van der Waals energy and pressure in dissipative media: Fluctuational electrodynamics and mode summation

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We derive the van der Waals energy and pressure in a planar multilayer system with arbitrary number of dissipative films between two half-spaces. A unique feature of this work is that the entire analysis is performed on the real frequency axis instead of summation over Matsubara frequencies on the imaginary frequency axis. The expression we obtain for van der Waals energy is a generalization of van Kampen and Schram’s result for dissipationless media. By considering a specific case of a vacuum gap between multilayer objects with dissipative films, we show that the van der Waals energy due to the vacuum gap can not be interpreted simply as a sum of free energy of normal modes.

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The phenomena of adhesion and cohesion play an important role in many areas of science and technology; they are responsible for stiction-related failure in microelectromechanical devices [1]; microbial adhesion is responsible for the formation of biofilms [2], and they contribute to friction and wear between surfaces [3]. Adhesion and cohesion can be loosely defined as the molecular attraction that holds together surfaces of two different substances or two identical substances, respectively. Of the interactions that are responsible for adhesion and cohesion, the van der Waals or Casimir (we will use the term “van der Waals” to refer to both van der Waals and Casimir types of interactions from now on) interaction is universal and exists between all types of atoms as well as macroscopic objects.

Lifshitz [4] and Casimir [5] determined the force between two half-spaces as a function of separation using two seemingly different methods. Lifshitz relied on Rytov’s theory of fluctuational electrodynamics [6] to determine the van der Waals pressure in the vacuum cavity between two half-spaces with frequency-dependent dielectric functions by evaluating the average electromagnetic stress tensor in vacuum due to thermal and zero-point fluctuations. Casimir evaluated the energy due to zero-point modes within a vacuum cavity between two parallel perfect electric conductors. The total free energy within this cavity is given by

$$E_c = k_B T \sum_n \ln \left[ 2 \sinh \left( \frac{\hbar \omega_n}{2 k_B T} \right) \right]. \quad (1)$$

where each value of $n$ corresponds to a different mode, $k_B$ is the Boltzmann constant, $2\pi\hbar$ is the Planck constant, and $T$ is the absolute temperature of the system. The force arises from the variation of the total free energy with thickness of the vacuum cavity. van Kampen et al. [7] and Schram [8] were the first to derive the Lifshitz formula for van der Waals pressure starting from summation of energy of electromagnetic modes in the vacuum cavity when the two half-spaces are dispersive but not dissipative. A good summary of the similarities and differences between the fluctuational electrodynamics method and the mode-summation method can be found in Ref. [9].

What happens to the van der Waals pressure when the vacuum gap is filled with a dissipative material? While Lifshitz’ original method can not be utilized directly because the stress tensor for arbitrary electromagnetic fields is not defined in dissipative media, Dzyaloshinskii, Lifshitz, and Pitaevskii [10] used techniques from quantum field theory to determine the van der Waals pressure in dissipative media. Barash and Ginzburg [11,12] justified the usage of Eq. (1) even in dissipative media on the grounds that it is possible to ascribe thermodynamic functions to electromagnetic fields in equilibrium with matter [12,13]. We derived a first-principles method, without using quantum field theory, of determining the van der Waals pressure in a dissipative and dispersive film within a multilayer structure by calculating the Maxwell stress tensor in fictitious layers of vacuum introduced in the structure [14]. Since the fictitious vacuum layers are eventually made to vanish, we retrieve the original system of interest. Using this method, the expression for van der Waals pressure in a dissipative film was shown to agree exactly with that obtained by Dzyaloshinskii, Lifshitz, and Pitaevskii [10]. Despite many works on the mode-summation method, determining van der Waals energy when at least one of the materials is dissipative is still a topic of active research [9,15–20] and has not been resolved entirely.

We, perhaps flippantly, remarked in Ref. [14] that the extension of our theoretical formalism to multilayer systems is simply an exercise in determining the appropriate Fresnel reflection and transmission coefficients. While there is some truth to that statement, as we will show here, it also underplays what can be learned from a complete analysis of the multilayer problem. The primary contribution of this paper is a derivation of an expression for van der Waals free energy of a planar multilayer system consisting of $N$ films with dissipative and dispersive dielectric functions and magnetic permeabilities between two half-spaces. The problem of van der Waals pressure and energy in planar multilayer systems has been considered before by many researchers. A subset of those works, that we are familiar with, is referenced here [21–26]. A unique feature of our derivation is that, even though it involves finding the pressure and energy in a dissipative

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material, it proceeds entirely along the real frequency axis.\textsuperscript{1}
Performing the analysis along the real frequency axis has (at least) three advantages over the analysis along the imaginary axis: (1) spectral contributions to the energy and pressure can be obtained\cite{27}, (2) contributions can be divided into propagating and evanescent waves\cite{27–29}, and (3) determination of thermal nonequilibrium van der Waals energy and pressure in a dissipative material, if at all possible to determine, will require analysis along the real frequency axis since the functions to be integrated are no longer analytic in the upper half of the complex frequency plane\cite{30,31}. The other important contribution to show that the van der Waals energy can not be expressed exclusively as a sum of free energy of normal modes when any of the materials is dissipative.

This paper is structured as follows: Expressions for van der Waals pressure and energy in a thin film as obtained from Lifshitz theory\cite{4} and the generalization by Dzyaloshinskii, Lifshitz, and Pitaevskii\cite{10,14} are given in Sec. I. In Sec. II, expressions for van der Waals energy of N-layered system with dissipative materials are obtained using fluctuational electrodynamics and the principle of conservation of energy. In Sec. III, we illuminate the similarities and differences between the fluctuational electrodynamics method and the mode-summation method to evaluate van der Waals energy when dissipation is present. We discuss the implications of our work in Sec. IV and outline some issues we have not been able to resolve to our satisfaction. We summarize our contributions in Sec. V.

