On a reformulation of the theory of Lifshitz–van der Waals interactions in multilayered systems

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In order to investigate the form of the van der Waals interaction in different multilayer geometries we reformulate the Lifshitz theory in terms of an algebra of 2×2 matrices. This device allows us to derive a closed form solution for the secular determinant of the modes in terms of simple quadratures with explicit N dependence. We specifically investigate (i) the van der Waals interactions between a substrate and a multilayer system as a function of the separation between the substrate and the multilayer system and (ii) the interaction between two multilayer systems over a medium of variable separation. [DOI: 10.1063/1.1578613]

I. INTRODUCTION

Recent experiments on bilayers adsorbed to rigid substrates have shown the complexity of interactions between a multilamellar lipid block close to a substrate.[1] Even neglecting the poorly understood effects of substrate roughness[2] there still remains much to learn regarding the interactions between a multilamellar lipid system and a rigid substrate.[3] Similar problems are raised also in other systems with multilayered geometry such as finite free standing smectic films[4] and smectic block copolymer layers.[5] Among the different forces acting in these multilayer systems van der Waals interactions are the most ubiquitous deserving to be studied in detail. We will formulate the theory of van der Waals forces in different multilayer geometries and derive closed form solutions that explicitly depend on the number of layers in the multilayer system.

Though some problems of this type have been addressed before,[7,8] the explicit dependence of the interaction on the number of layers, N, has remained hidden in implicit, recursion formulas. Here we go beyond this formulation that allows us to solve the recursion relation analytically and use this solution to write down the van der Waals interaction free energies in a form with explicit N dependence.

The plan of the paper is as follows: Following and expanding upon[7] we will first solve the electromagnetic wave equation in the case of a multilayer geometry with dielectrically homogeneous layers. The solution of the wave equation in this geometry will be obtained in terms of the 2×2 *transfer matrix* which will be decomposed into a product of two separate matrices, the diagonal *propagator matrix* and the symmetric *discontinuity matrix*, valid for the nonretarded as well as retarded cases of van der Waals interaction. The propagator matrix describes the propagation of the modes in the homogeneous regions of the multilayer geometry, while the discontinuity matrix describes the effects of the dielectric discontinuities on the electromagnetic modes. This straightforward decomposition, not noted before, allows us to create a simple mnemonic for constructing the transfer matrix in a wide variety of multilayer geometry contexts and to recast the Lifshitz theory into a simple and transparent form. We will then show how the (11) element of the transfer matrix is related to the secular determinant of the electromagnetic modes and that will allow us to write down the van der Waals free energy in terms of this element of the transfer matrix. This transparent formalism will allow us to treat the cases of (i) the van der Waals interactions between a substrate and a multilayer system as a function of the separation between the substrate and the multilayer system, and (ii) the interaction between two multilayer systems over a medium of variable separation.

The reformulation of the Lifshitz theory derived here simplifies and schematizes the calculation of the van der Waals interaction in multilayer systems into a transparent form particularly suitable for numerical computations. Because all results are derivable in terms of simple quadratures and contain explicit dependence on the number of layers in the multilayer system, the fundamental decomposition of the transfer matrix into a product of the propagator and the discontinuity matrices adds much-needed transparency and a convenient bookkeeping to the computation of van der Waals interactions in complicated multilayer geometries.

II. MODEL

Begin by focusing on a particular multilayer geometry in the z direction: a semi-infinite substrate (L) with a frequency

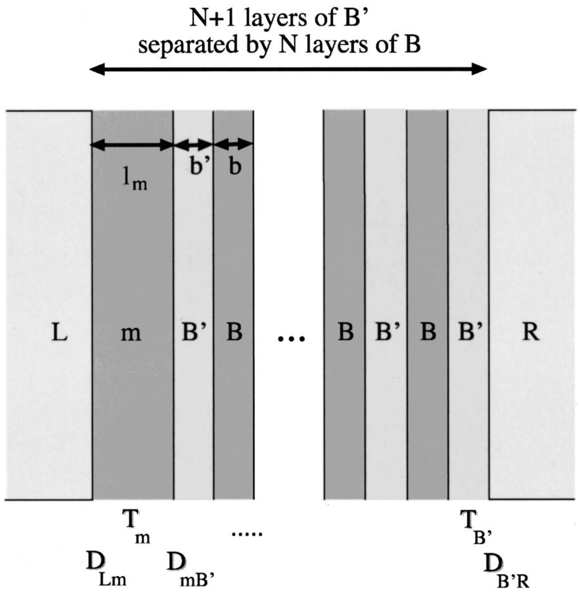

FIG. 1. A schematic presentation of the model. The multilayer slab composed of $N+1$ layers B' and N layers of B at a distance l_m away from the semi-infinite region (L) on the lhs, ending in a semi-infinite region (R) on the rhs. The matrices $\mathbb{D}_{ij}$ and $\mathbb{T}_{ij}$ are defined in the main text.

dependent dielectric function $\epsilon_L(\omega)$ separated by a layer of medium $\epsilon_m(\omega)$ with thickness l_m from an array composed of N layers (B',B) with dielectric functions $\epsilon_{B'}(\omega)$ and $\epsilon_B(\omega)$ and thicknesses b' and b, respectively (see Fig. 1). At the right hand boundary we have a semi-infinite dielectric medium (R) with $\epsilon_R(\omega)$. We will then generalize this geometry, case (i), to the case (ii) where on the lhs we also have a semi-infinite layer (L), covered with a multilayer stack composed of M (A,A') layers, interacting across the medium m, again of thickness l_m, with a multilayer stack of N (B',B) layers on the rhs ending in a semi-infinite substrate (R). If the materials A and B, as well as A' and B' are the same, the lhs multilayer is a mirror image of the rhs multilayer.

