van der Waals interactions between bodies having inhomogeneous dielectric permittivities

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Abstract
We present analytical results for the contribution of electromagnetic fluctuations in the distribution of interaction energy and pressure in isotropic systems whose properties depend only on one spatial coordinate. If we neglect the continuous inhomogeneity introduced here and consider the simplest case of two macroscopic homogeneous bodies separated by a homogeneous film our result reduces to the well-known Lifshitz formula. As a first application of theory, a one-dimensional modulated system with a homogeneous layer embedded in it is considered and a suitable perturbation theory for this system is developed. In the main part of this paper we limit the calculations to the non-retarded case, that is only the calculation of van der Waals interaction energy is given. As a second application of theory we consider the van der Waals interaction between two semi-infinite media across a planar region within which there is a thin film having an arbitrary variation of the dielectric permittivity. The importance of the precise evaluation of the transverse magnetic surface mode dispersion relation in inhomogeneous media is elucidated. For concreteness the influence of the transition layer between water and lipid in a symmetrical configuration is considered in some detail. The zero-frequency term and the dispersion-only contribution to the Hamaker coefficient are given analytically using some approximations and modelling of the dielectric constants reasonable for these dielectrics at room temperature. As a whole the results indicate the necessity of performing Lifshitz-type calculations on realistic inhomogeneous layered models, as are the models described here, for accurate interaction energy modelling. Of course further work is needed for real justification of the continuous variation of dielectric permittivities across phase interfaces.

1. Introduction

In recent years the Casimir effect has attracted a great deal of interest in different areas of contemporary physics starting from quantized scalar massless field theory [1], going through physical chemistry of colloids and interfaces [2] and ending with sophisticated biophysical

objects [3]. The basic result for Casimir effect between real materials in plane parallel geometry (the celebrated Lifshitz formula) [4] has been widely used in numerous investigations, simplified on physical grounds to surface-mode dispersion relation analysis only [5, 6, 12], and generalized by proximity force approximation or by more rigorous approaches [1] to non-plane parallel geometries. Transverse inhomogeneities such as periodic or statistically rough surfaces has also received a great deal of attention [7]. Even today a direct generalization of the Lifshitz approach [4] is still actual for anisotropic, multilayered and other complex systems [8, 9]. A good example in this direction is the calculation of the Casimir forces in modulated systems made recently in [10]. Here an appropriate perturbation scheme has been formulated and valuable estimations for the chemical potential in cholesteric liquid crystalline films have been obtained. In this paper we focus our efforts on a relatively simple problem: the calculation of the contribution of electromagnetic fluctuations to interaction energy in an isotropic system whose macroscopic description depends on the z-coordinate only. Of course this class of materials contains the simplest non-trivial case of two semi-infinite homogeneous bodies separated by a homogeneous film as well as the case of laminated multilayered media where the dielectric function is piece-wise constant in each slab. A brief exposition of general theory will be given in section 2 and appendix A. Section 3 is devoted to isotropic modulated systems interacting across a homogeneous layer of finite thickness L. In order to find the van der Waals interaction energy in closed form here we use the regular perturbation theory for small modulations (as in [10]). In section 4 a biophysical example is given for two symmetrical plane-parallel systems 'lipid/water/lipid' and 'water/lipid/water' by taking into account the thin transition layer between water and lipid substances where the dielectric permittivity is continuously varying function of the position. There and in appendix B we discuss the semiempirical determination of 'bulk' dielectric permittivities of the two constituents as well as the question of approximate additivity or non-additivity in the van der Waals interactions within these two structures.

2. Electromagnetic fluctuations in an inhomogeneous medium

Our first purpose here is to derive two scalar differential equations and boundary conditions to them. We will show that these two scalar equations determine the whole spatial information for the Green's dyadic function $D_{lk}(\vec{r}, \vec{r}'; \xi_n)$. According to general theory [4] the tensor D_{lk} is needed for calculation of the pressure (the force per unit area) acting in a medium having z-coordinate dependent dielectric permittivity $\varepsilon(\omega, z)$. The starting point is the equation for $D_{lk}(\vec{r}, \vec{r}'; \xi_n)$:

$$\left\{ \varepsilon(z; i\xi_n) \frac{\xi_n^2}{c^2} \delta_{jl} + \frac{\partial^2}{\partial x_j \partial x_l} - \Delta_3 \delta_{jl} \right\} D_{lk}(\vec{r}, \vec{r}'; \xi_n) = -4\pi \delta(\vec{r} - \vec{r}') \delta_{jk} \tag{2.1}$$

