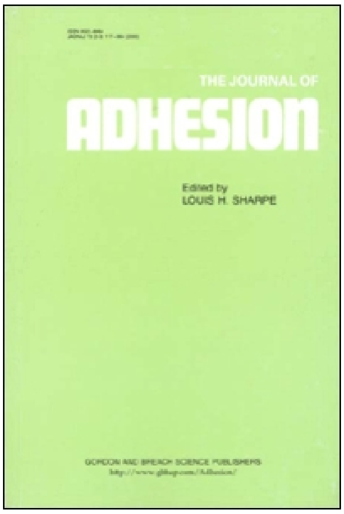

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Dielectric Anisotropy and the van der Waals Interaction between Bulk Media

V. A. Parsegian[a]; George H. Weiss[a]
[a] Department of Health, Education and Welfare, Physical Sciences Laboratory, Division of Computer Research and Technology, National Institutes of Health, Bethesda, Maryland, U.S.A.

To cite this Article Parsegian, V. A. and Weiss, George H.(1972) 'Dielectric Anisotropy and the van der Waals Interaction between Bulk Media', The Journal of Adhesion, 3: 4, 259 — 267
To link to this Article: DOI: 10.1080/00218467208072197
URL: http://dx.doi.org/10.1080/00218467208072197

J. Adhesion, 1972 Vol. 3, pp. 259–267

Printed in Northern Ireland

Dielectric Anisotropy and the van der Waals Interaction between Bulk Media

V. A. PARSEGIAN and GEORGE H. WEISS

Physical Sciences Laboratory, Division of Computer Research and Technology, National Institutes of Health, Department of Health, Education and Welfare, Bethesda, Maryland, 20014 U.S.A.

(*Received April* 17, 1971)

We derive the van der Waals interaction energy between two semi-infinite dielectrically anisotropic bodies acting across a planar slab filled with a third anisotropic material. The derivation, valid in the non-retarded limit, is performed by a summation of electromagnetic surface-mode fluctuations. The result is a free energy of interaction as a function of body separation and of rotation of the various media. The angular dependence of the energy predicts a torque between the two bodies; in some cases the van der Waals interaction between like substances will change from attraction to repulsion under rotation.

INTRODUCTION

Since E. M. Lifshitz'[1] formulation in 1955 of the van der Waals interaction between macroscopic bodies, several experimental measurements have confirmed the predicted interaction between isotropic solid bodies across a vacuum[2,3]. Good agreement has also been established between measured and calculated estimates of the interaction of water across a hydrocarbon medium[4,5,6]. Moreover, the original geometry considered by Lifshitz, two semi-infinite media acting across a planar slab, has been generalized to give estimates for interactions across triple-layer, and many-layer films[8,9].

These calculations and analyses show that the resulting van der Waals force between two large bodies can in no way be considered the additive pairwise sum of interactions between incremental parts of the two bodies[10]. In addition there may be strong temperature dependent forces when an intermediate material is of similar weight density but greatly different zero-frequency dielectric constant from that of the interacting bodies[11].

Such results suggest a more or less exhaustive discussion of van der Waals forces by means of the Lifshitz approach for the understanding of many-body effects. Besides the effect of different geometrical shapes there has been some question of the role of polarization anisotropy in van der Waals attraction[12]. In this paper we derive the van der Waals force between anisotropic bodies across an anisotropic planar slab. To do this we follow the method of surface mode summation explained elsewhere[13,14]. The resulting formulae, valid in the non-retarded limit, can be specialized to several cases which may obtain in practice. It is rather clear finally that only if material polarizability of the separating medium is very close to those of the interacting bodies will anisotropy be a noticeable feature. Otherwise, average polarizabilities suffice for calculation of the van der Waals forces between macroscopic bodies.