In the Lifshitz theory of van der Waals interactions the electromagnetic field fluctuation free energy $\mathcal{F}$ is obtained as[6]

$$\mathcal{F}=kT\sum_{\mathbf{Q}}\sum_{n=0}^{\infty}{}' \ln\mathcal{D}(i\xi_n,Q), \tag{1}$$

where the summation over the two-dimensional wave vector $\mathbf{Q}$ takes care of the homogeneity of the system in the (x,y) plane. The n summation is over the characteristic boson frequencies of the electromagnetic field given by $\xi_n=2\pi nkT/\hbar$, in standard notation. The prime in the summation indicates the fact that the $n=0$ term is given a weight 1/2. The secular mode equation $\mathcal{D}(\omega,Q)=0$ gives the eigenfrequencies of the EM field modes in the specified geometry.

In order to evaluate van der Waals interactions first one has to solve the wave equation with all the discontinuities implied by the system geometry. In this way one obtains a system of equations for the constant coefficients of the solution whose determinant gives the mode equation. From this *secular determinant* the van der Waals free energy emerges from Eq. (1).

III. SOLUTION OF THE WAVE EQUATION

A. The wave equation

We first derive the secular determinant for the EM modes between a half-space L and a multilayered half-space R (see Fig. 1). We use Maxwell equations in standard form (with $c^2=1/\epsilon_0\mu_0$)

$$\nabla^2\mathbf{E}(\mathbf{r})+\frac{\epsilon\mu\omega^2}{c^2}\mathbf{E}(\mathbf{r})=0,\quad \boldsymbol{\nabla}\cdot\mathbf{E}(\mathbf{r})=0, \tag{2}$$

for the electric field and

$$\nabla^2\mathbf{H}(\mathbf{r})+\frac{\epsilon\mu\omega^2}{c^2}\mathbf{H}(\mathbf{r})=0,\quad \boldsymbol{\nabla}\cdot\mathbf{H}(\mathbf{r})=0, \tag{3}$$

for the magnetic field. For succinctness we drop the explicit dependence on ω in $\mathbf{E}(\mathbf{r},\omega)$ and $\mathbf{H}(\mathbf{r},\omega)$, but it is always understood. Similarly for the displacement fields

$$\mathbf{D}(\mathbf{r})=\epsilon\epsilon_0\mathbf{E}(\mathbf{r}),\quad \mathbf{B}(\mathbf{r})=\mu\mu_0\mathbf{H}(\mathbf{r}), \tag{4}$$

valid in each homogeneous domain of the multilayer system.

We treat the electric field in detail then write the magnetic field results by analogy. Because the system is homogeneous in the (x,y) plane, the solution of the wave equation for the electric field, Eq. (2), has the form

$$\mathbf{E}(\mathbf{r})=\mathbf{e}(z)e^{\iota\mathbf{Q}\cdot\boldsymbol{\rho}},\quad \mathbf{H}(\mathbf{r})=\mathbf{h}(z)e^{\iota\mathbf{Q}\cdot\boldsymbol{\rho}}, \tag{5}$$

where $\boldsymbol{\rho}=(x,y)$ is the two dimensional radius vector and $\mathbf{Q}=(Q_x,Q_y)$. In each dielectric medium i the function $\mathbf{e}_i(z)$ must satisfy the Helmholtz equation

$$\frac{d^2\mathbf{e}_i(z)}{dz^2}+\left(\frac{\omega^2\epsilon_i\mu_i}{c^2}-Q^2\right)\mathbf{e}_i(z)=0, \tag{6}$$

whose solution has the form

$$\mathbf{e}_i(z)=\mathbf{A}_i e^{\rho_i z}+\mathbf{B}_i e^{-\rho_i z}, \tag{7}$$

with

$$\rho_i^2=Q^2-\frac{\epsilon_i\mu_i\omega^2}{c^2}. \tag{8}$$

Because both electric as well as magnetic fields are divergence free, the spatial components of $\mathbf{A}_i$, $\mathbf{B}_i$ satisfy

$$A_{i,z}=-\frac{\iota}{\rho_i}(Q_xA_{i,x}+Q_yA_{i,y}),$$
$$B_{i,z}=\frac{\iota}{\rho_i}(Q_xB_{i,x}+Q_yB_{i,y}). \tag{9}$$

In each homogeneous domain of the multilayer system, we write ϵ_i, μ_i, D_i, and B_i without explicit ω dependence. At the interfaces between these homogeneous domains the transverse components of $\mathbf{E}$, i.e., E_x and E_y, are continuous, while in the longitudinal direction it is the dielectric displacement $\mathbf{D}$ that is continuous

$$E_{i-1,x}=E_{i,x},\quad E_{i-1,y}=E_{i,y},\quad \text{and } D_{i-1,z}=D_{i,z}. \tag{10}$$

The same holds also for the $\mathbf{B}$ and $\mathbf{H}$. This constraint between coefficients reduces to enforcing the transitive relation between successive A_i, B_i, from $i=L$ to $i=R$ across the entire layered structure of Fig. 1. For two neighboring layers $i-1$, i Eqs. (10) and (9) yield

$$\begin{aligned} A_i &= \frac{\epsilon_{i-1}\rho_i + \epsilon_i\rho_{i-1}}{2\epsilon_i\rho_i}\left(e^{(\rho_{i-1}-\rho_i)l_{i-1/i}}A_{i-1}\right. \\ &\quad \left. -\overline{\Delta}_{i-1,i}e^{-(\rho_{i-1}-\rho_i)l_{i-1/i}}B_{i-1}\right), \\ B_i &= \frac{\epsilon_{i-1}\rho_i + \epsilon_i\rho_{i-1}}{2\epsilon_i\rho_i}\left(-\overline{\Delta}_{i-1,i}e^{(\rho_{i-1}-\rho_i)l_{i-1/i}}A_{i-1}\right. \\ &\quad \left. + e^{-(\rho_{i-1}-\rho_i)l_{i-1/i}}B_{i-1}\right), \end{aligned} \tag{11}$$

with

$$\overline{\Delta}_{i-1,i} = \frac{\epsilon_{i-1}\rho_i - \epsilon_i\rho_{i-1}}{\epsilon_{i-1}\rho_i + \epsilon_i\rho_{i-1}}. \tag{12}$$

