

A general theory of free energies of inhomogeneous spatially dispersive media: I†

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Abstract. A general formalism is developed to calculate free energies of inhomogeneous spatially dispersive media in terms of bulk dielectric properties. To illustrate the application we consider two semi-infinite half spaces separated by a vacuum. All previously known results for surface energies and interaction energies for dielectrics and electrolytes derived using continuum theories emerge as special cases.

We show that our result for the interaction free energy of two like media across a vacuum reduces to a form which is identical to that obtained by Lushnikov and Malov using diagrammatic methods. In addition we demonstrate that, subject to certain reasonable assumptions about the dielectric permittivity, it is equivalent to the results obtained using the method of surface modes.

1. Introduction

In the last few years much emphasis has been placed on extending and generalizing the Lifshitz theory of intermolecular forces to many systems of interest in areas ranging from solid state physics, surface physics, colloid chemistry to biology. It has been demonstrated that these energies can now be computed with a high degree of accuracy and good agreement with experiment can be obtained (Sabisky and Anderson 1973, Richmond and Ninham 1971a, b, Richmond *et al* 1973, Parsegian and Ninham 1970, Parsegian and Gingell 1972, Parsegian 1973). It is two decades since Lifshitz (1956) first formulated a theory of van der Waals interaction between macroscopic bodies separated by a vacuum. This was generalized to include the effects of an intervening medium by Dzyaloshinskii *et al* (1961). However, this subsequent approach based on quantum field theory was complex and a simpler approach which involved summing surface modes was evolved by van Kampen *et al* (1968). This approach was recently generalized to include effects due to added electrolyte (Davies and Ninham 1972). A more rigorous derivation of this latter result based on quantum statistical mechanics (but avoiding diagrammatic theory) which also yields bulk and surface energies as well

† After submitting this work for publication we received details of work in related areas from Wikborg and Inglesfield (1975a, b).

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as the interaction energies across an inhomogeneous dielectric and electrolyte system has been given by Gorelkin and Smilga (1973) and Mitchell and Richmond (1974a). A number of very recent reviews on all these recent developments are now available (see for example Israelachvili and Tabor 1973, Langbein 1974, Mahanty and Ninham 1975, Richmond 1975).

The introduction of electrolyte injects a new qualitative feature commonly referred to as spatial dispersion. The response of the system differs from that of a simple dielectric in that it is non-local. Now for bulk conducting systems, such as electrolytes or metals, this phenomenon has been studied and understood for a long time. In particular, the electrical free energy of such a system may be formulated in terms of a generalized dielectric permittivity which depends on wavenumber q as well as frequency ω (Nozières and Pines 1958). This result is of importance because it is independent of any model which may be used later to calculate the dielectric permittivity. Now the Lifshitz–van der Waals interaction energy across an inhomogeneous dielectric system may be formulated solely in terms of bulk permittivities and an obvious question is: can these results be generalized to cover spatially dispersive media without introducing models for the dielectric constant as is implicit in treatments based on Debye–Hückel theory or hydrodynamics (Richmond *et al* 1972, Chang *et al* 1971, Heinrichs 1973)? The question has been considered by Craig (1972) who appears to replace ϵ by $\epsilon(q, \omega)$ in the Lifshitz formulations. It is not at all obvious that this is a valid procedure. More recently Lushnikov and Malov (1974) have used diagrammatic methods to obtain an expression for the interaction free energy in terms of a coupling constant integration which unfortunately they did not evaluate. Furthermore they state that at short separations their result differs from any which would be obtained using the method of surface modes. This is due, they claim, to the existence of short-wave electron–hole pair excitations which are not true boson(s).

Using a general method developed by one of us (Mitchell and Richmond 1974a) to study dielectric and electrolytic systems we have demonstrated how a similar coupling constant integral may be evaluated to recover the surface mode result. In this paper we shall generalize the latter work to cover spatially dispersive media. We shall recover the result of Lushnikov and Malov as a special limit. Furthermore we demonstrate how the coupling constant integral may be evaluated to yield a result identical to that given by the method of surface modes. The paper is set out as follows. After a brief review of the theoretical formulation in §2, we discuss in §3 the response of a semi-infinite spatially dispersive medium and illustrate how the appropriate boundary conditions for the currents at the interface are taken into account. In §4 we consider the main problem of interest and derive expressions for the surface free energy of a single half space and interaction free energy for a pair of half spaces. Well established expressions for bulk free energies also emerge at this stage. In §5 we establish that our results satisfy a general formula which relates surface energies and interaction free energies. The paper ends with a brief discussion.

2. Theoretical formulation

Most of the details of the formulation we shall use have been given elsewhere (Mitchell and Richmond 1974a, Richmond 1974) and here we merely summarize the essential results. For our system the interaction Hamiltonian may be written as follows:

$$V = -\frac{1}{2} \int d^3r \mathbf{P}(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r}) \quad (2.1)$$