MODEL

The model to be studied is characterized by a planar slab of material of thickness L separating two semi-infinite media. All three media will be assumed to have anisotropic dielectric properties so that the displacement vector $\mathbf{D}$ is related to the electric vector by $\mathbf{D} = \boldsymbol{\epsilon}\mathbf{E}$ where $\boldsymbol{\epsilon}$ is a dielectric tensor. We will assume that the dielectric tensor in medium r can be represented by means of principal dielectric axes, in which form it will be written

$$\boldsymbol{\epsilon} = \begin{pmatrix} \epsilon_x^r & 0 & 0 \\ 0 & \epsilon_y^r & 0 \\ 0 & 0 & \epsilon_z^r \end{pmatrix}, \qquad r = 1,2,3. \tag{1}$$

The major assumption in the following analysis is that the "3" dielectric axis coincides with the z axis as defined by Figure 1. Although the analysis can be carried through when this condition does not obtain, the algebra becomes much more complicated. We believe that our analysis is sufficient to indicate the order of magnitude of effects due to anisotropy. The use of the assumption allows us to characterize the dielectric tensors by two angles, θ_2, θ_3 which represent the rotation around the z axis of materials 2 and 3 with respect to material 1. The case $\theta_2 = \theta_3 = 0$ refers to the situation

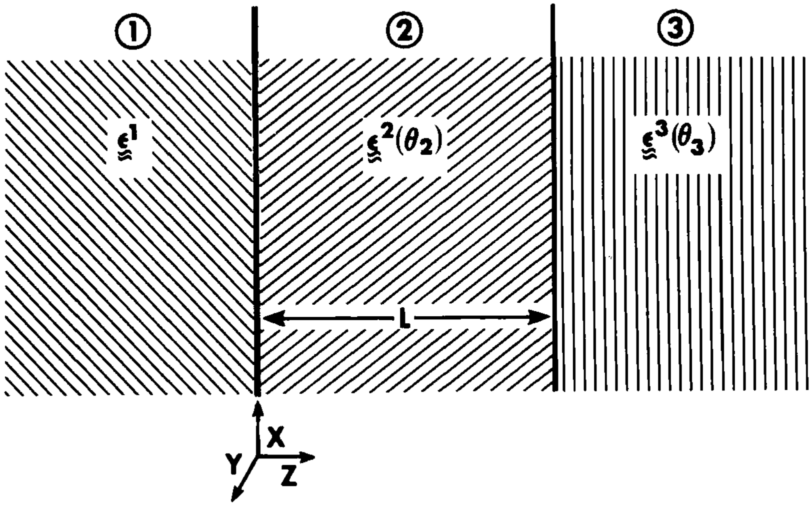

FIGURE 1 Two anisotropic bodies of substance "1" interacting across a planar slab of anisotropic material "2". All materials are assumed to have mutually orthogonal principal polarization axes. The principal axes of region 1 $(\epsilon_x^1, \epsilon_y^1, \epsilon_z^1)$ coincide with the axes (x,y,z) in the label. We consider the case where regions 2 and 3 are rotated by angles θ_2 and θ_3 about the z-axis (perpendicular to the planar slab) where θ_2 and θ_3 about the z-axis (perpendicular to the planar slab) where $\theta_2 = 0$, $\theta_3 = 0$ refer to the case where all principal "x-axes" are parallel.

in which the principal dielectric axes of all of the media are parallel. The effects of rotating materials 2 and 3 by amounts θ_2 and θ_3 can be represented through the use of dielectric tensors $\epsilon^2(\theta_2)$ and $\epsilon^3(\theta_3)$ where

$$\boldsymbol{\epsilon}^r(\theta_r) = \begin{bmatrix} \epsilon_x^r + (\epsilon_y^r - \epsilon_x^r)\sin^2\theta_r & (\epsilon_x^r - \epsilon_y^r)\sin\theta_r\cos\theta_r & 0 \\ (\epsilon_x^r - \epsilon_y^r)\sin\theta_r\cos\theta_r & \epsilon_y^r + (\epsilon_x - \epsilon_y^r)\sin^2\theta_r & 0 \\ 0 & 0 & \epsilon_z^r \end{bmatrix}. \quad (2)$$

It is understood that the various components ϵ_i^r also depend on the driving frequency ω. We also assume that only the dielectric properties are anisotropic and that the magnetic material properties are summarized by $\boldsymbol{\mu} = \mathbf{I}$ where $\mathbf{I}$ is the unit matrix.