I. LIFSHITZ THEORY OF VANDER WAALS ENERGY AND PRESSURE IN A PLANAR FILM

Consider a planar multilayer stack of N films sandwiched between two half-spaces L and R (see Fig. 1). All objects are at the same temperature T. The films are characterized by thickness \( d_k \), dielectric permittivity \( \varepsilon_k \), and magnetic permeability \( \mu_k \), where \( k \in \{1, 2, \ldots, N\} \). When \( k \) is replaced by \( L \) or \( R \), it refers to the properties of half-spaces \( L \) or \( R \). All dielectric permittivities and magnetic permeabilities are frequency dependent. At finite temperature, evaluation of van der Waals energy involves integration of functions over the real frequency axis or summation of an infinite sequence, each term of which is evaluated at a Matsubara frequency \( \Im = \frac{\pi n k_B T}{\hbar} \), \( n = 0, 1, 2, \ldots \). The integrals along the frequency axis are of the form \( \int_{0}^{\infty} d\omega \coth(\frac{\hbar \omega}{2 k_B T}) \Im f(\omega) \), where \( \Im f(\omega) \) stands for the imaginary part of \( f \), and \( f(\omega + i \xi) \) is an analytic function with no poles in the upper half complex frequency plane \( (\xi > 0) \), and the integral \( \int_{0}^{\infty} d\omega \equiv \lim_{\xi \to 0} f|_{\xi} \) d\omega is analytic. \( f(\omega) \) also satisfies the property that \( f(-\omega) = f(\omega) \). The analyticity of \( f \) can be exploited to replace the integral by a more (computationally) convenient sum \( -\sum_{\xi \to 0} f(i \xi_n) \). \( \sum_{\xi \to 0} \) indicates that the \( n = 0 \) term is multiplied by \( \frac{1}{2} \)\cite{4}. Both approaches yield identical values of van der Waals energy and pressure. In this paper, though, all mathematical entities are defined along the real frequency axis. Computations of integrals are also done along the real frequency axis.

The integral expression for van der Waals pressure in the \( k \)-th layer, i.e., that part of the fluctuational pressure that is influenced by the presence of discontinuities in electrical permittivity or magnetic permeability, is given by\cite{2}

\[
 p_k(z_k) = -\sum_{p=e,h} \int_{0}^{\infty} \frac{dk_k p_k}{2 \pi} \int_{0}^{\infty} d\omega \frac{\hbar}{\pi} \coth(\frac{\hbar \omega}{2 k_B T}) \times \Im \left[ ik_{z_k} \tilde{R}^{(p)}_{k,k-1}(\omega) \tilde{R}^{(p)}_{k,k+1}(\omega) e^{2k_z z_k} \right],
\]

where \( z_k \) is the thickness of the \( k \)-th layer, \( p_k \) is the \( \pm \) component of the in-plane wave vector, \( k_{z_k}(\omega) = \sqrt{\varepsilon_k(\omega) \mu_k(\omega) - k_p^2} \) is the \( z \)-component of wave vector in the \( k \)-th layer, and \( \tilde{R}^{(p)}_{k,k-1} \) is the generalized Fresnel reflection coefficients for \( p \)-polarized plane waves from film \( k \) incident at the interface with the multilayer to the left of \( k \) (composed of half-space \( L \) and films \( 1 \) through \( k - 1 \)). Similarly, \( \tilde{R}^{(p)}_{k,k+1} \) is the generalized Fresnel reflection coefficient for \( p \)-polarized plane waves from film \( k \) incident at the interface with the multilayer to the right (composed of films \( k + 1 \) through \( N \) and half-space \( R \)). \( p = e,h \) stand for transverse electric and transverse magnetic polarizations, respectively. \( \tilde{R}^{(p)}_{k,k \pm 1} \) can be determined from the following recursion relation\cite{32}:

\[
 \tilde{R}^{(p)}_{k,k \pm 1} = \frac{R^{(p)}_{k,k \pm 1} + R^{(p)}_{k,k \mp 1}[\pm 2] e^{2k_z z_k + j\xi n \pm 1}}{1 + R^{(p)}_{k,k \pm 1}[\pm 2] e^{2k_z z_k + j\xi n \pm 1}},
\]

where

\[
 R^{(p)}_{k,k \pm 1} = \frac{k_{k \pm 1}^{(p)} - k_{k \pm 1}^{(p)}}{k_{k \pm 1}^{(p)}} + \frac{k_{k \pm 1}^{(p)}}{k_{k \pm 1}^{(p)}}
\]

are Fresnel coefficients for \( p \)-polarized plane waves at the interface between layers of materials with properties \( \varepsilon_k, \mu_k \) and \( \varepsilon_{k \pm 1}, \mu_{k \pm 1} \). \( \varepsilon_k^{(p)} = \varepsilon_k \) and \( \mu_k \) for \( h \) and \( e \) polarized waves, respectively. Because of the proliferation of reflection coefficients in this paper, the different symbols are consolidated in Table I.

\textsuperscript{1}The transformation of the integral to summation of functions evaluated at Matsubara frequencies along the positive imaginary frequency axis, while not necessary, can be used eventually for computational expediency.

\textsuperscript{2}Most works give the equivalent expression for van der Waals pressure obtained by series summation over the Matsubara frequencies.
TABLE I. List of reflection coefficients used in this paper. See the equation numbers (if provided) for the definition of the reflection coefficient.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Equation</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{i,j}^{(p)}$</td>
<td>Eq. (4)</td>
<td>Reflection coefficient of a plane wave from half-space of material $i$ incident at an interface with half-space of material $j$, $i,j \neq V$ if one of the half-spaces is vacuum.</td>
</tr>
<tr>
<td>$\tilde{R}_{i,j}^{(p)}$</td>
<td>Eq. (3)</td>
<td>Reflection coefficient of a plane wave in material $i$ incident on the multilayer structure to the left of film $j$.</td>
</tr>
<tr>
<td>$\tilde{R}_{i}^{(p)}$</td>
<td>Eq. (3)</td>
<td>Reflection coefficient of a plane wave in material $i$ incident on the multilayer structure to the right of film $k$.</td>
</tr>
<tr>
<td>$\tilde{R}_{V,k}^{(p)}$</td>
<td>Eq. (10)</td>
<td>Reflection coefficient of a plane wave from vacuum incident at an interface of a thin film of material $k$ surrounded by vacuum on both sides.</td>
</tr>
<tr>
<td>$\tilde{R}_{V,[k-1]}^{(p)}$</td>
<td>Reflection coefficient of a plane wave in vacuum incident on the multilayer structure to the left of film $k-1$ (including film $k-1$).</td>
<td></td>
</tr>
<tr>
<td>$\tilde{R}_{V,[k]}^{(p)}$</td>
<td>Reflection coefficient of a plane wave in vacuum incident on the multilayer structure to the right of film $k$ (including film $k$).</td>
<td></td>
</tr>
</tbody>
</table>