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

$$F = F_0 - (1/\beta) \sum_{n=0}^{\infty} \int_0^1 \frac{d\lambda}{\lambda} \int d^3r \sum_{\alpha} G_{\alpha}(\mathbf{r}; i\xi_n; \lambda), \quad \alpha = x, y, z \quad (2.2)$$

where F_0 is the free energy in the absence of electrical interactions mediated by the interaction term (2.1). Now using linear response theory, the analytic continuation of G_{α} for real frequencies, ie $G_{\alpha}(\mathbf{r}; \omega; \lambda)$, can be shown to be the α th component of the polarization at \mathbf{r} induced by the α th component of a unit test dipole located at \mathbf{r} . This function may now be calculated semi-classically in terms of a macroscopic bulk dielectric permittivity $\epsilon(\mathbf{q}, \omega)$ which in general depends on wavenumber \mathbf{q} as well as frequency ω . Again within the framework of linear response theory, the coupling constant λ may be introduced by making the substitution

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

where $\chi(\mathbf{q}, \omega)$ is the macroscopic susceptibility which is independent of the coupling constant λ . At this point we comment that λ for a condensed medium need not necessarily be proportional to e^2 where e is the elementary electric charge. The choice given by equations (2.3) is determined by our initial interaction Hamiltonian (2.1) and the assumption that the macroscopic polarization responds linearly with the electric field. This point has also been discussed by Davies (1974).

The essential problem in formulating a macroscopic theory of van der Waals interactions across an inhomogeneous, spatially dispersive system is the characterization of the response of a finite or semi-infinite medium. In principle this involves solving a many-body problem which incorporates the effects of boundaries. Within the spirit of our macroscopic approach we shall formulate the response of our finite media in terms of the bulk dielectric response function $\epsilon(\mathbf{q}, \omega)$. For such a theory to be meaningful it is now necessary to impose an addition boundary condition relevant to the physical system under consideration. In our view, theories which purport to use only Maxwell's equations plus a certain constitutive relation involving the bulk permittivity have already specified a particular boundary condition (Agarwal *et al* 1971, Sein 1970). One must then ask the question: is this the appropriate boundary condition for the physical system under consideration? In the next section we shall discuss these points in some detail with reference to a semi-infinite half space.

3. The response of a semi-infinite half space

We shall consider a semi-infinite spatially dispersive medium which has a planar interface in contact with vacuum. (For convenience we choose a cartesian coordinate system and the medium occupies the half-space $z > 0$.) To proceed it is necessary to make certain assumptions about the nature of the interface.

First, within the spirit of our macroscopic approach we shall assume the medium is uniform up to the interface and, although charge fluctuations occur, charges and dipoles from the dispersive medium may not penetrate the interface into the vacuum or neighbouring medium. Furthermore, charges and dipoles may not accumulate at the interface. Thus the equilibrium charge density is zero everywhere. Secondly, we suppose that specular reflection of electric currents occurs at the interface and any quantum interference with phonons or other currents does not occur. These assumptions are not

essential but we maintain them for simplicity. We shall discuss the consequences of relaxing them in the final section.

We may now proceed to obtain the response function for such an inhomogeneous medium using a method proposed by Flores (1973). Let us introduce into the semi-infinite medium an oscillating external unit test charge at $\mathbf{r}_1 = (x_1, y_1, z_1)$. Polarization currents set up by this charge are reflected specularly at the interface. The solution we require may be constructed from the solutions to two auxiliary homogeneous systems. In system 1 the whole space is occupied with the spatially dispersive phase which has bulk dielectric constant $\epsilon_1(\mathbf{q}, \omega)$. (Henceforth we suppress the dependence of ϵ on ω .) In the plane $z = 0$ we place a sheet of oscillating surface charge with strength $\tilde{\sigma}_1(\mathbf{s})\delta(z)$, ($\mathbf{s} = (x, y)$). The oscillating unit test charge located at \mathbf{r}_1 now induces currents which of course travel into the half space $z < 0$. We now place another similar unit test charge at the image point $\bar{\mathbf{r}}_1 = (x_1, y_1, -z_1)$. This produces currents such that an observer situated in the half-space $z > 0$ would, if he were unaware of the test charge at the image point, imagine that currents from the test charge at \mathbf{r}_1 were being specularly reflected at the plane $z = 0$. The potential response $\varphi(\mathbf{r})$ and electric displacement $\mathbf{D}(\mathbf{r})$ for this system are readily obtained in terms of the certain Green functions. Thus if we introduce the two-dimensional Fourier transforms with respect to \mathbf{s}

$$\varphi(\mathbf{r}) = \int \frac{d^2\mathbf{K}}{(2\pi)^2} \exp(i\mathbf{K} \cdot \mathbf{s})\varphi(z) \quad (3.1)$$

and

$$\tilde{\sigma}(\mathbf{s}) = \int \frac{d^2\mathbf{K}}{(2\pi)^2} \exp(i\mathbf{K} \cdot \mathbf{s})\sigma(\mathbf{K}), \quad (3.2)$$

we have

$$\varphi(z) = 4\pi[G_1(z; z_1) \exp(-i\mathbf{K} \cdot \mathbf{s}_1) + G_1(z; -z_1) \exp(-i\mathbf{K} \cdot \mathbf{s}_1) + \sigma_1(\mathbf{K})G_1(z; 0)] \quad (3.3)$$

and

$$\mathbf{D}(z) = 4\pi[\mathbf{G}^D(z; z_1) \exp(-i\mathbf{K} \cdot \mathbf{s}_1) + \mathbf{G}^D(z; -z_1) \exp(-i\mathbf{K} \cdot \mathbf{s}_1) + \sigma_1(\mathbf{K})\mathbf{G}^D(z; 0)]. \quad (3.4)$$