DERIVATION

We will calculate the free energy of interaction by using a method first introduced by van Kampen Nijboer, and Schram[13] and later exploited by

Ninham, Parsegian and Weiss[14]. This consists first of representing the electromagnetic field by an ensemble of harmonic oscillators for which the Helmholtz free energy can be written

$$G(L,T) = kT\sum_j \ln\{2\sinh(\beta\hbar\omega_j/2)\} \tag{3}$$

in which T is the temperature, $\beta = 1/(kT)$ where k is Boltzmann's constant, $\hbar = h/(2\pi)$ where h is Planck's constant, and the ω_j are the electromagnetic surface modes in radians/sec. This expression for the free energy can be transformed into a contour integral over the dispersion relation, $D(\omega) = 0$, whose roots give the frequencies of standing waves. It is the integral form with which we will be dealing. The first step, however, is a derivation of the function $D(\omega)$.

In the nonretarded limit (i.e., the speed of light is considered to be infinite, limiting the validity of this analysis to configurations with $L \lesssim 100\,\text{Å}$) we start from Maxwell's equations, which are

$$\nabla\cdot(\boldsymbol{\epsilon}\mathbf{E}) = 0, \qquad \nabla\times\mathbf{E} = 0. \tag{4}$$

From the second of these equations we introduce a scalar potential by $\mathbf{E} = -\nabla\psi$ so that

$$\nabla\cdot(\boldsymbol{\epsilon}\nabla\psi) = 0. \tag{5}$$

This equation is to be solved subject to boundary conditions at the interfaces which state that the components E_x, E_y and $(\boldsymbol{\epsilon}\mathbf{E})_z$ are continuous there. A solution to Eq. (5) valid in material r can be obtained by substituting the form

$$\psi_r = f_r(z)\exp[i(ux+vy)], \qquad r = 1,2,3. \tag{6}$$

This leads to the following equation satisfied by the functions $f_r(z)$

$$\epsilon_z{}^r f_r''(z) - (\epsilon_{11}^r u^2 + 2\epsilon_{12}^r uv + \epsilon_{22}^r v^2)f_r(z) = 0 \tag{7}$$

where ϵ_{ij}^r is the ij element of the rotated matrix given in Eq. (2). This last equation can be rewritten

$$f_r''(z) - \beta_r{}^2(\theta)f_r(z = 0 \tag{8}$$

where

$$\beta_r^2\ (\theta) = \frac{\epsilon_x{}^r}{\epsilon_z{}^r}(u\cos\theta + v\sin\theta)^2 + \frac{\epsilon_y{}^r}{\epsilon_z{}^r}(v\cos\theta - u\sin\theta)^2. \tag{9}$$

Equation (8) has the solution

$$f_r(z) = A_r e^{\beta_r z} + B_r e^{-\beta_r z}. \tag{10}$$

Notice that since only surface modes have physical significance we can immediately set $B_1 = A_3 = 0$. The boundary conditions at $z = 0$ and $z = L$ can be written in terms of the $f_r(z)$ as

$$\begin{aligned} f_1(0) &= f_2(0), \qquad \epsilon_z^{1} f_1(0) = \epsilon_z^{2} f_2'(0) \\ f_2(L) &= f_3(L), \qquad \epsilon_z^{2} f_2'(L) = \epsilon_z^{3} f_3'(L). \end{aligned} \tag{11}$$

When the specific forms of Eq. (10) are substituted into this set of boundary conditions, then it is found that in order for the A_r and B_r to be nonzero it is necessary that

$$\left(\frac{a-1}{a+1}\right)\left(\frac{b-1}{b+1}\right) e^{-2\beta_2(\theta_2)L} - 1 = 0. \tag{12}$$

in which the parameters a and b are

$$a = \frac{\epsilon_z^{1} \beta_1}{\epsilon_z^{2} \beta_2(\theta_2)}, \quad b = \frac{\epsilon_z^{3} \beta_3(\theta_3)}{\epsilon_z^{2}\, \beta_2(\theta_2)}. \tag{13}$$

Equation (12) furnishes us with the dispersion relation $D(\omega) = 0$ since the ϵ's depend on ω. It is easy to verify that the dispersion relation derived above reduce to previously derived results for isotropic media. When $\epsilon_x^{r} = \epsilon_y^{r}$ the dispersion relation is independent of angle because of the isotropy in all planes perpendicular to the z axis.