$P_{k}(z_{k})$ can be obtained by differentiation of $U_{k}(z_{k})$ with respect to $z_{k}$, where $U_{k}(z_{k})$ is given by

$$U_{k}(z_{k}) = \sum_{p=e,h} \int_{0}^{\infty} \frac{dk_{p}k_{p}}{2\pi} \int_{0}^{\infty} d\omega \frac{\hbar}{2\pi} \coth \left[ \frac{\hbar\omega}{2k_{p}T} \right] \times \text{Im} \ln \left( 1 - \tilde{R}_{k,[k-1]}^{(p)} R_{k,[k-1]}^{(p)} e^{2k_{p}z_{k}} \right).$$

After integration by parts, Eq. (5) can be written as

$$U_{k}(z_{k}) = -\int_{0}^{\infty} \frac{dk_{p}k_{p}}{2\pi} \int_{0}^{\infty} d\omega \frac{\hbar}{2\pi} k_{p}T \left[ 2 \text{sinh} \frac{\hbar\omega}{2k_{p}T} \right] \times \sum_{p=e,h} \text{Im} \frac{\partial}{\partial \omega} \ln \left( 1 - \tilde{R}_{k,[k-1]}^{(p)} R_{k,[k-1]}^{(p)} e^{2k_{p}z_{k}} \right).$$

Although they do not appear as arguments of the function, $p_{k}$ and $U_{k}$ are in fact implicit functions of $z_{1}, z_{2}, \ldots, z_{k-1}, z_{k+1}, \ldots, z_{N}$ as well as $\varepsilon, \mu$ of all the materials. $U_{k}$, however, can not be interpreted as the van der Waals energy of the entire multilayer system since $U_{m}(z_{m}) \neq U_{p}(z_{n})$ if $m \neq n$ [25].

The question we ask here is as follows: what is the energy $U_{LR}^{(N)}$, which is a function of properties and dimensions of all materials in the multilayer system, from which the pressure in any constituent film can be obtained through the relation

$$p_{k}(z_{k}) = -\frac{\partial U_{LR}^{(N)}}{\partial z_{k}}, \quad k = 1,2,\ldots,N.$$  \hspace{1cm} (7)

Equation (7) can be interpreted as a system of $N$ first-order partial differential equations, the solution of which yields $U_{LR}^{(N)}$. Instead of trying to solve Eq. (7) directly, we will use conservation of energy to construct $U_{LR}^{(N)}$.

II. VAN DER WAALS ENERGY OF A PLANAR MULTILAYER SYSTEM

The method outlined in Ref. [14] can be summarized as a simple principle: the free energy of a planar multilayer system can be obtained by adding to the free energy of each component (half-spaces $L$ and $R$, and $N$ films) the work done in assembling them into the desired multilayer system. The mathematical statement of this principle is given by

$$U_{LR}^{(N)} = U_{LR}^{(0)} + \sum_{k=1}^{N} \left[ U_{V,V}^{(1)}(z_{k}) + W_{k}(z_{1},\ldots,z_{k}) \right] + U_{V,R}^{(0)} + W_{R}(z_{1},\ldots,z_{N}).$$  \hspace{1cm} (8)

where we use the following notation: the free energy of $N$ films bounded by half-spaces $L$ and $R$ is represented by $U_{LR}^{(N)}$; $U_{V,V}^{(1)}(z_{k})$ stands for the free energy of a thin film of thickness $z_{k}$ formed by the van der Waals pressure in vacuum from infinite separation to the surface of the rest of the multilayer structure in Fig. 1; $U_{LR}^{(0)}$ ($U_{V,R}^{(0)}$) is the free energy of a half-space of $L$ ($R$) adjacent to vacuum and is a constant. $U_{V,V}^{(0)}$ and $U_{V,R}^{(0)}$ do not play any role in determining the van der Waals pressure in any of the thin films. It is worth noting that the partial sum $U_{LR}^{(0)} + \sum_{k=1}^{N} U_{V,V}^{(1)}(z_{k}) + W_{k}(z_{1},\ldots,z_{k})$ is in fact $U_{V,V}^{(1)}$, the free energy of the multilayer system formed by the first $j$ films sandwiched between half-space $L$ and vacuum.

Apart from $U_{LR}^{(0)}$ and $U_{V,R}^{(0)}$, the terms in the right-hand side of Eq. (8) can be written in terms of appropriate generalized Fresnel reflection coefficients. $U_{V,V}^{(1)}(z_{k})$ can be written as [14]

$$U_{V,V}^{(1)}(z_{k}) = \sum_{p=e,h} \lim_{\Delta_{k} \to 0} \int_{0}^{\infty} \frac{dk_{p}k_{p}}{2\pi} \int_{0}^{\infty} d\omega \coth \left[ \frac{\hbar\omega}{2k_{p}T} \right] \times \frac{\hbar}{2\pi} \text{Im} \ln \left( 1 - R_{V,k}^{(p)} R_{V,k}^{(p)} e^{2k_{p}z_{k}} \right).$$  \hspace{1cm} (9)
where \( k_{z\omega}(\omega) = \sqrt{\frac{\omega^2}{c^2} - k^2} \), and