The Green functions G and \mathbf{G}^D (which are also functions of the transverse wavevector \mathbf{K}) are potential and electric displacement response functions to a single test charge of strength $(1/4\pi)$ for an isotropic bulk medium. If we Fourier transform with respect to the z coordinates

$$\left. \begin{matrix} G_1(z; z_1) \\ \mathbf{G}^D(z; z_1) \end{matrix} \right\} = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \exp[ik(z - z_1)] \left\{ \begin{matrix} \tilde{G}_1(\mathbf{q}) \\ \tilde{\mathbf{G}}^D(\mathbf{q}) \end{matrix} \right\} \quad \mathbf{q} = (\mathbf{K}, k) \quad (3.5)$$

then in the non-retarded limit we have

$$\tilde{G}_1(\mathbf{q}) = 1/q^2\epsilon_1(\mathbf{q}) \quad \text{and} \quad \tilde{\mathbf{G}}^D(\mathbf{q}) = -i\mathbf{q}/q^2. \quad (3.6)$$

Note that \mathbf{G}^D does not depend on the dielectric properties.

The second auxiliary homogeneous system we require for this case is a vacuum with dielectric permittivity equal to unity. We introduce another sheet of oscillating charge

in the plane $z = 0$ with strength $\tilde{\sigma}_2(\mathbf{s})$. The appropriate potential and electric displacement are now

$$\varphi(z) = 4\pi\sigma_2(\mathbf{K})G_2(z, 0) \quad (3.7)$$

$$\mathbf{D}(z) = 4\pi\sigma_2(\mathbf{K})\mathbf{G}^D(z, 0) \quad (3.8)$$

where the Fourier transform with respect to z of G_2 is

$$\tilde{G}_2(\mathbf{q}) = 1/q^2. \quad (3.9)$$

The essential step now is to assume that for the inhomogeneous system we may use the solutions (3.3), (3.4) in the domain $z > 0$ and solutions (3.7) and (3.8) in the domain $z < 0$. This construction as we have noted contains automatically the boundary condition on the currents, namely specular reflection at the interface, due to our particular choice of image test charge. Other choices conform to other boundary conditions. The surface charges now play the rôle of unknown constants to be determined by imposing the usual boundary conditions which are continuity of φ and D^z at the interface. Continuity of D^z from (3.4) and (3.8) yields immediately

$$\sigma_1(\mathbf{K}) = -\sigma_2(\mathbf{K}). \quad (3.10)$$

Imposing continuity of φ , we now obtain from equations (3.3), (3.7) and (3.10) that

$$\sigma_1(\mathbf{K}) = -\left[\frac{G_1(0; z_1) + G_1(0; -z_1)}{G_1(0; 0) + G_2(0; 0)} \right] \exp(-i\mathbf{K} \cdot \mathbf{s}_1) \quad (3.11)$$

and hence for our inhomogeneous system the potential response to a test charge located at z_1 is

$$\varphi(z; z_1) = \begin{cases} 4\pi \exp(-i\mathbf{K} \cdot \mathbf{s}_1) \left\{ G_1(z; z_1) + G_1(z; -z_1) \right. \\ \quad \left. - \left[\frac{G_1(0; z_1) + G_1(0; -z_1)}{G_1(0; 0) + G_2(0; 0)} \right] G_1(z; 0) \right\} & z > 0 \\ 4\pi \exp(-i\mathbf{K} \cdot \mathbf{s}_1) \left[\frac{G_1(0; z_1) + G_1(0; -z_1)}{G_1(0; 0) + G_2(0; 0)} \right] G_2(z; 0) & z < 0. \end{cases} \quad (3.12)$$

Similarly, the electric displacement response is

$$\mathbf{D}(z; z_1) = \begin{cases} 4\pi \exp(-i\mathbf{K} \cdot \mathbf{s}_1) \left\{ \underline{\mathbf{G}}^D(z; z_1) + \underline{\mathbf{G}}^D(z; -z_1) \right. \\ \quad \left. - \left[\frac{G_1(0; z_1) + G_1(0; -z_1)}{G_1(0; 0) + G_2(0; 0)} \right] \underline{\mathbf{G}}^D(z; 0) \right\} & z > 0 \\ 4\pi \exp(-i\mathbf{K} \cdot \mathbf{s}_1) \left[\frac{G_1(0; z_1) + G_1(0; -z_1)}{G_1(0; 0) + G_2(0; 0)} \right] \underline{\mathbf{G}}^D(z; 0) & z < 0. \end{cases} \quad (3.13)$$

In passing we note that these response functions contain singularities which yield the frequencies of both bulk and surface plasmon modes. The former are of course trivially obtained from the zeros of the appropriate bulk dielectric constants. The latter are given by the equation

$$G_1(0; 0) + G_2(0; 0) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \frac{1}{(K^2 + k^2)} \left[\frac{1}{\epsilon(\mathbf{K}, k)} + 1 \right] = 0 \tag{3.14}$$

which has been obtained by others (for example, Kliewer and Fuchs 1971, Ritchie and Marusak 1966).

