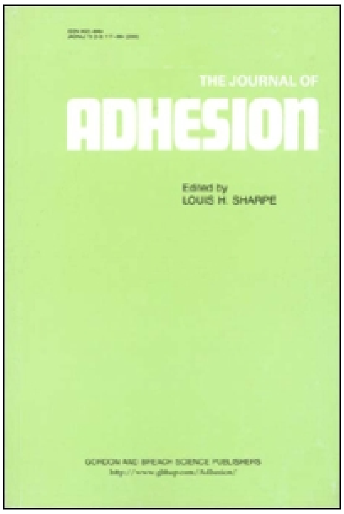


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## Van der Waals Attraction in Multilayer Structures-II

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# Van der Waals Attraction in Multilayer Structures—II

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The vdW attraction in multilayer structures is reconsidered on the basis of Green's function techniques and finite boundary conditions. No difficulties related to branch points are encountered in the course of integration. Electric and magnetic modes are considered. By applying Floquet's theorem an exact expression for the vdW energy between periodic multilayers is obtained. The relations of the present method to the surface mode hypothesis and to the reaction field approach are shown. Quantitative conclusions pertaining to the dependence of the vdW energy on the separation $d$ are drawn.

## I INTRODUCTION

Two alternative approaches to the elucidation of the van der Waals energy in multilayer systems have so far been reported[1–3]. First, there is the approach based on the surface mode hypothesis and van Kampen's integration method[4–6]; the second is the perturbation approach based on fluctuation fields[7,8]. The surface mode approach considers a finite array of layers and solves Maxwell's equations with respect to electromagnetic modes decreasing exponentially in the exterior[1,2]. Their energy gain with varying thickness of a distinct inner layer yields the van der Waals force across that layer. The restriction to exponentially decreasing modes provides mathematical simplicity, while completely neglecting the problem of the outgoing radiation. The true eigenvectors of Maxwell's equations in a homogeneous medium, the Hertzian modes, are known to possess a nonvanishing Poynting vector and thus are not normalizable in infinite space. We are now wondering whether there is any additional contribution of these modes to the van der Waals energy.

The perturbation approach to the van der Waals energy starts with the consideration of the instantaneous field fluctuations in the layer in question and satisfies Maxwell's equations by successively adding the fields reflected or transmitted by the different interfaces[3]. In a finite array of layers an outgoing radiation field is left, i.e. the instantaneous fluctuations continuously lose energy to the exterior. This energy dissipation is balanced by the random energy flow from the exterior to the fluctuations, which is the origin of the latter so that the mean intensity of fluctuations is obtained from the fluctuation-dissipation theorem. The perturbation approach thus accounts for both the ingoing and the outgoing radiation.

Despite these differing treatments of the radiation field in the two approaches, one finds similar final expressions for the van der Waals energy[1—3]. The dispersion energy is given by a frequency integral over the susceptibilities and structure factors of the layers considered. The frequency integration involved in the surface mode approach extends twice along the positive imaginary half-axis, while that of the perturbation approach extends once along the full imaginary axis. Both integrals agree if either the susceptibilities are symmetric with respect to the real frequency axis, or if advanced and retarded susceptibilities are used in symmetric manner. However, it is difficult to justify the mixed use of advanced and retarded susceptibilities within the surface mode approach which actually considers neither ingoing nor outgoing modes. There are better reasons to use different susceptibilities within the perturbation approach, where the instantaneous fields, by not being brought about by causality, may be treated by advanced susceptibilities, whereas retarded susceptibilities have to be used for all induced fields.

Attempts at solving this problem by considering non-retarded rather than retarded reaction fields are likewise unsuccessful. Treating electrostatic interaction fields avoids the question of ingoing and outgoing radiation, whereas the question of the correct final expression for the dispersion energy remains open.

A consistent treatment of all electromagnetic modes becomes possible on the basis of finite boundary conditions[9,10]. Let us avoid the distinction between ingoing and outgoing modes by introducing a large cavity, which reflects all modes anyway. It singles out those Hertzian modes whose normal components vanish on the surface of the cavity. We are left with normalizable modes and a discrete rather than a continuous energy spectrum. The discreteness of the spectrum greatly simplifies the summation over all modes, and we are able to replace this summation by a contour integral over the logarithmic derivative of the dispersion function. Returning to infinite size of the cavity not before this integration is shifted to the imaginary frequency axis, we wind up with a final energy expression containing the frequency integration over susceptibilities and structure factors along the full imaginary axis.