\[
\tilde{R}^{(p)}_{V,k} = \frac{R^{(p)}_{V,k}(1 - e^{i2k_z\delta_k})}{1 - R^{(p)}_{V,k} e^{2i2k_z\delta_k}}
\]

is the reflection coefficient of a plane wave in vacuum incident at the interface with a film of material \( k \) surrounded by vacuum on both sides. Although the integral in Eq. (9) has a singularity at \( \Delta_k = 0 \), it does not pose a problem when computing \( \partial U_{V,k}(z_k) / \partial z_k \) [see the discussion following Eq. (14) for an explanation; also see Ref. [14]]. \( W_k(z_1, \ldots, z_k) \) is given by

\[
W_k(z_1, \ldots, z_k) = -\sum_{p=0, h} \lim_{\delta_k \to 0} \int_0^\infty \frac{dk_p k_p}{2\pi} \int_0^\infty \frac{d\omega}{2\pi} \coth \left[ \frac{\hbar \omega}{2k_BT} \right] \Im \ln \left( 1 - \tilde{R}^{(p)}_{V,k} e^{i2k_z\delta_k} \right).
\]

where \( \tilde{R}^{(p)}_{V,[k-1]} \) is the generalized Fresnel reflection coefficient for a wave in vacuum at the interface between vacuum and the \( (k-1) \)th film. \( k-2 \) other films are present between the \( (k-1) \)th film and the half-space \( L \). \( \tilde{R}^{(p)}_{V,[k]} \) can be determined by using the recursion relation in Eq. (3). An important feature of Eqs. (9) and (11) is that both of them are obtained by calculating the Maxwell stress tensor only in vacuum, where the stress tensor is defined unambiguously [14].

Substituting Eqs. (9) and (11) into Eq. (8), \( U^{(N)}_{LR} \) is given by

\[
U^{(N)}_{LR} = \sum_{p=0, h} \int_0^\infty \frac{dk_p k_p}{2\pi} \int_0^\infty \frac{d\omega}{2\pi} \coth \left[ \frac{\hbar \omega}{2k_BT} \right] \lim_{\delta_k \to 0} \Im \ln \left[ 1 + \tilde{R}^{(p)}_{V,k} e^{i2k_z\delta_k} \right] + \sum_{k=1}^N \lim_{\delta_{k+1} \to 0} \Im \ln \left[ \left( 1 + R^{(p)}_{V,k} \tilde{R}^{(p)}_{V,[k-1]} e^{i2k_z\delta_k} \right) \left( 1 + R^{(p)}_{V,k+1} \tilde{R}^{(p)}_{V,[k]} e^{i2k_z\delta_k} \right) \right].
\]

It can be further simplified by realizing that

\[
(1 + R^{(p)}_{V,k} \tilde{R}^{(p)}_{V,[k-1]} e^{i2k_z\delta_k})(1 + R^{(p)}_{V,k+1} \tilde{R}^{(p)}_{V,[k]} e^{i2k_z\delta_k}) = (1 + R^{(p)}_{V,k} + R^{(p)}_{V,k} \tilde{R}^{(p)}_{V,[k-1]} e^{i2k_z\delta_k}) (1 + R^{(p)}_{V,k+1} + R^{(p)}_{V,k+1} \tilde{R}^{(p)}_{V,[k]} e^{i2k_z\delta_k})
\]

\[
= (1 + R^{(p)}_{V,k+1} R^{(p)}_{V,[k]} e^{i2k_z\delta_k}) (1 - R^{(p)}_{V,k} R^{(p)}_{V,[k]} e^{i2k_z\delta_k})
\]

\[
= (1 + R^{(p)}_{V,k+1} R^{(p)}_{V,[k]} e^{i2k_z\delta_k})(1 - R^{(p)}_{V,k} R^{(p)}_{V,[k]} e^{i2k_z\delta_k}).
\]

In going from the last-but-one equation to the last line in Eq. (13), we have used the fact that we will eventually take the limit as \( \delta_{k+1} \to 0 \) [see Eqs. (12) or (14)]. Using Eq. (13), Eq. (12) can be simplified to

\[
U^{(N)}_{LR} = -\sum_{p=0, h} \int_0^\infty \frac{dk_p k_p}{2\pi} \int_0^\infty \frac{d\omega}{2\pi} \coth \left[ \frac{\hbar \omega}{2k_BT} \right] \times \Im \left\{ \lim_{\delta_k \to 0} \sum_{k=0}^N \ln \left( 1 - R^{(p)}_{V,k+1} R^{(p)}_{V,[k]} e^{i2k_z\delta_k} \right) - \lim_{\Delta_k \to 0} \sum_{k=1}^N \ln \left( 1 - R^{(p)}_{k+1} e^{i2k_z\Delta_k} \right) + \sum_{k=1}^N \ln \left( 1 - R^{(p)}_{k+1} \tilde{R}^{(p)}_{k,[k]} e^{i2k_z\delta_k} \right) \right\}
\]

\[
= C - \sum_{p=0, h} \int_0^\infty \frac{dk_p k_p}{2\pi} \int_0^\infty \frac{d\omega}{2\pi} \coth \left[ \frac{\hbar \omega}{4k_BT} \right] \lim_{\Delta_k \to 0} \prod_{k=1}^N \ln \left( 1 - R^{(p)}_{k+1} \tilde{R}^{(p)}_{k,[k]} e^{i2k_z\delta_k} \right),
\]

where \( C \equiv C(\delta_1, \ldots, \delta_{N+1}; \Delta_1, \ldots, \Delta_N) \) is independent of all \( z_k \) (\( k = 1, \ldots, N \)). In Eq. (14), \( R_{N,N+1} = R_{N,R}, R_{R,0} = R_{R,L}, R_{R,N-1} = R_{R,V}, R_{V,N} = R_{V,L}, \) and \( \tilde{R}_{1,[0]} = R_{1,L} \). Only the second term contributes to van der Waals pressure in any of the layers. The implication of Eq. (14) is that the van der Waals energy of any planar multilayer system between two half-spaces can be split into two parts: a configuration-dependent part that contributes to van der Waals pressure, and a singular part that does not.