where Δ_3 is the 3D Laplace operator, $x_1 = x$, $x_2 = y$, $x_3 = z$. Here $\varepsilon(z) \equiv \varepsilon(z; i\xi_n)$,

$$\xi_n = n \frac{2\pi kT}{\hbar}, \qquad n = 0, 1, 2, \ldots \tag{2.2}$$

where k is the Boltzmann constant, T is the temperature, $j = 1, 2, 3$, $l = 1, 2, 3$. Let $\bar{D}_{lk}(\vec{r}, \vec{r}'; \xi_n)$ be the solution to (2.1) for a hypothetical homogeneous medium having for all z a scalar permittivity $\varepsilon(\omega, z_0)$. Then we introduce the notations

$$\tilde{D}_{lk}(\vec{r}, \vec{r}'; \xi_n) = D_{lk}(\vec{r}, \vec{r}'; \xi_n) - \bar{D}_{lk}(\vec{r}, \vec{r}'; \xi_n) \tag{2.3}$$

$$\tilde{D}_{lk}^H(\vec{r}, \vec{r}'; \xi_n) = \text{rot}_{l\mu} \text{rot}'_{k\nu} \tilde{D}_{\mu\nu}(\vec{r}, \vec{r}'; \xi_n) \tag{2.4}$$

where

$$\text{rot}_{l\mu} \equiv \varepsilon_{lp\mu} \frac{\partial}{\partial x_p}, \qquad \text{rot}'_{k\nu} \equiv \varepsilon_{ks\nu} \frac{\partial}{\partial x'_s}. \tag{2.5}$$

The force per unit area is given by the following formula:

$$F(z_0) = \frac{kT}{4\pi} \sum_{n=0}^{\infty}{}' \left\{ \frac{\xi_n^2}{c^2} \varepsilon(z_0) [\tilde{D}_{33}(\cdot) - \tilde{D}_{11}(\cdot) - \tilde{D}_{22}(\cdot)] + \tilde{D}_{11}^H(\cdot) + \tilde{D}_{22}^H(\cdot) - \tilde{D}_{33}^H(\cdot) \right\} \quad (2.6)$$

where $(\cdot) \equiv (\vec{\rho}, z_0; \vec{\rho}, z_0)$ and the prime indicates that the $n = 0$ term is to be multiplied by $1/2$. Due to homogeneity in the $x-y$ plane we introduce the following Fourier transform:

$$D_{lk}(\vec{r}, \vec{r}'; \xi_n) = \int \frac{d^2\vec{q}}{4\pi^2} e^{i\vec{q}\cdot(\vec{\rho}-\vec{\rho}')} d_{lk}(\vec{q}, \xi_n; z, z'), \qquad \vec{q}(q_x, q_y, 0), \quad \vec{\rho}(x, y, 0). \quad (2.7)$$

A further transformation is needed to replace the matrix $\bar{\bar{d}}$ with a new matrix $\bar{\bar{g}}$ depending only on $q = |\vec{q}| = (q_x^2 + q_y^2)^{1/2}$ and of course of z, z', ξ_n:

$$d_{sj} = (S^T)_{sp} g_{pr} (S)_{rj} \quad (2.8)$$

where

$$\bar{\bar{S}}(\vec{q}) = \frac{1}{q} \begin{pmatrix} q_x & q_y & 0 \\ -q_y & q_x & 0 \\ 0 & 0 & q \end{pmatrix}, \qquad \bar{\bar{S}}^T(\vec{q}) = \frac{1}{q} \begin{pmatrix} q_x & -q_y & 0 \\ q_y & q_x & 0 \\ 0 & 0 & q \end{pmatrix}. \quad (2.9)$$