Here A_i and B_i stand for $A_{i,z}$ and $B_{i,z}$ and l_i is the position of the discontinuity between the ith and the $i-1$st layers. The same analysis holds for the magnetic field starting from equation Eq. (3). The only difference compared to electric field is the substitution

$$\overline{\Delta}_{i-1,i} = \frac{\epsilon_{i-1}\rho_i - \epsilon_i\rho_{i-1}}{\epsilon_{i-1}\rho_i + \epsilon_i\rho_{i-1}} \rightarrow \Delta_{i-1,i} = \frac{\mu_{i-1}\rho_i - \mu_i\rho_{i-1}}{\mu_{i-1}\rho_i + \mu_i\rho_{i-1}}. \tag{13}$$

In this spirit we derive results only for the electric component of the EM modes and let the results for the magnetic component follow.

B. A mnemonic to construct the transfer matrix

Because of the transitive relation between successive A_i, B_i we can cast this result in a much more appealing form by introducing a vector $a_i^T = (A_i, B_i)$, in order to write Eq. (11) as

$$a_i = \mathbb{M}\cdot a_{i-1}, \tag{14}$$

where the newly introduced *transfer matrix* $\mathbb{M}$, apart from some multiplicative constant factors that are irrelevant for the subsequent analysis and have been absorbed into a redefinition of a_i, can be written in the form

$$\mathbb{M} = \begin{pmatrix} 1 & -\overline{\Delta}_{i-1,i}e^{-2\rho_{i-1}d_{i-1}} \\ -\overline{\Delta}_{i-1,i} & e^{-2\rho_{i-1}d_{i-1}} \end{pmatrix}, \tag{15}$$

with $d_{i-1} = l_{i-1,i} - l_{i-2,i-1}$.

We now observe that this transfer matrix can be factored into a product of two matrices describing the propagation of EM modes, *viz*.

$$\mathbb{M} = \begin{pmatrix} 1 & -\overline{\Delta}_{i,i-1} \\ -\overline{\Delta}_{i,i-1} & 1 \end{pmatrix} \times \begin{pmatrix} 1 & 0 \\ 0 & e^{-2\rho_{i-1}d_{i-1}} \end{pmatrix}. \tag{16}$$

With each discontinuity between media i and $i-1$, we can thus associate a symmetric matrix $\mathbb{D}_{i,i-1}$, of the form

$$\mathbb{D}_{i,i-1} = \begin{pmatrix} 1 & -\overline{\Delta}_{i,i-1} \\ -\overline{\Delta}_{i,i-1} & 1 \end{pmatrix}, \tag{17}$$

and a diagonal matrix $\mathbb{T}_i$ of the form

$$\mathbb{T}_{i-1} = \begin{pmatrix} 1 & 0 \\ 0 & e^{-2\rho_i d_{i-1}} \end{pmatrix}, \tag{18}$$

so that the transitive relation for the vector of the coefficients a_i between two successive media can be written as

$$\mathbb{M} = \mathbb{D}_{i,i-1}\times\mathbb{T}_{i-1}. \tag{19}$$

We can now easily generalize this relation to three consecutive media: $i-1$, $i-1$ and i. In this case the coefficients a_i are connected with the coefficients in the third layer a_{i-2} *via* a relation

$$a_i = \mathbb{M}\cdot a_{i-2}, \tag{20}$$

where one can now derive that the transfer matrix $\mathbb{M}$ is of the form

$$\begin{aligned} \mathbb{M} &= \begin{pmatrix} 1 & -\overline{\Delta}_{i,i-1} \\ -\overline{\Delta}_{i,i-1} & 1 \end{pmatrix} \times \begin{pmatrix} 1 & 0 \\ 0 & e^{-2\rho_{i-1}d_{i-1}} \end{pmatrix} \\ &\quad \times \begin{pmatrix} 1 & -\overline{\Delta}_{i-1,i-2} \\ -\overline{\Delta}_{i-1,i-2} & 1 \end{pmatrix} \\ &= \mathbb{D}_{i,i-1}\times\mathbb{T}_{i-1}\times\mathbb{D}_{i-1,i-2}, \end{aligned} \tag{21}$$

thus $\mathbb{M}$ is the product of matrices that enforce boundary conditions across interfaces and propagate fields traversing layers of finite thickness. These matrices are applied for regions starting on the lhs and ending on the rhs.

The meaning of the diagonal matrix $\mathbb{T}_{i-1}$ and the symmetric matrices $\mathbb{D}_{i-1,i}$ and $\mathbb{D}_{i-1,i-2}$ is as follows: $\mathbb{T}_{i-1}$, the *propagator matrix*, describes the propagation of the EM modes across the dielectrically homogeneous material of ϵ_{i-1} from the discontinuity ϵ_{i-2}, ϵ_{i-1} to the discontinuity ϵ_{i-1}, ϵ_i. $\mathbb{D}_{i-1,i}$ and $\mathbb{D}_{i-2,i-1}$, the *discontinuity matrices*, represent the jump in the material properties as the EM modes pass, respectively, from material $i-1$ to material i and from material $i-2$ to material $i-1$.

This notation can now be used for any number of layers, starting at the leftmost layer L and ending at the rightmost layer R with N layers in between

$$\begin{aligned} \mathbb{M} &= \mathbb{D}_{R,N-1}\times\mathbb{T}_{N-1}\times\mathbb{D}_{N-1,N-2}\times\mathbb{T}_{N-2} \\ &\quad \times\mathbb{D}_{N-2,N-3}\ldots\mathbb{T}_1\times\mathbb{D}_{1,L}. \end{aligned} \tag{22}$$

Still the relation between the coefficients in the first and the last media keeps the form

$$a_R = \mathbb{M}\cdot a_L. \tag{23}$$

We have thus found a simple *mnemonic* for constructing the transfer matrix for EM modes in an inhomogeneous system composed of a variable number of layers each with different dielectric properties. The mnemonic can be described as follows: with each discontinuity between media i and $i-1$ associate a symmetric matrix $\mathbb{D}_{i-1,i}$, with each homogeneous slab of material between the discontinuities $i-1$, i and $i-2$, $i-1$, associate a diagonal matrix $\mathbb{T}_{i-1}$. The transfer matrix $\mathbb{M}$ is then given by Eq. (22).