The modes themselves are obtained by setting the argument of the logarithm function in Eq. (14) to zero, i.e., the dispersion relation for the \( N \)-layer structure in Fig. 1 is given by \( \tilde{D}^{(p)}(\omega) = \prod_{k=1}^N (1 - R^{(p)}_{k+1} \tilde{R}^{(p)}_{k,[k]} e^{i2k_z\delta_k}) = 0 \).

Hence, the finite \( z_k \)-dependent part of the van der Waals energy in Eq. (14) can also be written as

\[
U^{(N)}_{LR} = -\int_0^\infty \frac{dk_p k_p}{2\pi} \int_0^\infty \frac{d\omega}{\pi} \coth \frac{\hbar \omega}{2k_BT} \ln \left[ 2 \sin \hbar \omega \right] \sum_{p=0, h} \frac{\partial}{\partial \omega} \Im \ln \tilde{D}^{(p)}(\omega, k_p).
\]
Equation (15) for $U_{LR}^{(N)}$ is a generalization of van Kampen’s and Schram’s expression for van der Waals energy of an $N$-layer medium at finite temperature [7,8,18,19,33]. However, two important features need to be kept in mind: (1) Eqs. (14) and (15) are obtained without having to rely on the assumption that computation of van der Waals free energy needs the summation of free energies of all fundamental modes of the system, and (2) unlike in all the literature regarding the mode-summation method we are aware of [7–9,16,18–20,33], the layer in which the van der Waals pressure is to be calculated can have dissipative properties.

III. EXCURSIONS INTO THE LOWER HALF PLANE
IN THE PRESENCE OF DISSIPATION

Since Eq. (15) is a generalization of van Kampen’s and Schram’s formula for van der Waals energy to the case of dissipative materials, it is natural to ask if we can also express it as a sum over normal modes, thereby lending legitimacy to the idea of mode summation in dissipative media. Specifically, we are interested in the van der Waals pressure in a vacuum gap between two multilayer objects which contain dissipative thin films. To show the relation between Eq. (15) and the sum of mode energies, the integration path along the real axis should be completed into a closed contour so as to include all the normal modes that contribute to van der Waals energy, which lie in the lower half of the complex frequency plane if at least one of the materials in the multilayer system is dissipative.

The vacuum gap of length $l_v$ in which the van der Waals pressure is to be determined is in-between multilayer objects marked 1 and 2 in Fig. 2. To simplify the analysis, the multilayer structure is placed inside a cavity with a perfect reflector at either end, marked “Schram’s perfect reflector” (SIR) in Fig. 2. This is done in order to eliminate branch points corresponding to the half-spaces $L$ and $R$ that would have otherwise been present [8]. In addition to the usual SPR employed by many, we added a layer of dissipative material to the surface of SPR to create “Schram’s imperfect reflector” (SIR in Fig. 2). In particular, SPR to the left has a coating of material $L$ and that to the right has a coating of material $R$. The dissipative layers, the thicknesses of which are immaterial, are present to ensure that the frequencies of normal modes of the two SIRs, with only vacuum in-between, are pushed from the real axis to the lower half of the complex frequency plane. If the materials $L$ and $R$ are vacuum, infinitesimal dissipation is added. The total thickness of multilayer object 1 is $l_1$ and that of multilayer object 2 is $l_2$. $L_v = l_1 + l_1 + l_2$ is the gap between the two SIRs. Eventually the thickness $z_L$ and $z_R$ of $L$ and $R$, respectively, and hence $l_1$ and $l_2$, are made to approach $\infty$ to recreate the multilayer system of interest. The assumption of vacuum cavity is not unduly restrictive as we have shown in Sec. II that each term in the right-hand side of Eq. (8) corresponds to the van der Waals energy of a multilayer system similar to the one shown in Fig. 2 (albeit without the reflectors at either end). Hence, if we can express the van der Waals energy of the vacuum cavity in Fig. 2 in terms of normal modes, then we can use the theory in Sec. II to express the energy of any planar multilayer system in terms of energy of normal modes.

The regularized van der Waals energy of the multilayers at a vacuum gap $l$ is the difference between (1) the work required to translate the two multilayer objects, including the reflectors, from $l_v \to \infty$ to $l_v = l$, and (2) the work done in translating the two SIRs, with only vacuum in-between, from $L_v \to \infty$ to $L_v = l + l_1 + l_2$. Denoting this van der Waals energy as $U_v(l)$, and by using Eq. (14), we can write

$$U_v(l) = \sum_{p=e,h} \int_0^\infty \frac{dk_zk_z}{2\pi} \int_0^{\infty} \frac{d\omega}{2\pi} \coth \left( \frac{\hbar\omega}{2k_BT} \right) \times \left[ \text{Im} \left[ \lim_{l_1 \to \infty} \left( \frac{D_{\text{SIR}}^{(p)}(\omega, k_z; l_1)}{D_{\text{SIR}}^{(p)}(\omega, k_z; l_1)} \right) \right] - \text{Im} \left[ \lim_{l_1 \to \infty} \left( \frac{D_{\text{SIR}}^{(p)}(\omega, k_z; l + l_1 + l_2)}{D_{\text{SIR}}^{(p)}(\omega, k_z; l_v)} \right) \right] \right].$$