Then the Green's dyadic problem (2.1) reduces to

$$\bar{\bar{B}}\bar{\bar{g}} = 4\pi\delta(z - z')\bar{\bar{I}} \quad (2.10)$$

where $(\bar{\bar{I}})_{lk} = \delta_{lk}$ is the unit 3×3 matrix and

$$\bar{\bar{B}} = \begin{pmatrix} -\varepsilon(z)\frac{\xi_n^2}{c^2} + \frac{\partial^2}{\partial z^2} & 0 & -iq\frac{\partial}{\partial z} \\ 0 & -\varepsilon(z)\frac{\xi_n^2}{c^2} - q^2 + \frac{\partial^2}{\partial z^2} & 0 \\ -iq\frac{\partial}{\partial z} & 0 & -\varepsilon(z)\frac{\xi_n^2}{c^2} - q^2 \end{pmatrix} \quad (2.11)$$

so that $\bar{\bar{g}}$ has only five non-zero elements:

$$\bar{\bar{g}} = \begin{pmatrix} g_{11} & 0 & g_{13} \\ 0 & g_{22} & 0 \\ g_{31} & 0 & g_{33} \end{pmatrix}. \quad (2.12)$$

The equation for $g_{22}(z, z')$

$$\left[\frac{d^2}{dz^2} - q^2 - \frac{\xi_n^2}{c^2}\varepsilon(z) \right] g_{22}(z, z') = 4\pi\delta(z - z') \quad (2.13)$$

corresponds to transverse-electric (TE) waves (or s-polarization). At every point $z \neq z'$ we require continuity of the function and its derivative:

$$g_{22}(z - 0, z') = g_{22}(z + 0, z'), \qquad \left(\frac{\partial g}{\partial z}\right)_{z-0} = \left(\frac{\partial g}{\partial z}\right)_{z+0}. \quad (2.14)$$

In the same time a jump $\varepsilon(z - 0) \neq \varepsilon(z + 0)$ is admitted. For transverse-magnetic (TM) waves we derive the following equation for $g_{11}(z, z')$:

$$\frac{d}{dz}\left(a(z)\frac{dg_{11}}{dz} \right) - \varepsilon(z)g_{11}(z, z') = 4\pi\frac{c^2}{\xi_n^2}\delta(z - z') \quad (2.15)$$

where

$$a(z) = \frac{\varepsilon(z)}{w^2(z)}, \qquad w^2(z) = q^2 + \frac{\xi_n^2}{c^2}\varepsilon(z) \quad (2.16)$$

and the boundary conditions to this equation are

$$g_{11}(z-0, z') = g_{11}(z+0, z'), \qquad \left(a(z)\frac{dg_{11}}{dz}\right)_{z-0} = \left(a(z)\frac{dg_{11}}{dz}\right)_{z+0}. \tag{2.17}$$

For the other three functions corresponding to TM waves we derive

$$g_{31}(z, z') = -\frac{iq}{w^2(z)}\frac{\partial g_{11}(z, z')}{\partial z} \tag{2.18}$$

$$g_{33}(z, z') = -\frac{iq}{w^2(z)}\frac{\partial g_{13}(z, z')}{\partial z} - \frac{4\pi}{w^2(z)}\delta(z - z') \tag{2.19}$$

$$\frac{d}{dz}\left(a(z)\frac{dg_{13}}{dz}\right) - \varepsilon(z)g_{13}(z, z') = -\frac{4\pi iqc^2}{\xi_n^2}\frac{d}{dz}\left(\frac{\delta(z - z')}{w^2(z)}\right). \tag{2.20}$$

Our second purpose is to construct for the scalar Green's functions (like $g_{22}(z, z')$ for the TE mode) appropriate analytical representations and finally to evaluate the pressure formula (2.6). Our results on this problem for the TE mode are collected in appendix A.

3. A modulated system with a homogeneous layer embedded in it

In this section we investigate only the TM mode. In the non-retarded limit (i.e., assuming an infinite speed of light) the contribution of the TE mode described in appendix A vanishes. First we give an important result which follows from equations (2.15) and (2.20):

$$g_{13}(z, z') = \frac{iq}{w^2(z')}\frac{\partial g_{11}(z, z')}{\partial z'}. \tag{3.1}$$

Formulae (2.6), (2.15)–(2.20) allow us to write the following quite general result:

$$F^{\text{TM}}(z_0) = \frac{kT}{8\pi^2}\sum_{n=0}^{\infty}{}' \int_0^{\infty} dq\, q\, I(\xi_n, q, z_0) \tag{3.2}$$

where

$$I(\xi_n, q, z_0) = \frac{\xi_n^2\varepsilon(z_0)}{c^2w^2(z_0)}\left(\frac{\partial^2\tilde{g}_{11}(z, z')}{\partial z\partial z'} - w^2(z_0)\tilde{g}_{11}(z, z')\right) \qquad (z = z' = z_0). \tag{3.3}$$