It is now a simple matter to obtain the appropriate dipole response function necessary to evaluate the free energy according to equation (2.2). In fact from equations (3.12) and (3.13) we have

$$\left. \begin{matrix} \varphi(\mathbf{r}, \mathbf{r}_1) \\ \mathbf{D}(\mathbf{r}, \mathbf{r}_1) \end{matrix} \right\} = \int \frac{d^2 \mathbf{K}}{(2\pi)^2} \exp(i\mathbf{K} \cdot \mathbf{s}) \left\{ \begin{matrix} \varphi(z; z_1) \\ \mathbf{D}(z; z_1) \end{matrix} \right\} \tag{3.15}$$

and

$$G_\alpha(\mathbf{r}) = \frac{1}{4\pi} \lim_{\mathbf{r} \rightarrow \mathbf{r}_1} \left[\frac{\partial}{\partial r_{1,\alpha}} D^\alpha(\mathbf{r}; \mathbf{r}_1) + \frac{\partial^2}{\partial r_\alpha \partial r_{1,\alpha}} \varphi(\mathbf{r}; \mathbf{r}_1) \right]. \tag{3.16}$$

We shall not evaluate the surface energy explicitly in this section. We shall see it emerge as a limiting case in the next section when we consider two spatially dispersive half spaces separated by a vacuum and the associated interaction free energy.

4. Free energy for the semi-infinite half spaces separated by a vacuum

Let us consider now two semi-infinite half spaces of spatially dispersive media separated by a vacuum. The bulk dielectric permittivities are $\epsilon_1(\mathbf{q}, \omega)$ and $\epsilon_3(\mathbf{q}, \omega)$. The vacuum layer has width $2l$ and we shall choose the z axis of a cartesian coordinate system perpendicular to the interfaces which coincide with the planes $z = \pm l$. Following the prescription outlined in the previous section we can immediately write down the potentials and displacement vectors for the case when a unit test charge is at \mathbf{r}_1 ($z_1 > l$). Thus

$$\varphi = \begin{cases} 4\pi[G_3(z; l) \sigma_4 + G_3(z; z_1) \exp(-i\mathbf{K} \cdot \mathbf{s}_1) + G_3(z; 2l - z_1) \exp(-i\mathbf{K} \cdot \mathbf{s}_1)] & z > l \\ 4\pi[G_2(z; -l) \sigma_2 + G_2(z, l) \sigma_3] & |z| < l \\ 4\pi G_1(z; -l) \sigma_1 & z < -l \end{cases} \tag{4.1}$$

and

$$\mathbf{D} = \begin{cases} 4\pi[\underline{G}^D(z; l) \sigma_4 + \underline{G}^D(z; z_1) \exp(-i\mathbf{K} \cdot \mathbf{s}_1) + \underline{G}^D(z; 2l - z_1) \exp(-i\mathbf{K} \cdot \mathbf{s}_1)] & z > l \\ 4\pi[\underline{G}^D(z; -l) \sigma_2 + \underline{G}^D(z; l) \sigma_3] & |z| < l \\ 4\pi \underline{G}^D(z; -l) \sigma_1 & z < -l \end{cases} \tag{4.2}$$

where

$$G_\alpha(z; z_1) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \exp[ik(z - z_1)]/q^2 \epsilon_\alpha(q) \quad \alpha = 1, 2, 3 (\epsilon_2(q) = 1). \tag{4.3}$$

It is now a simple matter to impose the boundary conditions. Thus, continuity of the potential at $z = \pm l$ gives

$$\sigma_1 G_1(-l^-; -l) = \sigma_2 G_2(-l^+; -l) + \sigma_3 G_2(-l^+; l) \quad (4.4)$$

$$\begin{aligned} &\sigma_2 G_2(l^-; -l) + \sigma_3 G_2(l^-; l) \\ &= \sigma_4 G_3(l^+; l) + [G_3(l^+; z_1) + G_3(l^+; 2l - z_1)] \exp(-i\mathbf{K} \cdot \mathbf{s}_1). \end{aligned} \quad (4.5)$$

Similarly, continuity of D^z at $z = \pm l$ gives

$$\sigma_1 G^z(-l^-; -l) = \sigma_2 G^z(-l^+; -l) + \sigma_3 G^z(-l^+; l) \quad (4.6)$$

$$\begin{aligned} &\sigma_2 G^z(l^-; -l) + \sigma_3 G^z(l^-; l) \\ &= \sigma_4 G^z(l^+; l) + [G^z(l^+; z_1) + G^z(l^+; 2l - z_1)] \exp(-i\mathbf{K} \cdot \mathbf{s}_1). \end{aligned} \quad (4.7)$$

If we introduce the notation

$$1/\hat{\epsilon}_\alpha(K) = 2K \int_{-\infty}^{\infty} \frac{dk}{2\pi} \frac{1}{q^2 \epsilon_\alpha(q)} \quad (\alpha = 1, 2) \quad (4.8)$$

and note that $1/\hat{\epsilon}_2 = 1$ then equations (4.4) may be rewritten to read

$$\sigma_1/\hat{\epsilon}_1 = \sigma_2 + \sigma_3 \exp(-2Kl) \quad (4.9)$$

$$\sigma_2 \exp(-2Kl) + \sigma_3 = \sigma_4/\hat{\epsilon}_3 + g(z_1) \quad (4.10)$$

$$-\sigma_1 = \sigma_2 - \sigma_3 \exp(-2Kl) \quad (4.11)$$

$$\sigma_2 \exp(-2Kl) - \sigma_3 = \sigma_4 \quad (4.12)$$

where

$$g(z_1) = 2K \int_{-\infty}^{\infty} \frac{dk}{2\pi} \left\{ \frac{\exp[ik(l - z_1)] + \exp[ik(z_1 - l)]}{q^2 \epsilon_3(q)} \right\}. \quad (4.13)$$