The above analysis renders the many layers problem efficiently solvable. By constructing the appropriate form of the transfer matrix, composed of the matrix products of the propagator matrix and the discontinuity matrix, we can now show how the transfer matrix is connected with the secular equation for the EM eigenmodes.

IV. THE SECULAR DETERMINANT

Because media (L) and (R) are both semi-infinite, the fields from surface modes must decay far from the outermost dielectric boundaries; hence $A_R=0$ and $B_L=0$, or $a_R^T=(0,B_R)$ and $a_L^T=(A_L,0)$. This can only happen if

$$a_R=\mathbb{M}a_L \rightarrow m_{11}\equiv\mathcal{D}_E(i\xi_N,Q)=0. \quad (24)$$

The unnormalized secular determinant is thus given *exactly* by the (11) element of the transfer matrix $\mathbb{M}$. The only excitations of the electric field that satisfy the boundary conditions are those obtained from solving the secular equation $m_{11}\equiv\mathcal{D}_E(i\xi_N,Q)=0$. For the magnetic part analogously $m_{11}\equiv\mathcal{D}_H(i\xi_N,Q)=0$. The complete electromagnetic spectrum of the problem can thus be deduced from the following EM mode secular equation

$$\mathcal{D}(i\xi_N,Q)=\mathcal{D}_E(i\xi_N,Q)\mathcal{D}_H(i\xi_N,Q)=0. \quad (25)$$

The free energy of the fluctuating EM modes is cast into a form containing the secular determinant of the electric and magnetic modes

$$\begin{aligned}\mathcal{F}&=kT\sum_{\mathbf{Q}}\sum_{n=0}^{\infty}{}'\ \ln\mathcal{D}(i\xi_N,Q)\\&=kT\sum_{\mathbf{Q}}\sum_{n=0}^{\infty}{}'\ \ln\mathcal{D}_E(i\xi_N,Q)\\&\quad+kT\sum_{\mathbf{Q}}\sum_{n=0}^{\infty}{}'\ \ln\mathcal{D}_H(i\xi_N,Q).\end{aligned} \quad (26)$$

If one is interested in the interaction free energy as a function of a variable spacing l_m, see Fig. 1, one has to consider the difference between the fluctuation free energy from Eq. (26) and its "zero," obtained at $l_m\rightarrow\infty$. This form of analysis completely reproduces the well known results on the van der Waals interactions across a single or double slab.[6]

V. A PERIODIC ARRAY OF SLABS BETWEEN TWO SEMI-INFINITE MEDIA

With this general theory where the transfer matrix is given as a product of propagator and discontinuity matrices we are now in a position to treat first the case (i) depicted on Fig. 1. The multilayer slab is composed of one layer of material m of thickness l_m and N periodic units of length $b+b'$, composed of material B and B'. All parameters are assumed to be independent of l_m.

A. Formulation through the transfer matrix

In this geometry the transfer matrix can be immediately written as

$$\mathbb{M}=\mathbb{D}_{RB'}\times\underbrace{\underbrace{\mathbb{T}_{B'}\times\mathbb{D}_{B'B}\times\mathbb{T}_B\times\mathbb{D}_{BB'}}_{\mathbb{A}}\times\cdots\times\underbrace{\mathbb{T}_{B'}\times\mathbb{D}_{B'B}\times\mathbb{T}_B\times\mathbb{D}_{BB'}}_{\mathbb{A}}}_{N}\times\mathbb{T}_{B'}\times\mathbb{D}_{B'm}\times\mathbb{T}_m\times\mathbb{D}_{mL}, \quad (27)$$

or

$$\mathbb{M}=\mathbb{D}_{RB'}\times\mathbb{A}^N\times\mathbb{T}_{B'}\times\mathbb{D}_{B'm}\times\mathbb{T}_m\times\mathbb{D}_{mL}, \quad (28)$$

where

$$\mathbb{A}=\mathbb{T}_{B'}\times\mathbb{D}_{B'B}\times\mathbb{T}_B\times\mathbb{D}_{BB'}=\begin{pmatrix}1-\overline{\Delta}_{BB'}^2e^{-2\rho_B b} & \overline{\Delta}_{BB'}(1-e^{-2\rho_B b})\\ -\overline{\Delta}_{BB'}e^{-2\rho_{B'}b'}(1-e^{-2\rho_B b}) & e^{-2\rho_{B'}b'}(e^{-2\rho_B b}-\overline{\Delta}_{BB'}^2)\end{pmatrix}. \quad (29)$$

Defining the elements of the power of the matrix $\mathbb{A}$

$$\mathbb{A}^N=\begin{pmatrix}a_{11}^{(N)} & a_{12}^{(N)}\\ a_{21}^{(N)} & a_{22}^{(N)}\end{pmatrix} \quad (30)$$

and introducing them into Eq. (28) yields the 11 element of matrix $\mathbb{M}$, i.e., the secular determinant

$$\begin{aligned}m_{11}&=(a_{11}^{(N)}-a_{21}^{(N)}\overline{\Delta}_{B'R})(1+\overline{\Delta}_{B'm}\overline{\Delta}_{B'R}^{(N)}e^{-2\rho_{B'}b'})\\&\quad\times\left(1-\overline{\Delta}_{Lm}\frac{\overline{\Delta}_{B'm}+\overline{\Delta}_{B'R}^{(N)}e^{-2\rho_{B'}b'}}{1+\overline{\Delta}_{B'm}\overline{\Delta}_{B'R}^{(N)}e^{-2\rho_{B'}b'}}e^{-2\rho_m l_m}\right),\end{aligned} \quad (31)$$

with

$$\overline{\Delta}_{B'R}^{(N)}=\frac{a_{12}^{(N)}-a_{22}^{(N)}\overline{\Delta}_{B'R}}{a_{11}^{(N)}-a_{21}^{(N)}\overline{\Delta}_{B'R}}. \quad (32)$$