As concerns the limit $c \to \infty$, it is evident from (2.15) that $g_{11} \propto c^2/\xi_n^2$ (the same is true for $\tilde{g}_{11}$) and in this limit $w(z)$ must be replaced by q. Let us consider now a physical system having the following distribution of the dielectric permittivity:

$$\varepsilon(i\xi_n, z) = \begin{cases} \varepsilon + g\Delta\varepsilon\cos(2q_0z), & -\infty < z < -L/2 \\ \varepsilon_3, & |z| < L/2 \\ \varepsilon + g\Delta\varepsilon\cos(2q_0z), & L/2 < z < \infty. \end{cases} \tag{3.4}$$

Here $|g| < 1, \varepsilon = \varepsilon(i\xi_n), \Delta\varepsilon = \Delta\varepsilon(i\xi_n), \varepsilon_3 = \varepsilon_3(i\xi_n)$. This is one-dimensional crystal in which an inclusion $|z| < L/2$ with permittivity $\varepsilon_3 = \varepsilon_3(i\xi_n)$ is embedded. If the modulation amplitude $g = 0$ we have the standard problem of interaction of two identical macroscopic bodies having permittivity $\varepsilon = \varepsilon(i\xi_n)$ and separated by a plane parallel slab of thickness L. We will develop a perturbation theory valid for small modulation taking into account terms which are linear with respect to g. If $-L/2 < z, z', z_0 < L/2$ the full g_{11} function will be given by the following expression:

$$g_{11}(z, z') = A(z')e^{-w_3z} + B(z')e^{w_3z} - 2\pi\frac{c^2w_3}{\xi_n^2\varepsilon_3}e^{-w_3|z-z'|} \tag{3.5}$$

where the sum of the first two terms in (3.5) is exactly the function $\tilde{g}_{11}(z, z')$ and the third term is the function $\bar{g}_{11}(z, z')$. In the leftmost half-space we have

$$g_{11}(z < -L/2) = A_{\text{left}}(z')y_-(z) = A_{\text{left}}(z')e^{wz} \left(1 + g\Delta\varepsilon \left[b_c c(z) + b_s s(z)\right]\right) \qquad (3.6)$$

where A_{left} is an arbitrary constant, $w = [q^2 + \frac{\xi_n^2}{c^2}\varepsilon]^{1/2}$, $c(z) \equiv \cos(2q_0 z)$, $s(z) \equiv \sin(2q_0 z)$ and the other two constants in (3.6) are

$$b_c = -\frac{1}{4}(w^2 + q_0^2)^{-1}\left(\frac{2q^2}{\varepsilon} + \frac{\xi_n^2}{c^2}\right), \qquad b_s = -\frac{1}{4}\left(w^2 + q_0^2\right)^{-1}\left(\frac{2q_0 q^2}{\varepsilon w} - \frac{w\xi_n^2}{q_0 c^2}\right). \qquad (3.7)$$

In the rightmost half-space we have

$$g_{11}(z > L/2) = A_{\text{right}}(z')y_-(-z). \qquad (3.8)$$

The four functions of z', i.e. $A, B, A_{\text{left}}, A_{\text{right}}$, are easily determined from boundary conditions (2.17) applied at the planes $z = \pm L/2$. After that calculation the result of equations (3.2) and (3.3) was calculated. We will give this result for the van der Waals pressure only, i.e. in the limit $c \to \infty$. Actually the pressure depends on the thickness L and temperature T, but not on z_0 itself. It is convenient to introduce instead of q-integration an x-integration where $2qL = x$, and for the pressure $F(L, T)$ we will have

$$F(L, T) = F(z_0) = \frac{kT}{8\pi L^3}\sum_{n=0}^{\infty}{}' \int_0^{\infty} \frac{x^2 \Delta^2 e^{-x}}{1 - e^{-x}\Delta^2}\,dx \qquad (3.9)$$

where

$$\Delta \equiv \Delta(i\xi_n, q_0 L, x) = \frac{\varepsilon_3 - \varepsilon_{\text{eff}}}{\varepsilon_3 + \varepsilon_{\text{eff}}}, \qquad \varepsilon_{\text{eff}} = -\left[\frac{\varepsilon(z)\partial g_{11}(z)}{q g_{11}(z)\partial z}\right] \quad \left(z = \frac{L}{2} + 0\right). \qquad (3.10)$$

