NON-RETARDED VAN DER WAALS INTERACTIONS BETWEEN TWO SPATIALLY DISPERSIVE MEDIA

D. CHAN* and P. RICHMOND

Unilever Research, Port Sunlight, Wirral, Merseyside L62 4XN, UK

Received 4 February 1975

A method is described which permits the derivation of the van der Waals interaction free energy between two spatially dispersive media separated by a vacuum. A result which agrees with that of Lushnikov and Malov is obtained. We demonstrate that subject to certain assumptions about the dielectric permittivity (which are reasonable for a macroscopic system) the results is equivalent to that given by applying the method of surface modes.

In recent years, considerable effort has been devoted to the experimental verification as well as theoretical extensions of Lifshitz theory [1]. Of particular interest is the problem of deriving an expression for the van der Waals interaction energy between media with non-local dielectric permittivities (e.g. conducting or strongly polar media). In this note we wish to outline a simple semi-classical method of deriving the bulk, surface and interaction free energy for two dissimilar planar half spaces of spatially dispersive media separated by a vacuum gap of width $2l$. The results are expressed in terms of the bulk dielectric permittivities of each medium.

The approach here follows closely the formalism developed by Mitchell and Richmond [3] to study inhomogeneous systems involving local dielectrics and electrolytes. Briefly, for our system, the interaction Hamiltonian may be written as

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

Where $\boldsymbol{P}(\boldsymbol{r})$ is the macroscopic polarisation density and $\boldsymbol{E}(\boldsymbol{r})$ the electric field. From standard statistical mechanics the change in free energy due to the interaction Hamiltonian V is [3]

$$\Delta F = -\frac{1}{\beta}\sum_{\xi_n}^{\infty}{}' \int_0^1 \frac{\mathrm{d}\lambda}{\lambda}\int \mathrm{d}\boldsymbol{r} \sum_{\alpha} G_\alpha(\boldsymbol{r};\mathrm{i}\xi_n;\lambda), \qquad \alpha = x,y,z\,. \tag{2}$$

In the regime of linear response $G_\alpha(\boldsymbol{r};\mathrm{i}\xi_n;\lambda)$ can be interpreted as the αth component of the polarisation density at $\boldsymbol{r}$ induced by the αth component of a unit test dipole located at the same position. This quantity may now be calculated classically in terms of the bulk dielectric permittivity $\epsilon(\boldsymbol{q},\omega)$ which depends on wave number $\boldsymbol{q}$ and frequency ω.

In order to use the bulk permittivity to characterise a finite medium, it is necessary to specify physical boundary conditions at the interface. For a vacuum-medium interface, it is reasonable to assume specular reflection of all currents at the boundary. With this boundary condition, Flores [4] has shown that the response within a non-local half space to a point charge situated in the spatially dispersive medium, can be replaced by the response of the bulk medium to the same point charge plus an identical point charge situated at the *image* position (with respect to what would have been the vacuum-medium interface) and an unknown surface charge located at the position of the interface. This procedure would ensure specular reflection of currents at the boundary. Using this prescription we can proceed to evaluate the quantity G_α needed in eq. (2) using classical electrodynamics. The unknown surface charges are determined by applying the usual boundary conditions on the field quantities $\boldsymbol{E}, \boldsymbol{D}, \boldsymbol{H}$ and $\boldsymbol{B}$.

* CSIRO Postdoctoral Fellow.

At this point we note that the dependence of $\epsilon(\boldsymbol{q}, \omega)$ on the coupling constant λ is obtained by the substitution

$$\epsilon(\boldsymbol{q},\omega) = 1+4\pi\chi(\boldsymbol{q},\omega) \rightarrow \epsilon(\boldsymbol{q},\omega|\lambda) = 1+4\pi\lambda\chi(\boldsymbol{q},\omega)\,, \tag{3}$$

where $\chi(\boldsymbol{q}, \omega)$ is independent of λ. This method of introducing the coupling constant is dictated by the assumption of linear response needed to interpret physically the meaning of the quantity $G_\alpha(\boldsymbol{r}; \omega;\lambda)$.