In addition to applying this exact retarded treatment to the dispersion energy in multilayers, we use Floquet's theorem. In periodic multilayers it is not necessary to satisfy the boundary conditions for the electromagnetic modes at all interfaces successively, as required by earlier treatments. The translational invariance of an infinite periodic lattice entails that the normalizable solutions of Maxwell's equations in this lattice merely pick up a phase factor on translation by one period. If a finite periodic lattice is considered, one obtains linear combinations of two modes with inverse phase factors. This theorem enables us to reduce the dispersion function of the allowed electromagnetic modes to a finite determinant whose order $n$ equals the number of layers per period. This relieves us from the tedious counting and summing of reflection and transmission fields reported earlier at the expense of evaluating a finite determinant. This evaluation is greatly simplified by the fact that due to the integration technique applied we do not need the eigenvectors but only the value of the determinant on the imaginary frequency axis. This enables several direct conclusions to be drawn on the qualitative behavior of the dispersion energy.



## II ARBITRARY MULTILAYERS

Let us consider an arbitrary system of parallel layers $j$ with the dielectric constant $\varepsilon_j(\omega)$, the magnetic permeability $\mu_j(\omega)$ and the thickness $d_j$ (see Figure 1). Solving Maxwell's equations in terms of plane waves we introduce electric fields of the form

$$\boldsymbol{E}_\varepsilon = \text{curl curl}\, \epsilon_j^{-1}\, \mathrm{e}^{i(k_x x + k_y y)}\{\boldsymbol{a}_j\, \mathrm{e}^{ik_j(z-z_j)} + \boldsymbol{b}_j\, \mathrm{e}^{-ik_j(z-z_j)}\} \tag{1}$$

$$\boldsymbol{E}_\mu = \text{curl}\, \mathrm{e}^{i(k_x x + k_y y)}\{\boldsymbol{a}_j\, \mathrm{e}^{ik_j(z-z_j)} + \boldsymbol{b}_j\, \mathrm{e}^{-ik_j(z-z_j)}\} \tag{2}$$

with $\mathbf{a}_j$, $\mathbf{b}_j$ being vectors normal to the interfaces

$$\boldsymbol{a}_j = (o, o, a_j)\,; \quad \boldsymbol{b}_j = (o, o, b_j) \tag{3}$$

and

$$\mathbf{K}_j^2 = k_x^2 + k_y^2 + k_j^2 = \left(\frac{\omega}{c}\right)^2 \epsilon_j \mu_j \tag{4}$$

At the interface $z = z_{j+1}$ between layers $j$ and $j+1$ we require continuity of the normal components of the electric displacement and of the magnetic induction and of the tangential components of the electric and of the magnetic field, which yields the boundary conditions

$$a_j\, \mathrm{e}^{ik_j d_j} + b_j\, \mathrm{e}^{-ik_j d_j} = a_{j+1} + b_{j+1} \tag{5}$$

$$x_j[a_j\, \mathrm{e}^{ik_j d_j} - b_j\, \mathrm{e}^{-ik_j d_j}] = x_{j+1}[a_{j+1} - b_{j+1}] \tag{6}$$

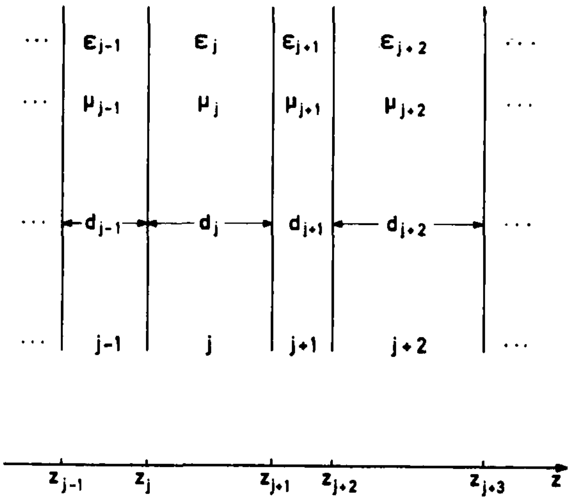


FIGURE 1 Multilayer system.



where

$$x_j = k_j \epsilon_j^{-1} \tag{7}$$

for the electric modes (1), and

$$x_j = k_j \mu_j^{-1} \tag{8}$$

for the magnetic modes (2).