In the case of a modulated system of the type (3.4) we have

$$\varepsilon_{\text{eff}} = \varepsilon + g\Delta\varepsilon\frac{x}{x^2 + 4q_0^2 L^2}\left[x\cos(q_0 L) - 2q_0 L\sin(q_0 L)\right]. \qquad (3.11)$$

Analogous oscillatory effects with respect to the factor $q_0 L$ for anisotropic modulated systems have recently been obtained in [10]. It can be easily seen that the pressure $F(L, T)$ can be expressed in terms of the energy per unit area $G(L, T)$ where

$$G(L, T) = \frac{kT}{8\pi L^2}\sum_{n=0}^{\infty}{}' \int_0^{\infty} x\ln[1 - e^{-x}\Delta^2]\,dx, \qquad F(L, T) = \partial G/\partial L \qquad (3.12)$$

even if Δ is x and L dependent as is in our case. This result also holds and in the nonsymmetric case $\varepsilon(z) \neq \varepsilon(-z)$ if we replace $\Delta^2 \to \Delta_1\Delta_2$, where $\Delta_j(i\xi_n, L, x)$, $j = 1, 2$ can be easily calculated.

4. van der Waals interactions involving lipid and water layers

Inspired by the recent calculation of van der Waals interactions involving lipid vesicles [13] we consider once again the symmetrical model (3.4) but with modified leftmost and rightmost half-spaces. For $z > L/2$ we write

$$\varepsilon(i\xi_n, z) = \varepsilon_1(i\xi_n, z) \qquad (4.1)$$

and for $z < -L/2$ we define $\varepsilon(i\xi_n, z) = \varepsilon_1(i\xi_n, -z)$. Between these inhomogeneous half-spaces we once again assume we have a homogeneous layer with dielectric permittivity $\varepsilon_3(i\xi_n)$. It turns out that formula (3.12) will have place provided that the symbol Δ in it is calculated in

the new conditions. We denote the unknown solution for $g_{11}(z)$ in the rightmost half-space by $\varphi(z)$ (see equation (2.15) in electrostatic approximation) and we define our model as follows:

$$\frac{\partial^2 \varphi}{\partial z^2} - q^2 \varphi + \frac{\partial \ln \varepsilon_1(z)}{\partial z} \frac{\partial \varphi}{\partial z} = 0, \qquad \frac{L}{2} \leqslant z \leqslant \frac{L}{2} + D \tag{4.2}$$

$$\varphi \left(z > \frac{L}{2} + D \right) = C_{\text{right}} e^{-qz}. \tag{4.3}$$

Equation (4.3) tells us that we have assumed $\varepsilon_1(i\xi_n, z) = \varepsilon_1(i\xi_n)$ in the whole region $z > L/2 + D$, whereas in a *transition layer* $(L/2, L/2 + D)$ *with thickness D* the dependence of $\varepsilon_1(i\xi_n, z)$ on z is arbitrary. In equation (4.2) we can make the substitution

$$y(z) = \frac{\varepsilon_1(z)\partial \varphi}{\varphi(z)\partial z} \tag{4.4}$$

so that the following first order differential equation is formulated for $y(z)$:

$$\frac{\partial y}{\partial z} = \varepsilon(z)q^2 - \frac{y^2(z)}{\varepsilon(z)}. \tag{4.5}$$

For our purposes it is sufficient to know only $y(L/2)$, where

$$y \left(\frac{L}{2} \right) = -q\varepsilon_1 - \int_{L/2}^{L/2+D} \left[q^2 \varepsilon_1(z) - \frac{y^2(z)}{\varepsilon_1(z)} \right] dz. \tag{4.6}$$

If $D/L \ll 1$ we can write

$$y \left(\frac{L}{2} \right) = -q\varepsilon_1 - q^2 \int_{L/2}^{L/2+D} \left[\varepsilon_1(z) - \frac{\varepsilon_1^2}{\varepsilon_1(z)} \right] dz. \tag{4.7}$$