Having derived an expression for the dispersion relation we can now use results derived in earlier papers[6-11,13,14] to rewrite the free energy as

$$\begin{aligned} G(L) &= \frac{kT}{4\pi^2} \sum_{n=0}^{\infty}{}' \iint_{-\infty}^{\infty} du\, dv \ln D(i\xi_n; u, v) \\ &= \frac{kT}{4\pi^2} \sum_{n=0}^{\infty}{}' \iint_{-\infty}^{\infty} du\, dv \ln \left[1 - \Delta_n^2(\xi_n, u, v, \theta) e^{-2\beta_2(\theta_2)L}\right] \end{aligned} \tag{14}$$

where we have explicitly included the dependence of the dispersion relation on u and v, $\xi_n = 2\pi nkT/\hbar$, the prime on the summation indicates that the $n = 0$ term is to be multiplied by $\frac{1}{2}$, and

$$\Delta_n^2(\xi_n, u, v, \theta) = \left(\frac{a-1}{a+1}\right)\left(\frac{b-1}{b+1}\right). \tag{15}$$

The double integrals in Eq. (14) can be reduced to single integrals by introducing polar coordinates, $u = \rho \cos \phi$, $v = \rho \sin \phi$, in which case the $\beta_r(\theta)$ can be written

$$\begin{aligned}\beta_r{}^2(\theta) &= \frac{\rho^2}{\epsilon_z{}^r}[\epsilon_x{}^r \cos^2(\theta - \phi) + \epsilon_y{}^r \sin^2(\theta - \phi)] \qquad (16)\\ &= \rho^2 g_r{}^2(\theta - \phi)\end{aligned}$$

where $g_r{}^2(\theta)$ is, by definition,

$$\frac{\epsilon_x{}^r}{\epsilon_z{}^r} + \frac{(\epsilon_y{}^r - \epsilon_x{}^r)}{\epsilon_z{}^r} \sin^2 \theta.$$

Since the ρ terms in the expressions for a and b cancel (Eq. (13)), the ρ integration can be expressed in the form

$$\iint_{-\infty}^{\infty} du\, dv \ln D(i\xi_n, u, v) = \int_0^{2\pi} d\phi \int_0^{\infty} \rho\, d\rho \ln \left[1 - \Delta_n{}^2(\theta, \phi) e^{-2\rho g_2(\theta - \phi) L}\right]. \qquad (17)$$

It is sometimes useful to take advantage of the fact that $\Delta_n{}^2(\theta, \phi) < 1$ to expand the logarithm and perform the ρ integration explicitly. This leads to the expression

$$G(L) = -\frac{kT}{16\pi^2 L^2} \sum_{n=0}^{\infty}{}' \sum_{m=1}^{\infty} \frac{1}{m^3} \int_0^{2\pi} \frac{\Delta_n^{2m}(\theta, \phi)}{g_2{}^2(\theta_2 - \phi)}\, d\phi. \qquad (18)$$

Both Eqs. (17) and (18) reduce in the isotropic limit, to results derived earlier by Ninham and Parsegian[6].

EXAMPLES AND DISCUSSION

We are now in a position to apply these results to some special cases in order to determine the circumstances under which dielectric anisotropy might lead to measurable orienting forces. We have searched the available literature to determine the amount of anisotropy in various crystals. The greatest variation was found in the uniaxial crystal of HgCl for which the two indices of refraction are 1.973 and 2.656, or the two corresponding dielectric susceptibilities are 3.893 and 7.054. If we assume that this crystal has only a single absorption peak in the *uv* at 1.83 × 10^{16} rad/sec for $\epsilon_x(\omega)$, $\epsilon_y(\omega)$ and $\epsilon_z(\omega)$ (derived from the ionization potential), then for the interaction of two such crystals across a vacuum ($\boldsymbol{\epsilon}^2 = \mathbf{I}$) the variation in energy with orientation is less than one percent over the entire range of angles.