In Eq. (16), $D_{\text{SIR}}^{(p)}(\omega, k_z; l_1)$ is the dispersion relation for modes in the entire structure confined between the two SIRs. $\tilde{R}_{\text{SIR}}^{(p)}(\nu_{l_1-1}^{\nu_{l_1+1}})$ and $\tilde{R}_{\text{SIR}}^{(p)}(\nu_{l_1}^{\nu_{l_1}^{\nu_{l_1}}})$ are the reflection coefficients of multilayer systems 1 and 2 inclusive of the corresponding SIR. As $\omega z_L/c \to \infty$, $\tilde{R}_{\text{SIR}}^{(p)}(\nu_{l_1-1}^{\nu_{l_1}^{\nu_{l_1}}} \to \tilde{R}_{\text{SIR}}^{(p)}(\nu_{l_1}^{\nu_{l_1}^{\nu_{l_1}}}$. Similarly, as $\omega z_R/c \to \infty$, $\tilde{R}_{\text{SIR}}^{(p)}(\nu_{l_1+1}^{\nu_{l_1+1}} \to 1 - \tilde{R}_{\text{SIR}}^{(p)}(\nu_{l_1}^{\nu_{l_1}^{\nu_{l_1}}}$. $D_{\text{SIR}}^{(p)}(\omega, k_z; l + l_1 + l_2) = 1 - \tilde{R}_{\text{SIR}}^{(p)}(\nu_{l_1}^{\nu_{l_1}^{\nu_{l_1}}} \tilde{R}_{\text{SIR}}^{(p)}(\nu_{l_1}^{\nu_{l_1}^{\nu_{l_1}}} \tilde{R}_{\text{SIR}}^{(p)}(\nu_{l_1}^{\nu_{l_1}^{\nu_{l_1}}} \tilde{R}_{\text{SIR}}^{(p)}(\nu_{l_1}^{\nu_{l_1}^{\nu_{l_1}}}$. The integral from $\omega = 0^+$ to $\omega = \infty$ can be rewritten as an integral over the entire real axis by appropriately defining the integrand along the negative real axis. We know that $e(-|\omega|) = e^{*}(|\omega|)$. The $z$ direction wave vectors $k_z$ obey the relation $k_z(-|\omega|) = -k_{z0}(|\omega|)$ for all $j$ (the behavior of the wave vector in vacuum is discussed specifically in Sec. III A). With this definition, we can see that $\text{Im} D_{\text{SIR}}^{(p)}(\omega, k_z; l)$ evaluated at $|\omega|$ and $-|\omega|$ are complex conjugates of each other. To see how Eq. (16) can be written as a sum over mode energies, let us rewrite Eq. (16) as an integral along the entire real frequency plane.
axis:
\[
U_{\alpha}(l) = \sum_{\rho = \alpha, h} \int_{0}^{\infty} \frac{dk_{p}k_{p}}{2\pi} \int_{0}^{\infty} d\omega \frac{\sqrt{\hbar \omega}}{4\pi} \coth \left( \frac{\hbar \omega}{2k_{p}T} \right) \\
\times \left[ \lim_{\beta \to \infty} \frac{1}{\beta} \left( \frac{D_{\beta}^{(p)}(\omega, k_{p}; l)}{D_{\beta}^{(p)}(\omega, k_{p}; l)} \right) \right] \\
- \left[ \lim_{L_{\alpha} \to \infty} \frac{1}{L_{\alpha}} \left( \frac{D_{\alpha}^{(p)}(\omega, k_{p}; L_{\alpha})}{D_{\alpha}^{(p)}(\omega, k_{p}; L_{\alpha})} \right) \right].
\]

(17)

The next section addresses questions related to the behavior of \(\lim_{\beta \to \infty} \frac{1}{\beta} \left( \frac{D_{\beta}^{(p)}(\omega, k_{p}; l)}{D_{\beta}^{(p)}(\omega, k_{p}; l)} \right)\) at different segments of the real frequency axis in the upper and lower half planes.

A. Branch cuts and contours of integration in upper and lower halves of complex frequency plane

Since \(k_{j}, j = 1, 2, \ldots, k = 1, v, k, \ldots, N\) are all relevant to the problem, it appears as though we have as many branch-point pairs as there are films. However, we will show that only the branch points corresponding to the vacuum region are important for evaluating \(D_{\beta}^{(p)}(\omega, k_{p}; l)\).

The complex frequencies corresponding to \(k_{0} = 0\) are valid branch points if we can show that the function \(D_{\beta}^{(p)}(\omega, k_{p}; l)\) takes on different values when the sign of \(k_{0}\) is changed. The effect of changing the sign of only \(k_{0}\), at the same \(\omega\) is \(R_{1}^{(p)}(k_{0}) = R_{1}^{(p)}(-k_{0})\). Keeping in mind that \(k_{0}\) affects only \(R_{0}^{(p)}\), the effect of changing the sign of only \(k_{0}\) is \(R_{0}^{(p)}(-k_{0}) = R_{0}^{(p)}(k_{0})\).

Hence,
\[
\tilde{V}_{\beta}^{(p)}(k_{0}) = \frac{R_{\beta}^{(p)}(k_{0}) + R_{\beta}^{(p)}(-k_{0})e^{2\beta k_{0}i\pi/4}}{1 + R_{\beta}^{(p)}(k_{0})R_{\beta}^{(p)}(-k_{0})e^{2\beta k_{0}i\pi/4}} = \tilde{V}_{\beta}^{(p)}(k_{0}).
\]

(18)

Similarly, we can also show that \(\tilde{V}_{\beta}^{(p)}(k_{0}) = \tilde{V}_{\beta}^{(p)}(-k_{0})\).

Clearly, the frequencies at which \(k_{0} = 0\) are branch points for evaluating \(D_{\beta}^{(p)}(\omega, k_{p}; l)\). Since \(R_{\beta}^{(p)}(k_{0}) = R_{\beta}^{(p)}(-k_{0})\), we have \(\tilde{V}_{\beta}^{(p)}(k_{0}) = \tilde{V}_{\beta}^{(p)}(-k_{0})\). Only \(R_{\beta}^{(p)}\) depends on \(k_{0}\) or other wave vectors \(k_{j}, j = 1, 2, \ldots, N\). By extension of Eq. (18), we see that \(\tilde{V}_{\beta}^{(p)}(k_{0}) = \tilde{V}_{\beta}^{(p)}(-k_{0})\). This analysis can be extended to show that \(\tilde{V}_{\beta}^{(p)}(k_{0})\) does not change when the sign of any of the wave vectors \(k_{j}, j = 1, 2, \ldots, N\) is changed. The same argument holds true for \(R_{\beta}^{(p)}(k_{0})\). Hence, the only branch points correspond to the frequencies at which \(k_{0} = 0\).