We can introduce the effective thickness D_{eff} of the transition layer with the following definition (see also formula (3.11)):

$$\frac{y(L/2)}{q} = -\varepsilon_1 - qD_{\text{eff}}. \tag{4.8}$$

Then the function Δ which appears in the formula for the interaction energy (3.12) will be

$$\Delta = \frac{\varepsilon_3 - \varepsilon_1 - qD_{\text{eff}}}{\varepsilon_3 + \varepsilon_1 + qD_{\text{eff}}} \approx \frac{\varepsilon_3 - \varepsilon_1}{\varepsilon_3 + \varepsilon_1} \left(1 - 2\frac{qD_{\text{eff}}\varepsilon_3}{\varepsilon_3^2 - \varepsilon_1^2} \right). \tag{4.9}$$

This formula together with (4.7), (4.8) is consistent with the two well-known cases where exact analytical solutions are available. The first case is for a triple film $\varepsilon_1(L/2 < z < L/2 + D) = \varepsilon_2$ [14] when

$$\Delta = \frac{\Delta_{32} + \Delta_{21}e^{-2qD}}{1 + \Delta_{32}\Delta_{21}e^{-2qD}}, \qquad \Delta_{ji} \equiv \frac{\varepsilon_j - \varepsilon_i}{\varepsilon_j + \varepsilon_i} \tag{4.10}$$

and the second case is for the exponential profile $\varepsilon_1(L/2 < z < L/2 + D) = \Gamma e^{-\lambda z}$ [15] when

$$D_{\text{eff}} = \frac{D(\varepsilon_3 - \varepsilon_1)^2}{\theta \varepsilon_3}, \qquad \theta \equiv \ln \frac{\varepsilon_3}{\varepsilon_1}. \tag{4.11}$$

For concreteness in evaluating equation (4.7) we choose the following linear profile:

$$\varepsilon_1(z) = \varepsilon_3 + \frac{(\varepsilon_1 - \varepsilon_3)}{D} \left[z - \frac{L}{2} \right] \tag{4.12}$$

so that the dielectric permittivity is continuous in the whole space (see figure 1).
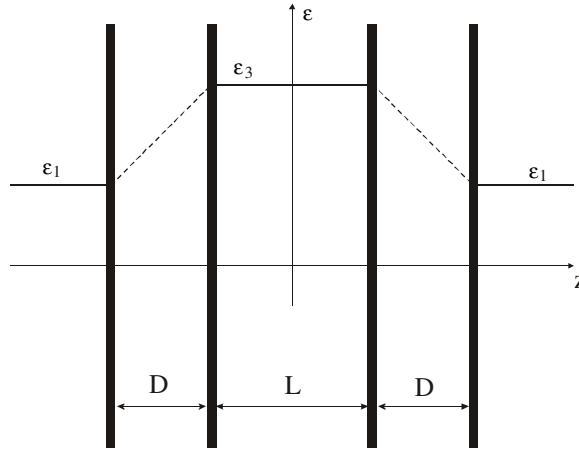
Figure 1. Schematic representation of the profile of the dielectric function $\varepsilon(z) = \varepsilon(-z)$ considered in section 4. The two phases $|z| < \frac{L}{2}$ and $|z| > \frac{L}{2} + D$ are separated by two transition layers both having thickness D. The dielectric permittivity in the region $\frac{L}{2} \leqslant z \leqslant \frac{L}{2} + D$ is given by equation (4.12).

Other analytical representations of $\varepsilon_1(z)$ important for real systems can be found in the recent paper by Podgornik and Parsegian [17]. In our case we have

$$D_{\text{eff}} = \frac{D}{\varepsilon_1 - \varepsilon_3} \left\{ \frac{\varepsilon_1^2 - \varepsilon_3^2}{2} + \varepsilon_1^2 \ln \frac{\varepsilon_3}{\varepsilon_1} \right\}. \qquad (4.13)$$

If we denote $x = 2qL$ as the meaning of x in (3.11) and also $a = D/L$ as well as $\chi \equiv \frac{\varepsilon_3}{\varepsilon_1}$, we will have

$$\Delta^2 = \left(\frac{\chi - 1}{\chi + 1} \right)^2 + x \frac{a\chi}{(\chi + 1)^2} \left(1 + 2 \ln \chi - \chi^2 \right). \qquad (4.14)$$