## III PERIODIC MULTILAYERS

Let us now turn to periodic layer systems, i.e. let us assume that layer $j + n$ has the same properties as layer $j$ for all $j$ and fixed $n$. In this case we know from Floquet's theorem that the periodic system of boundary conditions (5), (6) has the particular solutions

$$a_{j+n} = \xi a_j; \quad b_{j+n} = \xi b_j \tag{9}$$

Insertion of (9) into (5), (6) yields a finite secular determinant of the order of $2n$

$$
2^n A(\xi) =
\begin{vmatrix}
e^{ik_1d_1} & x_1^{-1}e^{-ik_1d_1} & 1 & x_2^{-1} & & & \\
-x_1e^{ik_1d_1} & e^{-ik_1d_1} & -x_2 & 1 & & & \\
 & & e^{ik_2d_2} & x_2^{-1}e^{-ik_2d_2} & \cdots & & \\
 & & -x_2e^{ik_2d_2} & e^{-ik_2d_2} & \cdots & & \\
 & & & & \cdots & 1 & x_n^{-1} \\
 & & & & \cdots & -x_n & 1 \\
\xi e^{inn} & x_1^{-1}\xi e^{inn} & & & & e^{ik_nd_n} & x_n^{-1}e^{-ik_nd_n} \\
-x_1\xi e^{inn} & \xi e^{inn} & & & & -x_ne^{ik_nd_n} & e^{-ik_nd_n}
\end{vmatrix}
\tag{10}
$$

Solving for $\xi$ we find

$$A(\xi) = \xi^2 - 2\xi\eta(n) + 1 = 0 \tag{11}$$

where

$$\eta(2) = \cos k_1d_1 \cos k_2d_2 - \frac{1}{2}\left(\frac{x_1}{x_2} + \frac{x_2}{x_1}\right)\sin k_1d_1 \sin k_2d_2 \tag{12}$$

$$
\begin{aligned}
\eta(3) = {} & \cos k_1d_1 \cos k_2d_2 \cos k_3d_3 \\
& - \frac{1}{2}\left(\frac{x_1}{x_2} + \frac{x_2}{x_1}\right)\sin k_1d_1 \sin k_2d_2 \cos k_3d_3 \\
& - \frac{1}{2}\left(\frac{x_2}{x_3} + \frac{x_3}{x_2}\right)\cos k_1d_1 \sin k_2d_2 \sin k_3d_3 \\
& - \frac{1}{2}\left(\frac{x_3}{x_1} + \frac{x_1}{x_3}\right)\sin k_1d_1 \cos k_2d_2 \sin k_3d_3
\end{aligned}
\tag{13}
$$

The quadratic Eq. (11) has two solutions $\xi$, one being the inverse of the other. If the susceptibilities in the different layers differ only slightly, so that $x_1 \simeq x_2 \simeq \ldots \simeq x_n$, we find $\eta\,(n) \simeq \cos \sum k_jd_j < 1$. In this case, $\xi$ is merely a phase factor.

The general solution of the linear system of boundary conditions (5), (6) can be written as follows

$$a_j = a_{i1}\xi^m + a_{i2}\xi^{-m} \tag{14}$$

$$b_j = b_{i1}\xi^m + b_{i2}\xi^{-m} \tag{15}$$

where $i$ and $m$ result from the reduction of $j$ to a basic period of layers,

$$i \equiv j(\mathrm{mod}\ n)\,; \qquad = mn + i \tag{16}$$

We know the amplitudes $a_j$, $b_j$ everywhere in the periodic multilayer once we know those in a basic period. As in the case of half-spaces, $a_j$, $b_j$ are built up from two inverse exponential terms.

## IV FINITE PERIODIC MULTILAYERS

On the basis of (14), (15) we are able to calculate the amplitudes $a_j$, $b_j$ on the right-hand side of a finite periodic multilayer from those on the left-hand side. We are interested in two types of external boundary conditions: in the finite boundary conditions imposed by a cavity (i) and in surface modes (ii).