In the non-retarded limit (velocity of light $\rightarrow\infty$) we obtain for the bulk energy per unit volume of each medium, the well known result:

$$\Delta F_{\mathrm{B}} = \frac{1}{\beta}\sum_{\xi_n}^{\infty}{}' \int \frac{\mathrm{d}^3\boldsymbol{q}}{(2\pi)^3} \int_0^1 \frac{\mathrm{d}\lambda}{\lambda}\left(1-\frac{1}{\epsilon(q,\mathrm{i}\xi_n)}\right) = \frac{1}{\beta}\sum_{\xi_n}^{\infty}{}' \int \frac{\mathrm{d}^3\boldsymbol{q}}{(2\pi)^3} \ln\epsilon(q,\mathrm{i}\xi_n)\,. \tag{4}$$

Similarly the surface energy per unit area of each surface is

$$\Delta F_{\mathrm{S}} = \frac{1}{\beta}\sum_{\xi_n}^{\infty}{}' \int \frac{\mathrm{d}^2\boldsymbol{K}}{(2\pi)^2}\left[\tfrac{1}{4}\ln\epsilon(\boldsymbol{K},0;\mathrm{i}\xi_n) + \ln\left(\frac{\hat{\epsilon}+1}{2\hat{\epsilon}}\right)\right]\,, \tag{5}$$

where

$$\frac{1}{\hat{\epsilon}(\boldsymbol{K},\mathrm{i}\xi_n)} = 2K\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{(2\pi)}\,\frac{1}{k^2+K^2}\,\frac{1}{\epsilon(\boldsymbol{q},\mathrm{i}\xi_n)}\,, \tag{6}$$

and $\boldsymbol{q} = (\boldsymbol{K}, k)$.

For the interaction energy per unit area, we obtain

$$\Delta F_{\mathrm{I}} = \frac{1}{\beta}\sum_{\xi_n}^{\infty}{}' \int \frac{\mathrm{d}^2\boldsymbol{K}}{(2\pi)^2} \int_0^1 \frac{\mathrm{d}\lambda}{\lambda}\left\{\left[\frac{\Delta_1(1+\Delta_3)}{\mathcal{D}}\exp(-4Kl)\frac{\hat{\epsilon}_3}{1+\hat{\epsilon}_3}\,2K\int_{-\infty}^{\infty}\frac{\mathrm{d}k}{2\pi}\frac{1}{q^2}\frac{1}{\epsilon_3}\left(1-\frac{1}{\epsilon_3}\right)\right] + [1\rightleftharpoons 3]\right\} \tag{7}$$

$$= \frac{1}{\beta}\sum_{\xi_n}^{\infty}{}' \int \frac{\mathrm{d}^2\boldsymbol{K}}{(2\pi)^2}\ln\mathcal{D}\,, \tag{8}$$

where

$$\mathcal{D} = 1-\Delta_1\Delta_2\exp(-4Kl)\,, \qquad \Delta_i = \frac{\hat{\epsilon}_i-1}{\hat{\epsilon}_i+1}\,, \tag{9, 10}$$

and the subscripts $i = 1,3$ refer to the two semi-infinite media. For two identical media interacting across a vacuum, eq. (7) reduces to the result given by Lushnikov and Malov [5] (apart from a factor of 2, due probably to a typographical error in their paper). We note also that after carrying out the coupling constant integration, the result for the interaction energy, eq. (8), coincides with that which would have been obtained from the surface mode method [6] adapted for spatially dispersive media. Furthermore for interacting non-spatially dispersive media or for interacting half spaces of Debey–Huckel electrolyte we recover well known results [3].

Full details of this work will be published elsewhere [7].

[1] E.M. Lifshitz, Sov. Phys., JETP 2 (1956) 73.
[2] A number of references to recent work may be found in B.W. Ninham and P. Richmond JCS Far. Trans. II 69 (1973) 658.
[3] D.J. Mitchell and P. Richmond, J. Coll. Int. Sci. 46 (1974) 118.
[4] F. Flores, Nuovo Cimento 14 (1973) 1.
[5] A.A. Lushnikov and V.V. Malov, Phys. Lett. 39A (1974) 317.
[6] N.G. van Kampen, B.R.A. Nijboer and K. Schram, Phys. Letters 25A (1968) 307.
[7] D. Chan and P. Richmond, J. Phys. C: Solid State Phys., submitted for publication.