With this example in mind it is of some interest to inquire whether there are *any* circumstances under which anisotropic dielectric properties will lead to substantially different energies as the media are rotated. We have been able to determine at least one possible situation in which this might be the case. Let us consider two identical uniaxial anisotropic media with principle axis dielectric susceptibility α and dielectric susceptibilities equal to β along the remaining two axes, interacting across an isotropic medium characterized by $\boldsymbol{\epsilon}^2 = \epsilon^2\mathbf{I}$. If we denote the combination $(\alpha - \beta)/\beta$ by γ, then the expression for the function $\Delta_n{}^2$ when the principal dielectric axis of the crystal is in the xy plane can be written

$$\Delta_n^2 = \left(\frac{\epsilon^2 - \beta\sqrt{1 + \gamma\cos^2\phi}}{\epsilon^2 + \beta\sqrt{1 + \gamma\cos^2\phi}}\right)\left(\frac{\epsilon^2 - \beta\sqrt{1 + \gamma\cos^2(\theta - \phi)}}{\epsilon^2 + \beta\sqrt{1 + \gamma\cos^2(\theta - \phi)}}\right) \tag{19}$$

in which we have set $\theta_3 = \theta$ for convenience. Let us assume, to begin with, that $\epsilon^2 = \beta$, and that γ is small. Then, to first order in γ we find that

$$\Delta_n{}^2 \approx \frac{\gamma^2}{16}\cos^2\phi\cos^2(\theta - \phi) \tag{20}$$

where γ contains the dependence on m. For an isotropic dielectric the function $g_2(\theta)$ is identically equal to 1. Hence the $m = 1$ term in Eq. (18) can be carried out exactly, and we find that to a good approximation

$$G(L) = -\frac{kT}{1024\pi L^2}[1 + 2\cos^2\theta]\sum_n{}'\gamma_n{}^2 . \tag{21}$$

The angular factor varies from 3 to 1 as θ varies from 0 to 90°, although the absolute value of the free energy is quite small in this case because of the factor $\overset{n}{\Sigma}{}'\gamma_n{}^2$. However, the simplified model calculation suffices to suggest that in order to emphasize anisotropy it is necessary that $\epsilon^2 \approx \beta$.

In order to test this idea we have used the parameters for HgCl, *i.e.*, we have chosen

$$\begin{aligned} \alpha &= 1 + 2.893/(1 + (\xi/\xi_0)^2) \\ \beta &= 1 + 6.054/(1 + (\xi/\xi_0)^2) \end{aligned} \tag{22}$$

where $\xi_0 = 1.83 \times 10^{16}$ rad/sec. The dielectric properties of the intermediate material were assumed to be those of a melt, such that ϵ^2 was chosen to be

$$\epsilon^2 = \frac{1}{3}(\alpha + 2\beta) = 1 + 5.0/(1 + (\xi/\xi_0)^2). \tag{23}$$

For this set of parameters the value of γ is not necessarily small, but it is true that $\epsilon^2 \approx \beta$. The sum over n in Eq. (14) can be converted into an integral over $\xi = 2\pi nkT/\hbar$, and to a good approximation, $G(L)$ is given by

$$\begin{aligned} G(L) &= -\frac{\hbar}{32\pi^3 L^2} \int_0^\infty d\xi \int_0^{2\pi} \Delta^2(\xi, \theta, \phi)\, d\phi \\ &= -\frac{\hbar}{32\pi^3 L^2}\, s(\theta). \end{aligned} \tag{24}$$

A curve of the function $s(\theta) \times 10^{-14}$ is plotted in Figure 2. It is obvious on physical grounds that $s(\theta + \pi/2) = s(\theta - \pi/2)$ so that the curve shown covers the entire range. The most striking feature is that the free energy changes sign indicating that the attractive force at $\theta = 0$ changes to a repulsive force by $\theta = 90°$.