Let us consider the finite multilayer shown in Figure 2. Introducing the cavity implies that we have to put $\underset{\sim}{E} = 0$ on the left-hand surface and $x_l = \infty$.

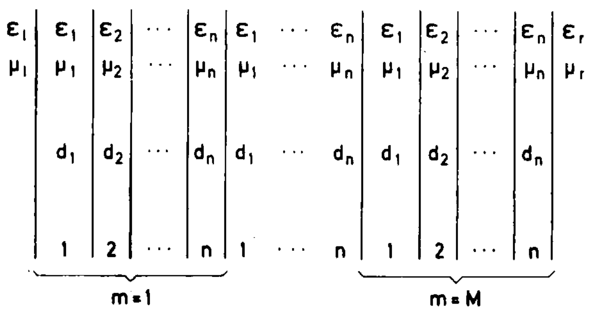


FIGURE 2 Finite periodic multilayer.

The surface mode condition, on the other hand, requires that $\underset{\sim}{E}$ decreases exponentially in the exterior for positive imaginary values of $k_j$, i.e. we have to assume $a_e = 0$. According to (5), (6) we can satisfy both conditions by putting

$$(x_l + x_1)a_1 + (x_l - x_1)b_1 = 0 \tag{17}$$

$x_l = \infty$ corresponds to finite boundary conditions, $x_l \neq \infty$ corresponds to surface modes.

The dissection of $a_1$, $b_1$ according to (14), (15) is achieved by allowing for the fact that the initial values of the particular solutions (9) satisfy

$$a_{11}A_{2n2}(\xi) + b_{11}x_1A_{2n1}(\xi) = 0 \tag{18}$$

$$a_{12}A_{2n2}(\xi^{-1}) + b_{12}x_1A_{2n1}(\xi^{-1}) = 0 \qquad (19$$

where the subdeterminants $A_{ij}(\xi)$ result from $A(\xi)$ by omission of row $i$ and column $j$.
At the right-hand side of the finite multilayer shown in Figure 2 we find according to (5), (6) and (14), (15)

$$(a_{11} + b_{11})\xi^{M+1} + (a_{12} + b_{12})\xi^{-(M+1)} = a_r + b_r \tag{20}$$

$$x_1(a_{11} - b_{11})\xi^{M+1} + x_1(a_{12} - b_{12})\xi^{-(M+1)} = x_r(a_r - b_r) \tag{21}$$

Combining (17) to (21) we wind up with

$$\frac{a_r}{b_r} = \frac{\begin{vmatrix} \xi^M \begin{vmatrix} x_r - x_1 & A_{2n2}(\xi) \\ x_r + x_1 & x_1 A_{2n1}(\xi) \end{vmatrix} \begin{vmatrix} x_l + x_1 & A_{2n2}(\xi) \\ x_l - x_1 & x_1 A_{2n1}(\xi) \end{vmatrix} \\ \xi^{-M} \begin{vmatrix} x_r - x_1 & A_{2n2}(\xi^{-1}) \\ x_r + x_1 & x_1 A_{2n1}(\xi^{-1}) \end{vmatrix} \begin{vmatrix} x_l + x_1 & A_{2n2}(\xi^{-1}) \\ x_l - x_1 & x_1 A_{2n1}(\xi^{-1}) \end{vmatrix} \end{vmatrix}}{\begin{vmatrix} \xi^M \begin{vmatrix} x_r + x_1 & A_{2n2}(\xi) \\ x_r - x_1 & x_1 A_{2n1}(\xi) \end{vmatrix} \begin{vmatrix} x_l + x_1 & A_{2n2}(\xi) \\ x_l - x_1 & x_1 A_{2n1}(\xi) \end{vmatrix} \\ \xi^{-M} \begin{vmatrix} x_r + x_1 & A_{2n2}(\xi^{-1}) \\ x_r - x_1 & x_1 A_{2n1}(\xi^{-1}) \end{vmatrix} \begin{vmatrix} x_l + x_1 & A_{2n2}(\xi^{-1}) \\ x_l - x_1 & x_1 A_{2n1}(\xi^{-1}) \end{vmatrix} \end{vmatrix}} \tag{22}$$