For a given value of \(k_{p}\), these frequencies correspond to \(\omega = \pm c_{k_{p}}\). We draw branch cuts extending from \(c_{k_{p}}\) to \(-\infty\) and from \(-c_{k_{p}}\) to \(-\infty\). The presence of branch cuts implies that \(D_{\beta}^{(p)}(\omega, k_{p}; l)\) takes on different values in the upper and lower half planes because of the changing sign of \(k_{0}\). \(k_{0}\) is defined such that \(\text{Im}(k_{0}) \geq 0\) all over the complex frequency plane. In the upper half plane,
\[
k_{0}(\omega) = \left\{ \begin{array}{ll}
|k_{0}|, & \omega > c_{k_{p}} \\
|k_{0}|, & \omega < -c_{k_{p}}
\end{array} \right.
\]

(19)

In the lower half plane,
\[
k_{0}(\omega) = \left\{ \begin{array}{ll}
-k_{0}, & \omega > c_{k_{p}} \\
-k_{0}, & \omega < -c_{k_{p}}
\end{array} \right.
\]

(20)

The definition of \(k_{0}\) in Eqs. (19) and (20) is in agreement with the relationship between z-component wave vectors at \(|\omega|\) and \(-|\omega|\), which is given by \(k_{z}(\pm |\omega|) = -k_{z}'(|\omega|)\).

Using the definitions of \(k_{0}\), the values of \(I^{(p)}(\omega, k_{p}) = \lim_{\beta \to \infty} \frac{1}{\beta} \left( \frac{D_{\beta}^{(p)}(\omega, k_{p}; l)}{D_{\beta}^{(p)}(\omega, k_{p}; l)} \right)\) in different segments of the real frequency axis in the upper half plane can be related to the corresponding values at appropriate positions in the upper half plane and positive frequencies. For \(0 < \omega < c_{k_{p}}\), the reflection coefficients \(\tilde{V}_{\beta}^{(p)}(k_{0})\) and \(\tilde{V}_{\beta}^{(p)}(k_{0})\) as well as \(e^{2\beta k_{p}i}\) are evaluated at \(k_{0} = |k_{0}|\).

\[
I^{(p)}(\omega, k_{p}) = \lim_{\beta \to \infty} \frac{1}{\beta} \left( \frac{D_{\beta}^{(p)}(\omega, k_{p}; l)}{D_{\beta}^{(p)}(\omega, k_{p}; l)} \right)
\]

(21)

The subscript \(\text{ahp}\) stands for “upper half plane.” In the lower half plane, \(I^{(p)}(\omega, k_{p})\) for \(\omega < c_{k_{p}}\) is evaluated by calculating \(\tilde{V}_{\beta}^{(p)}(k_{0})\) and \(\tilde{V}_{\beta}^{(p)}(k_{0})\) using the definition \(k_{0} = -|k_{0}|\). By using Eq. (18), \(I^{(p)}(\omega, k_{p})\) in the lower half plane can be related to \(I_{\text{ahp}}^{(p)}(\omega, k_{p})\) as
\[
I^{(p)}(\omega, k_{p}) = I_{\text{ahp}}^{(p)}(\omega, k_{p})
\]

\[
= \lim_{\beta \to \infty} \frac{1}{\beta} \left( \frac{1 - \tilde{V}_{\beta}^{(p)}(k_{0})\tilde{V}_{\beta}^{(p)}(k_{0})e^{-2\beta k_{p}i}}{1 - \tilde{V}_{\beta}^{(p)}(k_{0})\tilde{V}_{\beta}^{(p)}(k_{0})e^{-2\beta k_{p}i}} \right).
\]

(22)

The subscript \(\text{ahp}\) stands for “lower half plane.” The function \(I^{(p)}(\omega, k_{p})\) in the left half plane can be obtained through the following symmetry relation: \(I^{(p)}(-|\omega|, k_{p}) = I^{(p)}(|\omega|, k_{p})\).
$I^p(\omega, k_\rho)$ as evaluated along the real frequency axis in the upper and lower half planes are not equal, the difference comes from the $i2[k_\rho^2(l - i\varepsilon)]$ term in Eq. (23). However, $U_c$, as we defined in Eq. (17), does not suffer from this term since the $i2[k_\rho^2(l - i\varepsilon)]$ term is common to both $\lim_{\varepsilon\to -\infty} \ln \left( \frac{D_m^p(\omega, k_\rho; l)'}{D_m^p(\omega, k_\rho; l_\rho)} \right)$ and $\lim_{\varepsilon\to -\infty} \ln \left( \frac{D_m^p(\omega, k_\rho; l + i\varepsilon)}{D_m^p(\omega, k_\rho; l_\rho)} \right)$ and cancel each other.

The singularities of the integrand correspond to poles of $\coth \left( \frac{h\omega_{m,k\rho}}{2k_BT} \right)$ and branch points of the ln function at zeros of $D_m^p(\omega, k_\rho; l_\rho)$ (modes of the electrodynamic system shown in Fig. 2). Following the arguments of Diaz and Alexopoulos [34], $D_m^p(\omega, k_\rho; l)$ can have only zeros or pole singularities.

We further assume that poles of $D_m^p(\omega, k_\rho; l)$, if present, are independent of $l$ and hence cancel with the contribution from $D_m^p(\omega, k_\rho; l \to \infty)$. Because of the analyticity of $D_m^p(\omega, k_\rho; l)$, it can be written as

$$D_m^p(\omega, k_\rho; l) = \left( 1 - \frac{\omega}{\omega_{m,k\rho}(l)} \right) D_m^p(\omega, k_\rho; l_\rho)$$

(24)

in a neighborhood of $\omega_{m,k\rho}(l)$ in which $D_m^p(\omega, k_\rho; l)$ is a regular function. Because of the ln function, a branch cut of the form shown in Fig. 3 is present at each normal mode $\omega_{m,k\rho}$.