After some simple algebra we obtain

$$\sigma_4 = -\exp(-i\mathbf{K} \cdot \mathbf{s}_1) g(z_1) \frac{[1 + \Delta_1 \exp(-4Kl)]}{\mathcal{D}} \frac{\hat{\epsilon}_3}{1 + \hat{\epsilon}_3} \quad (4.14)$$

where

$$\mathcal{D} = 1 - \Delta_1 \Delta_3 \exp(-4Kl) \quad (4.15)$$

and

$$\Delta_\alpha = \frac{\hat{\epsilon}_\alpha - 1}{\hat{\epsilon}_\alpha + 1} \quad \alpha = 1, 3. \quad (4.16)$$

This is sufficient since we only require the response function at the point $r = r_1$. We may now apply the prescription according to equation (3.16) to obtain

$$\sum_\alpha G_\alpha(\mathbf{r}) = \int \frac{d^2\mathbf{K}}{(2\pi)^2} G(\mathbf{K}|z) \quad (4.17)$$

where

$$\begin{aligned}
G(\mathbf{K}|z) = & 2K^3 \frac{\hat{\epsilon}_3}{1 + \hat{\epsilon}_3} \frac{[1 + \Delta_1 \exp(-4Kl)]}{\mathcal{D}} \int \frac{dk'}{2\pi} \int \frac{dk}{2\pi} \frac{1}{q'^2 \epsilon_3(q')} \frac{[1 - 1/\epsilon_3(q)]}{q^2} \\
& \times \{ \exp[i(k+k')(z-l)] + \exp[i(k-k')(z-l)] \} \\
& - 2K \frac{\hat{\epsilon}_3}{1 + \hat{\epsilon}_3} \frac{[1 + \Delta_1 \exp(-4Kl)]}{\mathcal{D}} \int \frac{dk'}{2\pi} \int \frac{dk}{2\pi} \frac{kk'}{q'^2 \epsilon_3(q')} \frac{1 - 1/\epsilon_3(q)}{q^2} \\
& \times \{ \exp[i(k-k')(z-l)] - \exp[i(k+k')(z-l)] \} \\
& + \int \frac{dk}{2\pi} \frac{\exp[2ik(z-l)]}{q^2} (K^2 - k^2) \left(\frac{1}{\epsilon_3(q)} - 1 \right) \\
& + \int \frac{dk}{2\pi} \left(\frac{1}{\epsilon_3(q)} - 1 \right) \quad z > l. \tag{4.18}
\end{aligned}$$

To evaluate the complete free energy we also require $G(\mathbf{K}|z)$ in the region $z < -l$. This may be readily obtained by symmetry and we finally obtain

$$\begin{aligned}
\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \left[\int_{-\infty}^{-l} dz G(\mathbf{K}|z) + \int_l^{\infty} dz G(\mathbf{K}|z) \right] = & \left\{ V_3 \int \frac{dk}{2\pi} \left(\frac{1}{\epsilon_3(q)} - 1 \right) \right. \\
& - \frac{1}{4} \left(1 - \frac{1}{\epsilon_3(K, 0)} \right) + \left(\frac{2K\hat{\epsilon}_3}{1 + \hat{\epsilon}_3} \right) \frac{[1 + \Delta_1 \exp(-4kl)]}{\mathcal{D}} \int \frac{dk}{2\pi} \frac{1}{q^2 \epsilon_3(q)} \\
& \left. \times \left(1 - \frac{1}{\epsilon_3(q)} \right) \right\} + \{ \epsilon_3 \rightarrow \epsilon_1; \epsilon_1 \rightarrow \epsilon_3 \}. \tag{4.19}
\end{aligned}$$

In evaluating the z intergral, we have used the following identities:

$$\begin{aligned}
\int_{-\infty}^{\infty} \frac{dk}{2\pi} \int_{-\infty}^{\infty} \frac{dk'}{2\pi} \int_0^{\infty} dz \exp[i(k-k')z] f(k, k') = & \frac{1}{2} \int \frac{dk}{2\pi} f(k, k) \\
\text{for } f(k, k') = & f(-k, -k') \tag{4.20}
\end{aligned}$$

and

$$\int_{-\infty}^{\infty} \frac{dk}{2\pi} \int_0^{\infty} dz e^{ikz} f(k) = \frac{1}{2} f(0) \quad \text{if } f(k) \text{ is even.} \tag{4.21}$$

We have also made the assumption that $\epsilon(q, \omega)$ is only a function of the magnitude $q = |\mathbf{q}|$ of the wavevector. This is valid provided the bulk response is only a function of $|\mathbf{r} - \mathbf{r}'|$ where \mathbf{r} and \mathbf{r}' refer respectively to the field and source point.

Separating out the l dependent terms we may write the total free energy as a sum of bulk, surface and interaction free energies. Thus the bulk free energy is

$$F_B = \sum_{\alpha} \frac{V_{\alpha}}{\beta} \sum_{n=0}^{\infty} \int \frac{d^3 \mathbf{q}}{(2\pi)^3} \int_0^1 \frac{d\lambda}{\lambda} \left(1 - \frac{1}{\epsilon_{\alpha}(q|\lambda)} \right) \quad \alpha = 1, 2 \tag{4.22}$$

where V_{α} is the volume of medium α . Expressions of this type were first obtained by Nozières and Pines (1958).