The ratio of the amplitudes $a_r/b_r$ at the right-hand side of the multilayer under consideration is an even function of all interior wave numbers $k_j$, $j = 1, 2, \ldots, n$, according to

$$\left.\begin{aligned} [A(\xi)]_{-kj} &= [A(\xi)]_{kj} \\ [x_1 A_{2n1}(\xi)]_{-kj} &= [A_{2n2}(\xi)]_{kj} \\ [x_1 A_{2n1}(\xi)]^* &= A_{2n2}(\xi^{-1}) \end{aligned}\right\} \tag{23}$$

A change in sign of the wave number $k_r$ at the right-hand side yields the inverse ratio $b_r/a_r$.

## V TWO PERIODIC MULTILAYERS

In order to find the allowed electromagnetic modes in the presence of two periodic multilayers, we have to assume agreement of the amplitudes $a_r$, $b_r$ in the interspace. We now consider the two finite periodic multilayers shown in Figure 3, and number the layers within multilayer 1 from the left to the right, and those within multilayer 2 from the right to the left.

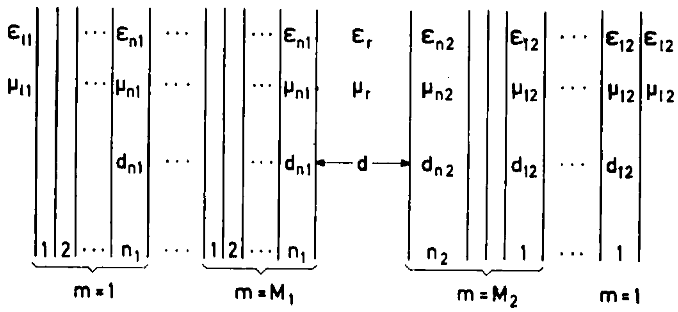


FIGURE 3 Attracting multilayers.

Taking into account this inversion of multilayer 2, we have to write

$$\left.\begin{aligned} a_{r1}\,e^{ik_r d} &= b_{r2} \\ b_{r1}\,e^{-ik_r d} &= a_{r2} \end{aligned}\right\} \tag{24}$$

We thus obtain the dispersion relation

$$e^{ik_r d}a_{r1}a_{r2} - e^{-ik_r d}b_{r1}b_{r2} = 0 \tag{25}$$

where $a_{rj}$, $b_{rj}$, $j = 1,2$ result from (22) by adding the second subscript $j$, which refers to multilayers 1 and 2, to all relevant quantities.

Dispersion relation (25) is valid both for finite boundaries and for surface modes. By means of properties (23) we find relation (25) to be real on the real frequency axis, if we assume the susceptibilities $\varepsilon_j(\omega)$, $\mu_j(\omega)$ to be real there, and if we consider the limit $x_{l1}$, $x_{l2} = \infty$. In this case all eigenfrequencies $\omega$ are also real.

The application of the finite boundary conditions $x_{l1}$, $x_{l2} = \infty$ provides us with a set of completely decoupled electromagnetic modes. Any imaginary part of the eigenfrequencies $\omega_m$ results exclusively from the properties of the susceptibilities $\varepsilon_j(\omega)$, $\mu_j(\omega)$, i.e. there is an energy dissipation to the electron states of the multilayers under investigation, but no direct energy exchange between the electromagnetic modes.

The application of the surface mode condition $x_{l1}$, $x_{l2} \neq \infty$, on the other hand, yields complex eigenfrequencies $\omega_m$ even if the susceptibilities $\varepsilon_j(\omega)$, $\mu_j(\omega)$ are real on the real frequency axis, i.e. we are left with directly coupled electromagnetic modes. This shows that the surface mode hypothesis is not at all convenient for selecting allowed electromagnetic modes. It will be demonstrated to cause additional difficulties in the following calculations of the vdW energy between multilayers 1 and 2.