As written m_{11} includes physically irrelevant l_m independent factors that will add a constant term to Eq. (26), and will thus not contribute to the interaction free energy. The l_m dependent part of the secular determinant can be on the other hand written as

$$m_{11}(l_m)\rightarrow(1-\overline{\Delta}_{Lm}\overline{\Delta}_{mR}^{\mathrm{eff}}(N)e^{-2\rho_m l_m}), \quad (33)$$

where obviously

$$\overline{\Delta}_{mR}^{\mathrm{eff}}(N)=\frac{\overline{\Delta}_{B'm}+\overline{\Delta}_{B'R}^{(N)}e^{-2\rho_{B'}b'}}{1+\overline{\Delta}_{B'm}\overline{\Delta}_{B'R}^{(N)}e^{-2\rho_{B'}b'}}. \quad (34)$$

In the case of $N=0$ layers this result straightforwardly reduces to the case of interactions in the $Lmb'R$ slab.

B. Connection with a recursion formula

We will now show that the above formulation is not only equivalent to an earlier recursion relation formulation[7] but also gives an explicit analytical solution of the recursion relation.

What differs between the cases of $N-1$ and N layers between L and R? Consider first the following recursion relation:

$$\overline{\Delta}^{(N)}_{B'R}=\frac{p_{12}+p_{11}\overline{\Delta}^{(N-1)}_{B'R}}{p_{22}+p_{21}\overline{\Delta}^{(N-1)}_{B'R}}, \tag{35}$$

with p_{ik} the elements of a matrix $\mathbb{P}$. Let the boundary condition be $\overline{\Delta}^{(0)}_{B'R}=\overline{\Delta}_{B'R}$. This recursion relation can be solved exactly using the form

$$\overline{\Delta}^{(N)}_{B'R}=\frac{g^{(N)}+f^{(N)}\overline{\Delta}_{B'R}}{h^{(N)}+e^{(N)}\overline{\Delta}_{B'R}}. \tag{36}$$

Inserting this *ansatz* into Eq. (35) and defining

$$\mathcal{C}^{(N)}=\begin{pmatrix} f^{(N)} & g^{(N)} \\ e^{(N)} & h^{(N)} \end{pmatrix}, \tag{37}$$

we find

$$\mathcal{C}^{(N)}=\mathbb{P}\mathcal{C}^{(N-1)}, \tag{38}$$

or, taking into account the boundary condition for $N=0$

$$\mathcal{C}^{(N)}=\mathbb{P}^{N}. \tag{39}$$

The recursion relation Eq. (35) becomes

$$\overline{\Delta}^{(N)}_{B'R}=\frac{p^{(N)}_{12}+p^{(N)}_{11}\overline{\Delta}_{B'R}}{p^{(N)}_{22}+p^{(N)}_{21}\overline{\Delta}_{B'R}}, \tag{40}$$

the $p^{(N)}_{ik}$ now stand for the elements of the matrix $\mathbb{P}^{N}$. From this we see that Eq. (32) is equivalent to a recursion relation of the form

$$\overline{\Delta}^{(N)}_{B'R}=\frac{a_{12}-a_{22}\overline{\Delta}^{(N-1)}_{B'R}}{a_{11}-a_{21}\overline{\Delta}^{(N-1)}_{B'R}}. \tag{41}$$

If the elements of matrix $\mathbb{A}$, a_{ik}, are taken from Eq. (29), the above recursion relation can be written in the following form:

$$\begin{aligned}\overline{\Delta}^{(N)}_{B'R}&=\frac{\overline{\Delta}_{B'B}+\overline{\Delta}^{(N)}_{BR}e^{-2\rho_B b}}{1+\overline{\Delta}_{B'B}\overline{\Delta}^{(N)}_{BR}e^{-2\rho_B b}},\\ \overline{\Delta}^{(N)}_{BR}&=\frac{\overline{\Delta}_{BB'}+\overline{\Delta}^{(N-1)}_{B'R}e^{-2\rho_{B'}b'}}{1+\overline{\Delta}_{BB'}\overline{\Delta}^{(N-1)}_{B'R}e^{-2\rho_{B'}b'}},\end{aligned} \tag{42}$$

with the boundary condition $\overline{\Delta}^{(1)}_{B'R}=\overline{\Delta}_{B'R}$. This recursion relation coincides with the result derived by Parsegian and Ninham.[8]

C. Application of the Abelès formula

With the secular determinant for the multilayer problem derived in terms of the elements of the matrix $\mathbb{A}^{N}$, Eq. (32), we now invoke an identity[9] valid for square matrices

$$\mathbb{A}^{N}=\frac{(\det\mathbb{A})^{N/2}}{\sinh\xi}\begin{pmatrix} \sinh N\xi\,\dfrac{a_{11}}{\sqrt{\det\mathbb{A}}}-\sinh(N-1)\xi & \sinh N\xi\,\dfrac{a_{12}}{\sqrt{\det\mathbb{A}}} \\ \sinh N\xi\,\dfrac{a_{12}}{\sqrt{\det\mathbb{A}}} & \sinh N\xi\,\dfrac{a_{11}}{\sqrt{\det\mathbb{A}}}-\sinh(N-1)\xi \end{pmatrix}, \tag{43}$$

where

$$\cosh\xi=\frac{1}{2}\,\frac{\mathrm{Tr}\,\mathbb{A}}{\sqrt{\det\mathbb{A}}}. \tag{44}$$