The surface free energy per unit area is

$$F_s = \frac{1}{\beta} \sum'_{n=0} \int \frac{d^2 \mathbf{K}}{(2\pi)^2} \int_0^1 \frac{d\lambda}{\lambda} \left[\frac{1}{4} \left(1 - \frac{1}{\epsilon_1(K, 0)} \right) + \frac{1}{4} \left(1 - \frac{1}{\epsilon_3(K, 0)} \right) - \left(\frac{2K\hat{\epsilon}_1}{1 + \hat{\epsilon}_1} \right) \right. \\ \left. \int \frac{dk}{2\pi} \frac{1}{q^2 \epsilon_1(q)} \left(1 - \frac{1}{\epsilon_1(q)} \right) - \left(\frac{2K\hat{\epsilon}_3}{1 + \hat{\epsilon}_3} \right) \int \frac{dk}{2\pi} \frac{1}{q^2 \epsilon_3(q)} \left(1 - \frac{1}{\epsilon_3(q)} \right) \right] \quad (4.23)$$

and, finally, the interaction free energy per unit area is

$$F_i(l) = - (1/\beta) \sum'_{n=0} \int \frac{d^2 \mathbf{K}}{(2\pi)^2} \int_0^1 \frac{d\lambda}{\lambda} \left[\frac{\Delta_1 (1 + \Delta_3) \exp(-4Kl)}{\mathcal{D}} \left(\frac{\hat{\epsilon}_3}{1 + \hat{\epsilon}_3} \right) 2K \int \frac{dk}{2\pi} \right. \\ \times \frac{1}{q^2 \epsilon_3(q)} \left(1 - \frac{1}{\epsilon_3(q)} \right) + \frac{\Delta_3 (1 + \Delta_1) \exp(-4Kl)}{\mathcal{D}} \left(\frac{\hat{\epsilon}_1}{1 + \hat{\epsilon}_1} \right) \\ \left. \times 2K \int \frac{dk}{2\pi} \frac{1}{q^2 \epsilon_1(q)} \left(1 - \frac{1}{\epsilon_1(q)} \right) \right]. \quad (4.24)$$

At this point we note that for two identical media ($\epsilon_1 = \epsilon_3 = \epsilon$) equation (4.24) may be recast to read:

$$F_i(l) = \frac{-2}{\beta} \sum'_{n=0} \int \frac{d^2 \mathbf{K}}{(2\pi)^2} \int_0^1 \frac{d\lambda}{\lambda} \frac{M_K (1 - \hat{\epsilon}) / (1 + \hat{\epsilon}) + 1}{[(\hat{\epsilon} + 1) / (\hat{\epsilon} - 1)]^2 \exp(4Kl) - 1} \quad (4.25)$$

where

$$M_K = (4K/m) [\hat{\epsilon} / (\hat{\epsilon} - 1)]^2 \int_0^\infty dk [1 - 1/\epsilon(q)]^2 q^{-2} - 1 \quad (4.26)$$

which is formally identical to the result obtained by Lushnikov and Malov (1974). (The difference of a factor of two between our results and theirs is due probably to a typographical error in their paper.)

At this stage we use equation (2.3) to introduce the explicit dependence of ϵ on the coupling constant λ . It then follows that

$$\frac{\lambda d\epsilon(q)}{d\lambda} = \epsilon(q) - 1 \quad (4.27)$$

and

$$\frac{d\hat{\epsilon}}{d\lambda} = 2K\hat{\epsilon}^2 \int \frac{dk}{2\pi} \frac{1}{q^2 \epsilon(q)} \left(1 - \frac{1}{\epsilon(q)} \right). \quad (4.28)$$

From equations (4.22) and (4.27) we then obtain the bulk free energy

$$F_B = \sum_\alpha \frac{V_\alpha}{\beta} \sum'_{n=0} \int \frac{d^3 \mathbf{q}}{(2\pi)^3} \ln \epsilon_\alpha(q). \quad (4.29)$$

Similar results for the bulk electron gas within the random phase approximation have been obtained by Wentzel (1957).

The surface free energy may be evaluated in a similar manner. Thus, from equations (4.23), (4.27) and (4.28) we have

$$\begin{aligned}
F_s = \frac{1}{\beta} \sum_{n=0}^{\infty} \int \frac{d^2\mathbf{K}}{(2\pi)^2} \int_0^1 d\lambda \left\{ \frac{1}{4} \left[\frac{1}{\epsilon_1(K,0)} \frac{d\epsilon_1(K,0)}{d\lambda} + \frac{1}{\epsilon_3(K,0)} \frac{d\epsilon_3(K,0)}{d\lambda} \right] \right. \\
\left. - \left[\frac{1}{\hat{\epsilon}_1(1+\hat{\epsilon}_1)} \frac{d\hat{\epsilon}_1}{d\lambda} + \frac{1}{\hat{\epsilon}_3(1+\hat{\epsilon}_3)} \frac{d\hat{\epsilon}_3}{d\lambda} \right] \right\} = \frac{1}{\beta} \sum_{n=0}^{\infty} \int \frac{d^2\mathbf{K}}{(2\pi)^2} \\
\times \left\{ \frac{1}{4} \left(\ln \epsilon_1(K,0) + \ln \epsilon_3(K,0) \right) + \ln \left(\frac{\hat{\epsilon}_1 + 1}{2\hat{\epsilon}_1} \right) + \ln \left(\frac{\hat{\epsilon}_3 + 1}{2\hat{\epsilon}_3} \right) \right\}. \quad (4.30)
\end{aligned}$$