## VI VAN DER WAALS ENERGY

Having found a complete set of allowed electromagnetic modes we are now able to calculate the vdW energy $\Delta E$ between multilayers 1 and 2. We have to provide each eigenfrequency with its free quantum energy $kT\, ln\, 2\sinh(\hbar\omega/2kT)$ and to sum the change in energy relative to the limit $d = \infty$.

$$\Delta E = \mathrm{Re} \sum_m \left[ kT\, ln2 \sinh \frac{\hbar\omega_m}{2kT} \right]_\infty^d \tag{26}$$

By restricting ourselves to summing only the real part of the energy gain, we account for the continuous energy exchange between electromagnetic modes and electrons. The energy dissipation from the electromagnetic modes (photons) to the electrons is made up, in thermal equilibrium, by an equivalent energy dissipation from the electrons to the electromagnetic modes. The true dispersion relation of the coupled system electrons plus photons is hermitic, its eigenfrequencies are real. A semi-classical decoupling of electrons and photons on the basis of susceptibilities has to allow for retarded and advanced susceptibilities as well. This is most appropriately done by calculating only the real part of the photon energy gain[9,10]



## VII COMPLEX INTEGRATION

The most convenient method of carrying out the summation (26) is the Green's function technique introduced by van Kampen *et al.*[4]. It makes use of the analytical identity

$$\sum_{\text{zeros}} f(\omega_m) - \sum_{\text{poles}} f(\omega_n) = \frac{1}{2\pi i} \oint d\omega f(\omega) \frac{d}{d\omega}\, ln\, g(\omega) \tag{27}$$

where $\omega_m$ runs over all zeros and $\omega_n$ runs over all poles of $g(\omega)$ within the contour of integration. This contour, on the other hand, must not contain poles of $f(\omega)$. If $g(\omega)$ is chosen such that its zeros and poles yield the eigenfrequencies of the allowed electromagnetic modes for separations $d$ and $\infty$ of the multilayers, respectively, we can use (27) directly for summing (26).

This is done by introducing a dispersion function (Green's function) $D(\omega, k_r)$ which is the ratio of dispersion relations (25) for finite and infinite separation

$$D(\omega,k_r) = 1 - e^{2ik_r d} \frac{a_{r1}}{b_{r1}} \frac{a_{r2}}{b_{r2}} \tag{28}$$

and putting[9,10]

$$(\omega) = kT\,ln \sinh \frac{\hbar\omega}{2kT} \tag{29}$$

$$g(\omega) = (D_\epsilon^{\mathrm{ret}} D_\epsilon^{\mathrm{adv}} D_\mu^{\mathrm{ret}} D_\mu^{\mathrm{adv}})^{\frac{1}{2}} \tag{30}$$

The subscripts ε and $\mu$ in (30) refer to the electric and magnetic modes (1) and (2), respectively. The superscripts ret and adv require the use of retarded and advanced susceptibilities.

Since the poles of the retarded and advanced dispersion functions $D_{\epsilon,\mu}^{ret}$ and $D_{\epsilon,\mu}^{adv}$ lie in the lower and upper half frequency plane, respectively, we choose the contour of integration in (27) to enclose the full right-hand half plane. It runs along the imaginary axis from $+\,i\infty$ to $-\,i\infty$ and is closed by a semicircle. Since the integral on the semicircle vanishes, we find

$$\Delta E = -\frac{1}{2\pi}\int_0^\infty dkk \frac{1}{4\pi i}\int_{-i\infty}^{+i\infty} d\omega\, kT\, ln \sinh \frac{\hbar\omega}{2kT}\frac{d}{d\omega}\, ln\; D_\epsilon^{\mathrm{ret}} D_\epsilon^{\mathrm{adv}} D_\mu^{\mathrm{ret}} D_\mu^{\mathrm{adv}} \tag{31}$$

The integration over $k$ in (31) is that over the tangential wave numbers $k_x$, $k_y$. After integration by parts and making use of the fact that $D_\epsilon^{ret} D_\epsilon^{adv}$ and $D_\mu^{ret} D_\mu^{adv}$ are even functions on the imaginary frequency axis, we obtain

$$\Delta E = \frac{1}{2\pi}\int_0^\infty dkk \frac{\hbar}{4\pi i}\int_{-i\infty}^{+i\infty} d\omega\, \mathrm{ctgh} \frac{\hbar\omega}{2kT}\, ln\; D_\epsilon(\omega, k_r) D_\mu(\omega, k_r) \tag{32}$$