Following Abelès[9] this formula can be reproduced via induction starting from the rather trivial case of $N=2$. If we define

$$U^{(-)}_{ik}\equiv a_{ik}-e^{-\xi}\sqrt{\det\mathbb{A}}\quad\text{and}\quad U^{(+)}_{ik}\equiv a_{ik}-e^{\xi}\sqrt{\det\mathbb{A}}, \tag{45}$$

then we obtain for $\overline{\Delta}^{(N)}_{B'R}$ of Eq. (32),

$$\overline{\Delta}_{B'R}^{(N)}=\frac{U_{22}^{(-)}-e^{-2N\xi}U_{22}^{(+)}\dfrac{\dfrac{-a_{12}}{U_{22}^{(+)}}+\overline{\Delta}_{B'R}}{\dfrac{-a_{12}}{U_{22}^{(-)}}+\overline{\Delta}_{B'R}}}{-a_{21}\left(1-e^{-2N\xi}\dfrac{\dfrac{-U_{11}^{(+)}}{a_{21}}+\overline{\Delta}_{B'R}}{\dfrac{-U_{11}^{(-)}}{a_{21}}+\overline{\Delta}_{B'R}}\right)}$$

$$=\frac{(a_{22}^{*}-e^{-\xi})\left(1-e^{-2N\xi}\dfrac{-a_{21}^{*}+\overline{\Delta}_{B'R}(a_{22}^{*}-e^{\xi})}{-a_{21}^{*}+\overline{\Delta}_{B'R}(a_{22}^{*}-e^{-\xi})}\right)}{-a_{21}^{*}\left(1-e^{-2N\xi}\dfrac{(a_{11}^{*}-e^{\xi})-a_{12}^{*}\overline{\Delta}_{B'R}}{(a_{11}^{*}-e^{-\xi})-a_{12}^{*}\overline{\Delta}_{B'R}}\right)}. \tag{46}$$

Here we have substituted $a_{ik}^{*}=a_{ik}/\det\mathbb{A}$ to normalize $\mathbb{A}$. Then e^{ξ} and $e^{-\xi}$ are nothing but eigenvalues of this matrix with the property (see below)

$$(a_{11}^{*}-e^{-\xi})(a_{22}^{*}-e^{-\xi})=a_{12}^{*}a_{21}^{*}, \tag{47}$$

which is just a different way of writing down Eq. (44). Clearly in the limit of a very large number of layers, $N\to\infty$, the limiting value of $\overline{\Delta}_{B'R}^{(N)}$ should not depend on the presence of the $b'R$ discontinuity, i.e., on the value of $\overline{\Delta}_{B'R}$. This expectation is verified directly from Eq. (46) in the specified limit

$$\overline{\Delta}_{B'R}^{(N\to\infty)}=\frac{U_{22}^{(-)}}{-a_{21}}=\frac{(a_{22}^{*}-e^{-\xi})}{-a_{21}^{*}}. \tag{48}$$

This limit can be reached also *via* the recursion relation Eq. (42) which shows that for large N there is no difference in the solution of the recursion relation between the $(N-1)$st and Nth iteration. In other words the recursion relation has a *fixed point* defined by $\overline{\Delta}_{B'R}^{(N-1)}=\overline{\Delta}_{B'R}^{(N)}$ which leads immediately to Eq. (48). This can be seen as follows: inserting the ansatz $\overline{\Delta}_{B'R}^{(N-1)}=\overline{\Delta}_{B'R}^{(N)}$ back into Eq. (42) we obtain the following equation satisfied at the fixed point $\overline{\Delta}_{B'R}^{(N\to\infty)}$,

$$\overline{\Delta}_{B'R}^{(N\to\infty)}=\frac{a_{12}-a_{22}\overline{\Delta}_{B'R}^{(N\to\infty)}}{a_{11}-a_{21}\overline{\Delta}_{B'R}^{(N\to\infty)}}, \tag{49}$$

or equivalently, if we divide the numerator and the denominator on the rhs by $\det\mathbb{A}$

$$(\overline{\Delta}_{B'R}^{(N\to\infty)})^2a_{21}^{*}+(a_{22}^{*}-a_{11}^{*})\overline{\Delta}_{B'R}^{(N\to\infty)}-a_{12}^{*}=0. \tag{50}$$

Solving this quadratic equation and taking into account that by definition $\det a_{ik}^{*}=1$, we immediately obtain back Eq. (48) exactly.

VI. GENERALIZATIONS AND SPECIALIZATIONS

We can now write results for the following cases pertinent to the multilayer geometry: (i) interactions between a substrate and a multilayered slab and (ii) interactions between two multilayered slabs.

A. Interactions between a substrate and a multilayered slab

For this geometry we derive the secular determinant by putting together the secular determinant Eq. (33) and the form of the $\overline{\Delta}_{B'R}^{(N)}$ derived in Eq. (46). Disregarding now all the physically irrelevant terms that do not depend on l_m we derive the secular equation for the EM modes in this case in the form

$$m_{11}\to(1-\overline{\Delta}_{Lm}\overline{\Delta}_{mR}^{\rm eff}(N)e^{-2\rho_m l_m}). \tag{51}$$

This result can also be written in the form explicitly containing the properties of the individual layers making up the system. We first introduce the associated unitary matrix

$$\mathbb{A}^{*}=\frac{\mathbb{A}}{\sqrt{\det\mathbb{A}}}=\begin{pmatrix}a_{11}^{*} & a_{12}^{*}\\ a_{21}^{*} & a_{22}^{*}\end{pmatrix} \tag{52}$$

derived from Eq. (29). $\mathbb{A}^{*}$ has two eigenvalues $\lambda_{\pm}$ such that $\lambda_{+}\lambda_{-}=1$. These can be represented by

$$\lambda_{+}=e^{\xi}\quad\text{and}\quad\lambda_{-}=e^{-\xi}, \tag{53}$$

so that the eigenfunction equation becomes

$$\cosh\xi=\tfrac{1}{2}\,{\rm Tr}\,\mathbb{A}^{*}. \tag{54}$$

Written *in extenso*

$$\lambda_{\pm}=\frac{1}{2}\frac{{\rm Tr}\,\mathbb{A}}{\sqrt{\det\mathbb{A}}}\left(1\pm\sqrt{1-4\frac{\det\mathbb{A}}{({\rm Tr}\,\mathbb{A})^2}}\right). \tag{55}$$