The contour path for integrating $\lim_{\varepsilon\to -\infty} \ln \left( \frac{D_m^p(\omega, k_\rho; l + i\varepsilon)}{D_m^p(\omega, k_\rho; l_\rho)} \right)$ is shown in Fig. 3. Because of Eq. (23), the integrals along $C_{R,L}^-$ and $C_{R,U}^+$ (and $C_{R,U}^-$ and $C_{R,L}^+$) cancel each other. As $\omega + i\xi \to \infty$, $\varepsilon \to 1$ for all materials and all reflection coefficients vanish. Hence, the integrands along $C_{\infty,U}$ and $C_{\infty,L}$ vanish. Since the integral along the contour in Fig. 3 is zero, the sum of residues at all poles of the integrand within the contour must also equal zero by Cauchy’s residue theorem.

![FIG. 3. (Color online) The zeros of $D(\omega, k_\rho)$, are labeled $\omega_{1,k_\rho}$, $\omega_{2,k_\rho}, \ldots$, $\omega_{N,k_\rho}$, and $-\omega_{1,k_\rho}$, $-\omega_{2,k_\rho}, \ldots$, $-\omega_{N,k_\rho}$. The poles on the $\xi$ axis are poles of $\coth(h\omega/2k_BT)$. The red lines are contours for integration.](image)

The contribution from each normal mode at $\omega_{m,k\rho}$ to the contour integral is given by

$$\frac{i\hbar}{4\pi} \int_0^\infty dx \left( 0 - i2\pi \right) \coth \left( \frac{h\omega_{m,k\rho}(l + x)}{2k_BT} \right)$$

$$- \coth \left( \frac{h\omega_{m,k\rho}(l \to \infty)}{2k_BT} \right)$$

$$- \lim_{\varepsilon\to -\infty} \ln \left( \frac{D_m^p(\omega, k_\rho; l + i\varepsilon)}{D_m^p(\omega, k_\rho; l_\rho)} \right)$$

(25)

Clearly, the contribution in Eq. (25) is the change in free energy of a normal mode as the vacuum gap is changed from $l_\rho = l$ to $l_\rho \to \infty$. The $i0$ and $i2\pi$ terms in Eq. (25) are contributions from either side of the branch cut at normal mode frequencies. In deriving Eq. (25), we are assuming that $\omega_{m,k\rho}$ does not coincide with any of the Matsubara frequencies. The contribution from $-\omega_{m,k\rho}^*$ is the complex conjugate of Eq. (25). The contribution from all the Matsubara frequencies is given by

$$-k_BT \sum_{n=0}^\infty \int_0^\infty \frac{dk_\rho k_\rho}{2\pi} \sum_{\varepsilon,h} \lim_{l_\rho \to \infty} \ln \left[ \frac{D_m^p(i\xi_n,k_\rho;l_\rho)}{D_m^p(i\xi_n,k_\rho;l')} \right].$$

(26)

In both Eqs. (25) and (26), the contributions of cavity modes corresponding to the imperfect mirror alone are suppressed in order to make the expression compact. The Lifshitz formula for $U_c$, corresponding to the contributions from positive Matsubara frequencies, is given by

$$U_c(l) = -k_BT \sum_{n=0}^\infty \int_0^\infty \frac{dk_\rho k_\rho}{2\pi} \sum_{\varepsilon,h} \lim_{l_\rho \to \infty} \ln \left[ \frac{D_m^p(i\xi_n,k_\rho;l_\rho)}{D_m^p(i\xi_n,k_\rho;l')} \right].$$

(27)

From Eqs. (25)–(27), we can relate $U_c$ to the free energies of normal modes as follows:

$$U_c(l) = U_{nor}(l) + \frac{k_BT}{2} \sum_{n=0}^\infty \int_0^\infty \frac{dk_\rho k_\rho}{2\pi} \sum_{\varepsilon,h} \lim_{l_\rho \to \infty} \ln \left[ \frac{D_m^p(i\xi_n,k_\rho;l_\rho)}{D_m^p(i\xi_n,k_\rho;l')} \right].$$

(28)

where $U_{nor}(l)$ is the sum of free energy of each normal mode and is given by

$$U_{nor}(l) = k_BT \int_0^\infty \frac{dk_\rho k_\rho}{2\pi} \sum_{\varepsilon,h} \lim_{l_\rho \to \infty} \ln \left[ \frac{\sinh \left( h\omega_{m,k\rho}(l)/2k_BT \right)}{\sinh \left( h\omega_{m,k\rho}(l_\rho)/2k_BT \right)} \right].$$

(29)

In Eq. (29), the $\sum_m$ is performed over modes only in the right half plane. Equations (28) and (29) imply that the van der Waals energy is not only composed of the sum of free energies of normal modes but also contributions from poles at negative Matsubara frequencies. Only when $D_m^p(i\xi_n,k_\rho;l) = \frac{D_m^p(i\xi_n,k_\rho;l_\rho)}{D_m^p(i\xi_n,k_\rho;l')} = \frac{D_m^p(i\xi_n,k_\rho;l')}{
is dissipative. An analogy to this observation can be seen even when correction of the form suggested by Intravaia et al. by Ninham [33], is that the van der Waals energy of the multilayer system with dissipative materials is insufficient to capture the van der Waals energy of the multilayer system with dissipative materials.

V. SUMMARY

We have derived a method to determine the van der Waals energy and pressure in a dissipative material within a planar multilayer object with arbitrary number of layers. It is shown to be a hybrid of the fluctuational electrodynamics (Lifshitz) method and energy conservation. Like Lifshitz, we use Rytov’s theory of fluctuational electrodynamics and like Casimir (and others) we use principle of energy conservation to extend Lifshitz’ theory to the case of dissipative materials. Unlike Casimir (and others), we do not rely on the assumption that the van der Waals free energy can be computed by adding the free energy of each mode. We have also shown that van der Waals energy and pressure in a dissipative material can be obtained by performing the analysis entirely along the real frequency axis.
solved only when the question of finite dissipation is addressed in its entirety. To the best of our understanding, nothing new is gained by employing the mode-summation method over the fluctuational electrodynamics method.

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