The frequency integration in (32) by-passes the poles of $\mathrm{ctgh}(\hbar\omega/2kT)$ from the right, i.e. we obtain alternatively

$$\Delta E = \frac{kT}{4\pi}\int_0^\infty dkk \sum_{n=-\infty}^{+\infty} ln\; D_\epsilon(i\omega_n, k_r) D_\mu(i\omega_n, k_r) \tag{33}$$

where

$$\hbar\omega_n = 2\pi nkT \tag{34}$$

## VIII BOUNDARY CONDITIONS

With $\omega$ being imaginary, we find the normal wave numbers $k_j$ for all values of the parallel wave numbers $k_x$, $k_y$ to become imaginary, too. In this case, $\xi$ is no longer a phase factor, but causes a real exponential increase or decrease of the amplitudes $a_j$, $b_j$. Returning to infinite multilayers in the final expressions (32), (33), therefore, enables us to omit all negative powers of $\xi$ in the ratios $a_{rj}/b_{rj}$ according to (22), $j = 1,2$. The dispersion function (28) becomes independent of the normal wave numbers $k_{1j}$ in the exterior, i.e. independent of our choice of boundary conditions.

This independence of the final energy expressions (32), (33) of the choice of boundary conditions in the case of infinite multilayers seems to justify the use of the cavity and of the surface mode hypothesis to the same extent. However, this would be an erroneous conclusion. The above procedure actually applies only to the boundary conditions imposed by the cavity.

We emphasized in Section 5 that the dispersion relation (25) yields real eigenfrequencies, i.e. decoupled electromagnetic modes, only in the limit $x_{l1}, x_{l2} = \infty$. The application of the surface modes condition rather leaves us with directly coupled electromagnetic modes. This entails that the dispersion function (28) is not analytic in a single frequency plane. We find branch points at $x_{l1} = 0$, $x_{l2} = 0$ which connect four different Riemann surfaces $\pm x_{l1}$, $\pm x_{l2}$.

The missing decoupling of electromagnetic modes raises severe doubts as to the applicability of Bose statistics. The existence of branch points impedes the application of the complex integration techniques. There is no obvious principle of how to integrate around the branch points and the respective intersections. Consideration of outgoing plane waves only means an intuitive selection of that Riemann surface in which the integral along the imaginary axis converges. This applies to Lifshitz's[11,12] and van Kampen's[4-6] procedure as well.

Having been satisfied that only the application of finite boundaries enables a consistent utilization of the dispersion relation, of Bose statistics and of the contour integration, we conclude that the correct contour of integration in the final energy expression (32) is from $-i\infty$ to $+i\infty$, rather than twice from 0 to $+i\infty$, as suggested by investigations based on the surface mode hypotheses[4-6].

## IX QUANTITATIVE CONCLUSIONS

In principle, Eqs. (22), (28) and (33) would enable an exact integration of the vdW energy between periodic multilayers. Actually, this integration is hampered by the lack of reliable experimental data relating to the frequency dependence of the susceptibilities involved. In order to obtain quantitative results it is necessary to dissect the exact integrals into integrals related only to adjacent layers. In view of the fact that the dispersion relation (28) enters the final energy expressions only at imaginary values of $\omega$ and of the normal wave numbers $k_j$, it is logical to expand it in terms of $exp(ik_jd_j)$. We may expect all resulting integrals to converge rapidly.

This expansion method turns out to be equivalent to the perturbation approach reported earlier.[3] For the geometric situation shown in Figure 3 we obtain successively

$$D(\omega, ik_r) = 1 - e^{-2k_r d}\frac{x_r - x_{n1}^{\text{eff}}}{x_r + x_{n1}^{\text{eff}}}\frac{x_r - x_{n2}^{\text{eff}}}{x_r + x_{n2}^{\text{eff}}} \tag{35}$$

and

$$x_{ij}^{\text{eff}} = x_{ij}\frac{x_{ij} + x_{i-1j}^{\text{eff}} \operatorname{ctgh} k_{ij}d_{ij}}{x_{ij} \operatorname{ctgh} k_{ij}d_{ij} + x_{i-1j}^{\text{eff}}} \tag{36}$$

for $i = 1, \ldots, n_j$ and $j = 1,2$. We can describe each multilayer by an effective inverse susceptibility $x_{nj}^{\text{eff}}$ which depends explicitly on the normal wave numbers $k_{ij}$.