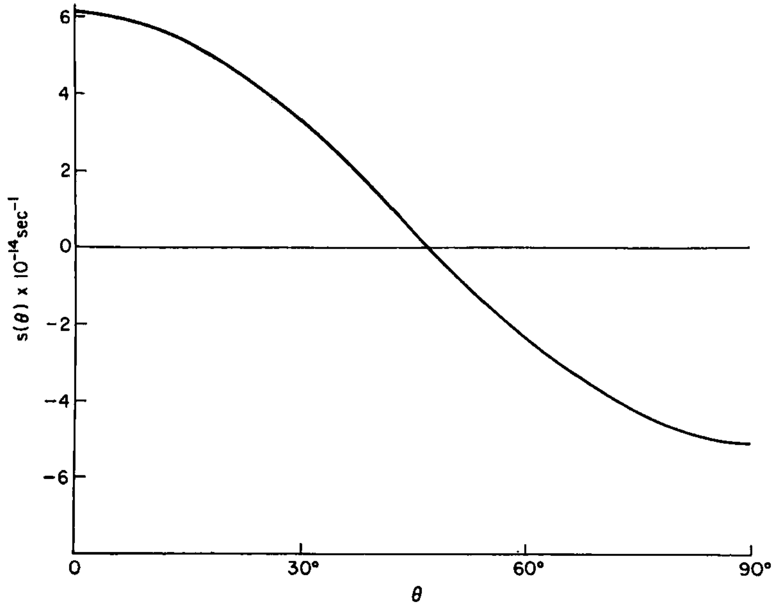

FIGURE 2 A curve of the function s(θ) that contains the angular dependence of the free energy for two crystals of HgCl acting across an isotropic medium with properties that are an arithmetic mean of the properties of the three dielectric axes.

It should be noted that energies involved in this anisotropic effect are quite small in comparison with the weakly anisotropic energy that results when the intermediate medium is a vacuum. For this latter case the values of $s(\theta)$ range from 8.89×10^{16} sec^{-1} at $\theta = 0$ to 8.83×10^{16} sec^{-1} at $\theta = 90°$ and the energy is therefore two orders of magnitude greater. The value of energy/unit area for a separation of 25 Å (with a melt as the intermediate medium) is 1.05×10^{-2} erg/cm^2 at $\Delta\theta = 0°$ and 90° respectively. Although the two systems show a qualitative difference in behavior with respect to forces it is interesting to notice that the difference in energy due to rotation through 90° is roughly 2×10^{-2} ergs/cm^2 for an intermediate melt and 1×10^{-2} ergs/cm^2 for the intermediate vacuum. The interesting point about these numbers is that they are of the same order of magnitude. Whether this order of magnitude equality is a more general phenomenon can only be investigated by doing calculations for many more sets of parameters. It does appear from the present calculations that anisotropic dielectric properties can lead to significant forces for orienting crystals in a melt. It is also possible that these long range orientation forces act to align regions of smectic liquid-crystal phases[15].

Although we have exhibited a situation in which anisotropic dielectric properties lead to a significant orientation force, it is not clear how general this effect might be. The properties of HgCl are more anisotropic than those of most other crystals, and we obtained a very small effect unless the intermediate zone has very special properties that tend to null certain isotropic properties of the crystal. We do not believe that any qualitative effects will be changed if the theory is developed with retardation, but we have not yet made detailed calculations to verify this.

References

1. E. M. Lifshitz, *Soviet Physics JETP* **2,** 73 (1958) [Zh. Eksp: Teor Fiz 29, 95 (1955)].
2. B. Derjaguin, I. I. Abrikosova, and E. M. Lifshitz, *Quarterly Reviews* (*London*) **10,** 295 (1956).
3. D. Tabor and R. H. S. Winterton, *Proc. Roy. Soc.* (*London*) **A312,** 435 (1969).
4. D. A. Haydon and J. Taylor, *Nature* (*London*) **224,** 1197 (1969).
5. I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, *Advances in Physics* **10,** 165 (1959)
6. B. W. Ninham and V. A. Parsegian, *Biophys. J.* **10,** 646 (1970).
7. B. W. Ninham and V. A. Parsegian, *J. Chem. Phys.* **52,** 4578 (1970).
8. B. W. Ninham and V. A. Parsegian, *J. Chem. Phys.* **53,** 3398 (1970).
9. V. A. Parsegian and B. W. Ninham, *J. Theor. Brol.* in press.
10. V. A. Parsegian and B. W. Ninham, *J. Colloid* and *Interface Sci.* in press.
11. V. A. Parsegian and B. W. Ninham, *Biophys. J.* **10,** 664 (1970).
12. H. Krupp, *Advan. Colloid and Interface Sci.* **1,** 111 (1967).
13. N. G. van Kampen, B.R.A. Nijboer and K. Schram, *Phys Letters* **26A,** 307 (1968).
14. B. W. Ninham, V. A. Parsegian and G. H. Weiss, *J. Statistical Physics* **2,** 323 (1970).
15. A. G. De Rocco, personal communication.