Finally the interaction free energy may be similarly integrated. We have from equations (4.24), (4.27) and (4.28)

$$\begin{aligned}
F_I(l) = (1/\beta) \sum_{n=0}^{\infty} \int \frac{d^2\mathbf{K}}{(2\pi)^2} \int_0^1 d\lambda \left(- \left\{ \frac{\Delta_1 \exp(-4Kl)}{\mathcal{D}} \left[\frac{1 + \Delta_3}{(1 + \hat{\epsilon}_3)\hat{\epsilon}_3} \right] \frac{d\hat{\epsilon}_3}{d\lambda} \right\} - \{1 \Rightarrow 3\} \right) \\
= (1/\beta) \sum_{n=0}^{\infty} \int \frac{d^2\mathbf{K}}{(2\pi)^2} \int_0^1 d\lambda \left(\frac{\partial \ln \mathcal{D}}{\partial \Delta_3} \frac{d\Delta_3}{d\hat{\epsilon}_3} \frac{d\hat{\epsilon}_3}{d\lambda} + \frac{\partial \ln \mathcal{D}}{\partial \Delta_1} \frac{d\Delta_1}{d\hat{\epsilon}_1} \frac{d\hat{\epsilon}_1}{d\lambda} \right) \\
= (1/\beta) \sum_{n=0}^{\infty} \int \frac{d^2\mathbf{K}}{(2\pi)^2} \ln \mathcal{D}(\mathbf{k}; i\xi_n). \quad (4.31)
\end{aligned}$$

Now we note that $\mathcal{D}(\mathbf{k}, \omega)$ is the secular determinant whose zeros yield the surface modes and equation (4.31) is precisely that result which one would obtain by applying the well known methods of surface modes to this system (van Kampen *et al* 1968, Richmond and Ninham 1971c). Thus within the limits of our approximation for the dielectric permittivities we see that the comments of Lushnikov and Malov about bosons etc are not valid.

It is a trivial matter to see that our expression (4.31) for the interaction free energy reduces to the limiting cases valid for pure dielectrics and Debye–Hückel electrolytes respectively. In the former case we simply have $\hat{\epsilon}_\alpha(K, \omega) \rightarrow \epsilon_\alpha(\omega)$ and clearly we obtain the conventional Lifshitz energy. In the latter case we use the fact that the bulk dielectric permittivity for an electrolyte is $\epsilon(q) = 1 + \kappa^2/q^2$ where κ is the conventional inverse Debye screening length. (We assume there is no background dielectric.) A simple integral using equation (4.8) then yields $\hat{\epsilon}_\alpha = \hat{\epsilon} = s/K$ where $s = (K^2 + \kappa^2)^{1/2}$. The appropriate result for the interaction of electrolytes across a vacuum then follows immediately (Davies and Ninham 1972, Mitchell and Richmond 1974a, Richmond 1974).

5. Cohesion—surface and interaction energies

Consider two identical semi-infinite media separated by a distance $2l$. As we have seen in the previous section, the total free energy may be expressed as a sum of bulk, surface and interaction free energies. The bulk energy is independent of l . When l is infinite, the interaction free energy per unit area, $F_I(\infty)$, is zero. The total surface free energy per unit area is 2γ , γ being the surface energy per unit area. Now let us bring the two surfaces into contact so that the interface heals to give one piece of bulk material filling the whole space. Clearly the decrease of surface energy has been achieved at the expense of a reduction of interaction energy and we have therefore

$$2\gamma = -F_I(0). \quad (5.1)$$

Relations of this type have been known for a long time (Young 1855). It is easy to see that

the Lifshitz interaction free energy (for a non-spatially dispersive media) satisfies this relation. In this case we have

$$F_1(l) = (1/\beta) \sum_{n=0}^{\infty} \int \frac{d^2 \mathbf{K}}{(2\pi)^2} \ln \left[1 - \left(\frac{\epsilon - 1}{\epsilon + 1} \right)^2 \exp(-4Kl) \right]$$

and therefore

$$-F_1(0) = (1/\beta) \sum_{n=0}^{\infty} \int \frac{d^2 \mathbf{K}}{(2\pi)^2} \ln \left[\frac{(\epsilon + 1)^2}{4\epsilon} \right]. \quad (5.2)$$

This is clearly seen to be equal to 2γ (Craig 1972, Mitchell and Richmond 1974a.) Now it is clearly of interest to check that our theory for spatially dispersive media satisfies the general relation, equation (5.1). If now we consider two identical media then we see immediately from equations (4.15) and (4.31) that the interaction free energy at zero separation is

$$-F_1(0) = (1/\beta) \sum_{n=0}^{\infty} \int \frac{d^2 \mathbf{K}}{(2\pi)^2} \ln \left[\frac{(\hat{\epsilon} + 1)^2}{4\hat{\epsilon}} \right]. \quad (5.3)$$