From Eq. (29),

$$\begin{aligned}{\rm Tr}\,\mathbb{A}&=1-\overline{\Delta}_{B'B}^2(e^{-2\rho_{B'}b'}+e^{-2\rho_B b})+e^{-2(\rho_{B'}b'+\rho_B b)},\\ \det\mathbb{A}&=(1-\overline{\Delta}_{B'B}^2)^2e^{-2(\rho_{B'}b'+\rho_B b)},\end{aligned} \tag{56}$$

so that $\overline{\Delta}_{B'R}^{(N)}$, Eq. (46), can be written

$$\overline{\Delta}_{B'R}^{(N)}=\frac{(a_{22}^{*}-\lambda_{-})\left(1-\lambda_{-}^{2N}\dfrac{-a_{21}^{*}+\overline{\Delta}_{B'R}(a_{22}^{*}-\lambda_{+})}{-a_{21}^{*}+\overline{\Delta}_{B'R}(a_{22}^{*}-\lambda_{-})}\right)}{-a_{21}^{*}\left(1-\lambda_{-}^{2N}\dfrac{(a_{11}^{*}-\lambda_{+})-a_{12}^{*}\overline{\Delta}_{B'R}}{(a_{11}^{*}-\lambda_{-})-a_{12}^{*}\overline{\Delta}_{B'R}}\right)}. \tag{57}$$

Because $\lambda_{-}<1$ in the limit of $N\to\infty$ we derive

$$\overline{\Delta}_{mR}^{\rm eff}(N\to\infty)=\frac{\overline{\Delta}_{B'm}\overline{\Delta}_{B'B}e^{-2\rho_{B'}b'}(1-e^{-2\rho_B b})+(e^{-4\rho_{B'}b'}(e^{-2\rho_B b}-\overline{\Delta}_{B'B}^2)-\lambda_{-}(1-\overline{\Delta}_{B'B}^2)e^{-(\rho_B b+3\rho_{B'}b')})}{\overline{\Delta}_{B'B}e^{-2\rho_{B'}b'}(1-e^{-2\rho_B b})+\overline{\Delta}_{B'm}(e^{-4\rho_{B'}b'}(e^{-2\rho_B b}-\overline{\Delta}_{B'B}^2)-\lambda_{-}(1-\overline{\Delta}_{B'B}^2)e^{-(\rho_B b+3\rho_{B'}b')})}, \tag{58}$$

where we have used the explicit form of the Tr and det from Eq. (56). The van der Waals interaction free energy in this case can thus be written as

$$\mathcal{F} = kT\sum_{\mathbf{Q}} \sum_{n=0}^{\infty}{}' \ \ln(1-\overline{\Delta}_{Lm}\overline{\Delta}^{\mathrm{eff}}_{mR}(N\to\infty)e^{-2\rho_m l_m}). \quad (59)$$

We have omitted the magnetic terms of an analogous form. This form of the interaction free energy becomes more simple in the asymptotic limit of large l_m. In this case we derive after some heavy algebra that

$$\mathcal{F} = -kT\sum_{\mathbf{Q}} \sum_{n=0}^{\infty}{}' \ \overline{\Delta}_{Lm}\overline{\Delta}_{mB'}e^{-2\rho_m l_m} - kT\sum_{\mathbf{Q}} \sum_{n=0}^{\infty}{}' \ \overline{\Delta}_{Lm} \times \frac{1-\overline{\Delta}^2_{B'B}e^{2\rho_B b}-\lambda_-(1-\overline{\Delta}^2_{B'B})e^{(\rho_B b+\rho_{B'}b')}}{\overline{\Delta}_{BB'}(1-e^{-2\rho_B b})} \times e^{-2(\rho_m l_m+\rho_{B'}b'+\rho_B b)}. \quad (60)$$

To the lowest order in l_m we are simply back to the interactions between two semi-infinite slabs L and B' over m, the first term in the above equation, plus a first order correction because of the finite thickness of the region B'.

The approach to the limit $N\to\infty$ is governed by the terms $e^{-2N\xi}$ in Eq. (46), where as we know, Eq. (53), $\xi = \log\lambda_+$. We can get two explicit limiting forms of ξ in the case of the zero order $n=0$ van der Waals term, that shows the N dependence most prominently. First of all for small b, b' we get $\xi\sim\sqrt{2(1+\overline{\Delta}^2_{BB'}/1-\overline{\Delta}^2_{BB'})}Q\sqrt{bb'}$. In the opposite limit of large b, b' we get $\xi\sim Q(b+b')$. Introducing now the dimensionless form of the wave vector, $u=Ql_m$, we obtain the correlation length in the first limit as $\zeta_< \sim l_m\sqrt{1-\overline{\Delta}^2_{BB'}/2(1+\overline{\Delta}^2_{BB'})}(b+b')/\sqrt{bb'}$ and in the second limit as $\zeta_>\sim l_m$. Thus for small b, b', if the total thickness of the multilayers $N(b+b')$ is larger then $\zeta_<$ we have Eq. (59) and *mutatis mutandis* for large b, b'.