Inserting (35) into (33) and replacing the integration over the tangential wave number $k$ by that over the normal wave number $k_r$ in the interspace according to (4) we obtain

$$\Delta E = \frac{kT}{4\pi}\sum_{n=-\infty}^{+\infty}\int_{Kr}^{\infty} dk_r k_r \left\{ ln\left(1 - e^{-2k_r d}\frac{x_r - x_{n1}^{\text{eff}}}{x_r + x_{n1}^{\text{eff}}}\frac{x_r - x_{n2}^{\text{eff}}}{x_r + x_{n2}^{\text{eff}}}\right)_\varepsilon + ln\left(1 - e^{-2k_r d}\frac{x_r - x_{n1}^{\text{eff}}}{x_r + x_{n1}^{\text{eff}}}\frac{x_r - x_{n2}^{\text{eff}}}{x_r + x_{n2}^{\text{eff}}}\right)_\mu \right\} \tag{37}$$

($K_r = (\omega/c_n)\sqrt{\varepsilon_r\mu_r}$. We find an electric as well as a magnetic contribution to the dispersion energy. The electric contribution usually predominates the magnetic contribution, i.e., the variation of the dielectic constant $\varepsilon_j(\omega)$ is larger than that of the magnetic permeability $\mu_j(\omega)$.

The relative contribution by the different layers to the dispersion energy (37) depends sensitively on the width $d$ of the interspace. If $d$ is small compared to the thickness $d_{n1}$, $d_{n2}$ of the first left-hand and right-hand layers, we find ctgh $k_{nj}d_{nj}$ to be approximately equal to 1 throughout the region of integration in (32), (33), i.e. we may put $x_{nj}^{\text{eff}} = x_{nj}$. In that case we recover the findings reported by Lifshitz for the dispersion energy between half-spaces[11,12]. The exact frequency integration extends along the full imaginary axis rather than twice along the upper half axis.

For studying the behavior of the dispersion energy with varying thickness $d_{ij}$ of the different layers it is convenient to rewrite (36) in the form

$$x_{ij}^{\text{eff}} = x_{ij}\frac{1 - e^{-2k_{ij}d_{ij}}\dfrac{x_{ij} - x_{i-1j}^{\text{eff}}}{x_{ij} + x_{i-1j}^{\text{eff}}}}{1 + e^{-2k_{ij}d_{ij}}\dfrac{x_{ij} - x_{i-1j}^{\text{eff}}}{x_{ij} + x_{i-1j}^{\text{eff}}}} \tag{38}$$

Expanding (38) with respect to the exponentials $exp(-2k_{ij}d_{ij})$ or with respect to the relative change in susceptibility $(x_{ij} - x^{eff}_{i-1j})/(x_{ij} + x^{eff}_{i-1j})$ we learn that (37) is built up from a power series with respect to these quantities, too. The total exponentials arising are linear combinations of all distances $d_{ij}$ occurring in the multilayer system, i.e., all effective phase shifts $k_{ij}d_{ij}$ of the interacting modes on their motion between the interfaces have to be added. The total dispersion energy is given by a sum over contributions of all closed paths which result from the repeated reflections and transmissions of the modes at all interfaces. This is just the way in which the dispersion energy arises when the perturbation approach is applied. Exact agreement with the findings reported earlier[3] is obtained if the nonretarded limit $c \to \infty$, $k_{ij} = k_r$ of expression (37) is taken.

The contribution of a distinct layer to the dispersion energy (37) depends on the relative phase shift, which the layer imposes on the radiation field. The layers next to the interspace in Figure 3 cause a small and large relative phase shift if their thickness is small and large compared to the width of the interspace, respectively. A significant contribution of an adsorbate layer to the dispersion energy may be expected only if its thickness exceeds the separation $d$. In the opposite case the main contribution to the dispersion energy arises from the bulk material. This has first been concluded from investigations on the effect of layers adsorbed at the surface of interacting spheres,[13,14] and was experimentally verified by Tabor and Israelachvili for the example of stearic acid films on mica[15].

If, in particular, we consider a periodic double layer, where the susceptibility of the second neighboring layers equals that of the interspace, we find the vdW energy to decrease more rapidly with increasing separation than in the case of half-spaces, i.e. more rapidly than $d^{-2}$. This has also been found by Ninham and Parsegian[2].



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