However, from equation (4.30) we have the surface free energy and it is apparent that for two identical media, this expression may be written

$$F_s = 2\gamma = (1/\beta) \sum_{n=0}^{\infty} \int \frac{d^2 \mathbf{K}}{(2\pi)^2} \left[\ln \left\{ \frac{(\hat{\epsilon} + 1)^2}{4\hat{\epsilon}} \right\} + \frac{1}{2} \ln \epsilon(\mathbf{K}, 0) - \ln \hat{\epsilon} \right]. \quad (5.4)$$

Clearly equations (5.3) and (5.4) are not equal. After a little thought it becomes clear why. In bringing the surfaces together to obtain equation (5.3) we have not completely healed the interface to obtain a uniform block of bulk material. The currents at the 'interface' are still specularly reflected. We must therefore evaluate the energy involved in effectively removing the barrier which maintains this boundary effect, thereby completely healing the interface. Using the methods of previous sections this is easy. We consider two identical spatially dispersive media with bulk dielectric permittivity $\epsilon(\mathbf{q}, \omega)$ separated by a barrier at $z = 0$ which ensures the currents are specularly reflected. The derivation of the response function necessary to evaluate the free energy follows that given in §3. We obtain

$$\begin{aligned} \varphi(z, z_1) = 4\pi \exp(-i\mathbf{K} \cdot \mathbf{s}_1) & \left[G_1(z; z_1) + G_1(z; -z_1) \right. \\ & \left. - \frac{[G_1(0; z_1) + G_1(0; -z_1)]}{2G_1(0; 0)} G_1(z; 0) \right] \end{aligned} \quad (5.5)$$

$$\begin{aligned} \mathbf{D}(z, z_1) = 4\pi \exp(-i\mathbf{K} \cdot \mathbf{s}_1) & \left\{ \mathbf{G}^D(z; z_1) + \mathbf{G}^D(z; -z_1) \right. \\ & \left. - \frac{[G_1(0; z_1) + G_1(0; -z_1)]}{2G_1(0; 0)} \mathbf{G}^D(z; 0) \right\} \end{aligned} \quad (5.6)$$

where

$$G_1(z; z_1) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \frac{\exp[ik(z - z_1)]}{q^2 \epsilon(q)}. \quad (5.7)$$

Applying the prescription (3.16) to equations (5.5)–(5.7) and inserting the result into equation (2.2) we obtain (after dropping bulk energies proportional to the volume) the healing free energy

$$F_H = (1/\beta) \sum'_{n=0} \int \frac{d^2 \mathbf{K}}{(2\pi)^2} \int_0^1 \frac{d\lambda}{d} \left[\frac{1}{2} \left(1 - \frac{1}{\epsilon(\mathbf{K}, 0)} \right) - 2K\hat{\epsilon} \int \frac{dk}{2\pi q^2 \epsilon^2(q)} (\epsilon(q) - 1) \right]. \quad (5.8)$$

Now using the relations (4.27) and (4.28) we do the coupling constant integration to obtain

$$F_H = (1/\beta) \sum'_{n=0} \int \frac{d^2 \mathbf{K}}{(2\pi)^2} \left[\frac{1}{2} \ln \epsilon(\mathbf{K}, 0) - \ln \hat{\epsilon} \right]. \quad (5.9)$$

Now we see that if we bring two surfaces together from infinite separation and also heal the join completely, then the appropriate free energy to be used on the right-hand side of equation (5.1) is

$$-F_1(0) + F_H = (1/\beta) \sum'_{n=0} \int \frac{d^2 \mathbf{K}}{(2\pi)^2} \left[\ln [(\hat{\epsilon} + 1)^2 / 4\hat{\epsilon}] + \frac{1}{2} \ln \epsilon(\mathbf{K}, 0) - \ln \hat{\epsilon} \right], \quad (5.10)$$

which is identical to equation (5.4). Thus we see that providing we account correctly for the boundary effects, our theory is self-consistent and satisfies the general relation, equation (5.1).

6. Discussion

In this paper we have developed a general theory of free energies of inhomogeneous spatially dispersive media. Our theory yields the free energy components. Although we have considered two different spatially dispersive media separated by a vacuum it is trivial to include a simple dielectric in the gap. It is more difficult to include a spatially dispersive medium. However, it can be done and in a later paper we shall consider the case of a spatially dispersive medium between two dielectrics. This system is of particular interest in colloidal and biological systems where particles are separated by electrolytes. The general case of three spatially dispersive media could be done but in this case it is not clear what the boundary condition on the currents at the surface should be without more details of the nature of the interacting media. Of course, even in the case we have considered here, the currents may not always be reflected specularly due to coupling with phonons or other excitations. Other types of systems which our results derived here do not cover are those where, as a result of establishing a surface, large structural changes occur or, alternatively, surface charges or dipoles are formed. Omission of the former effect implies that our expressions probably do not hold close to critical points. The latter effects occur in the electrolyte systems referred to above and we hope to study systems of this type in future publications (see also Mitchell and Richmond 1974b, Barnes and Davies 1975.)

Finally we comment on the feature discussed in § 5, namely the boundary effect which occurs as one brings two media together. This arises in our semi-macroscopic formulation because of our neglect of tunnelling of charges which may occur between interfaces as they come into contact. To handle this effect properly, a more complete microscopic treatment is necessary. However, it may be possible to build into our method a boundary condition which takes into account in a phenomenological way this tunnelling pheno-

menon and thereby obtain an interaction free energy which models better the behaviour in the final few Ångströms before contact.

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