B. Interactions between two multilayered slabs

By symmetry we can generalize the above results also to the case of two multilayered slabs interacting over the region m of thickness l_m, where on the lhs we have a semi-infinite layer (L), covered with a multilayer stack composed of M (A,A') layers, interacting across the m with a multilayer stack of N (B',B) layers on the rhs ending in a semi-infinite substrate (R). Using our mnemonic for constructing the transfer matrix or applying symmetry arguments directly to Eq. (59) we arrive at

$$m_{11}\to(1+\overline{\Delta}^{\mathrm{eff}}_{Lm}(M)\overline{\Delta}^{\mathrm{eff}}_{mR}(N)e^{-2\rho_m l_m}), \quad (61)$$

where $\overline{\Delta}^{\mathrm{eff}}_{Lm}(M)$, $\overline{\Delta}^{\mathrm{eff}}_{mR}(N)$ are

$$\overline{\Delta}^{\mathrm{eff}}_{mR}(N) = \frac{\overline{\Delta}_{B'm}+\overline{\Delta}^{(N)}_{B'R}e^{-2\rho_{B'}b'}}{1+\overline{\Delta}_{B'm}\overline{\Delta}^{(N)}_{B'R}e^{-2\rho_{B'}b'}} \quad (62)$$

and

$$\overline{\Delta}^{\mathrm{eff}}_{Lm}(M) = \frac{\overline{\Delta}_{A'm}+\overline{\Delta}^{(N)}_{A'L}e^{-2\rho_{a'}a'}}{1+\overline{\Delta}_{A'm}\overline{\Delta}^{(M)}_{A'L}e^{-2\rho_{a'}a'}}. \quad (63)$$

$\overline{\Delta}^{(N)}_{B'R}$ is given by Eq. (57). $\overline{\Delta}^{(N)}_{A'L}$, on the other hand, is given by the same formula but with reversed direction of the discontinuities, which amounts to the transformation $\overline{\Delta}_{B'm}, \overline{\Delta}_{B'R} \to -\overline{\Delta}_{A'm}, -\overline{\Delta}_{A'R}$.

In the limit of a large number of layers N, $M\to\infty$ with furthermore $N=M$, the same limiting expressions apply as in the previous case except that they can now be obtained for the left multilayered slab as well as for the right-hand side. We thus get

$$m_{11}\to(1+(\overline{\Delta}^{\mathrm{eff}}_{Lm}(M\to\infty)\overline{\Delta}^{\mathrm{eff}}_{mR}(N\to\infty))e^{-2\rho_m l_m}). \quad (64)$$

The interaction free energy is thus obtained in the form

$$\mathcal{F} = kT\sum_{\mathbf{Q}} \sum_{n=0}^{\infty}{}' \ \ln(1+(\overline{\Delta}^{\mathrm{eff}}_{Lm}(M\to\infty)\overline{\Delta}^{\mathrm{eff}}_{mR}(N\to\infty)) \times e^{-2\rho_m l_m}), \quad (65)$$

plus an equivalent magnetic term. In the asymptotic limit of large l_m and for the case that the multilayers to the left and to the right of m are symmetric we obtain in complete analogy with the analysis in the preceding sections that

$$\mathcal{F} = -kT\sum_{\mathbf{Q}} \sum_{n=0}^{\infty}{}' \ \overline{\Delta}^2_{mB'}e^{-2\rho_m l_m} - kT\sum_{\mathbf{Q}} \sum_{n=0}^{\infty}{}' \times \left(\frac{1-\overline{\Delta}^2_{B'B}e^{2\rho_B b}-\lambda_-(1-\overline{\Delta}^2_{B'B})e^{(\rho_B b+\rho_{B'}b')}}{\overline{\Delta}_{BB'}(1-e^{-2\rho_B b})}\right)^2 \times e^{-2(\rho_m l_m+\rho_{B'}b'+\rho_B b)}, \quad (66)$$

plus again an analogous magnetic term. To the lowest order in l_m we are simply back to the interactions between two semi-infinite slabs B' over m, the first term in the above equation, plus a first order correction because of the finite thickness of the region B'.

VII. CONCLUSIONS

We have reformulated the theory of van der Waals forces to treat interactions within finite and infinite multilayered arrays by a straightforward and simple formalism that connects the secular mode equation with properties of the transfer marix for the EM field.

The key is to decompose the 2×2 transfer matrix into a product of propagator and discontinuity matrices in such a way that the Gaussian boundary conditions at successive interfaces of the different layers are properly enforced. The decomposition of the transfer matrix into a product of propagator and discontinuity matrices allowed us to create a simple but powerful mnemonic for constructing the secular determinant and consequently the free energy of van der Waals interactions in general multilayer geometries. This mnemonic works for the retarded as well as nonretarded cases and reduces the formula for the van der Waals free energy to simple quadratures involving explicitly the number of layers. We applied this novel formulation of the Lifshitz–van der Waals interaction to two different cases involving multilayer geometries, but it can be used in many other multilayer geometries.

If the multilayer geometry contains a repeating motif, e.g., in our case the repeating (BB') layers, the transfer matrix is then reduced to an explicit form by invoking the Abelès formula for the power of a 2×2 matrix. This device allowed us to derive the secular determinant of the EM modes in multilayer geometries in a form explicitly involving the number of these repeating layers. Our procedure is formaly equivalent to an exact solution of the implicit recursion relation obtained in the previous work.[8]

In the case of van der Waals interactions between a multilayer slab and a substrate we were able to show that the slab can be represented by an effective value of the dielectric response of the slab as a whole, as described by $\overline{\Delta}_{mR}^{\mathrm{eff}}$. In the limit of a large number of layers in the slab we derived an explicit form for this quantity dependent on the dielectric response of the B' and the B layers and their respective thicknesses. Similar arguments can be used for the interaction between two semi-infinite mirror symmetric slabs of (BB') composites interacting across m. In this case as well the interaction formula reduces to the form of interaction between two semi-infinite homogeneous layers where their effective dielectric properties depend again on the dielectric response of the (B') and the (B) layers and their respective thicknesses.

The formal reduction of the van der Waals interaction problem onto an algebra of 2×2 matrices, presented in this work, allows us to succinctly and effectively formulate the evaluation of the van der Waals interactions in complicated multilayer geometries that are much more difficult to treat in the framework of the standard approach.

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