The energy per unit area (3.12) is usually written in the following canonical form:

$$G(L, D, T) = -\frac{A(a, T)}{12\pi L^2}, \qquad A(a, T) = -\frac{3kT}{2} \sum_{n=0}^{\infty}{}' \int_0^{\infty} x \ln(1 - \Delta^2 \mathrm{e}^{-x}) \, \mathrm{d}x \qquad (4.15)$$

where the Hamaker coefficient $A(a, T)$ is given by a double (s, n) summation:

$$A(a, T) = \frac{3kT}{2} \sum_{n=0}^{\infty}{}' \sum_{s=1}^{\infty} \frac{(\chi - 1)^{2s}}{(\chi + 1)^{2s}} \left[1 + 2a \frac{\chi(1 + 2 \ln \chi - \chi^2)}{(\chi - 1)^2(\chi + 1)} \right] \qquad (4.16)$$

and terms of the order $O(a^2)$ are neglected in the above three formulae. In appendix B we explain how (4.15) can be evaluated for the system lipid/water/lipid (abbreviated as lwl) at room temperature $kT = 0.404 \times 10^{-20}$ J. This means $\varepsilon_3 = \varepsilon_{\text{water}}$, $\varepsilon_1 = \varepsilon_{\text{lipid}}$. Because the coefficient before a in (4.16) is not invariant upon the replacement $\chi \to \chi^{-1}$ the system water/lipid/water (abbreviated as wlw) is also considered ($\varepsilon_3 = \varepsilon_{\text{lipid}}$, $\varepsilon_1 = \varepsilon_{\text{water}}$) in appendix B. The result of calculations depicted in figure 2 can be approximated with the following expressions:

$$A_{\text{lwl}} = (0.62\text{–}0.58a) \times 10^{-20} \text{ J}, \qquad A_{\text{wlw}} = (0.62\text{–}2.25a) \times 10^{-20} \text{ J}. \qquad (4.17)$$

The important question of approximate additive dispersion molecular interactions in these systems is also discussed in appendix B. The zero-frequency term and separately the dispersion-only contribution to the Hamaker function (4.16) are also given there.
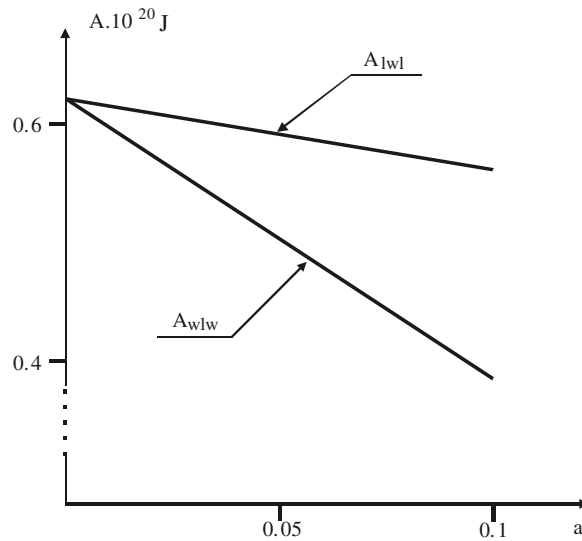
Figure 2. The function $A(a, kT = 0.404 \times 10^{-20}$ J). For thin transition layers such that $0 \leqslant a = \frac{D}{L} \leqslant 0.1$ the theory predicts a linear decrease of the Hamaker coefficient $A(a, T)$ with increase of a, which is different for lwl and wlw systems.

5. Conclusion

In this paper we have studied the effect of continuous spatial inhomogeneity on Casimir forces and especially on van der Waals interactions in various planar geometries. Prominent examples of isotropic modulated system (section 3) and lipid layers interacting across water (section 4) are considered in some detail. In section 4 we have calculated approximate analytical results for the interaction of lipid acting across a slab of water with thin intermediate layers having dielectric properties varying smoothly between the properties of both media. If a (see (4.17)) is estimated to be approximately 0.1 [15] the effect of inhomogeneity can be relatively large—between 10 and 30%. This result indicate the necessity of performing Lifshitz-type calculations on realistic layered models without the simplifying assumption that dielectric properties change discretely at the material interfaces, being constant within each material region.

Appendix A. The contribution of TE modes to the force formula (2.6)

If we rewrite equation (2.13) as

$$\left(\frac{d^2}{dz^2} - w^2(z) \right) g_{22}(z, z') = 4\pi \delta(z - z') \tag{A.1}$$

where

$$w(z) = \left[q^2 + \frac{\xi_n^2}{c^2} \varepsilon(i\xi_n, z) \right]^{1/2} \tag{A.2}$$

we can easily derive its general solution:

$$g_{22}(z, z') = A(z') f_+(z) + B(z') f_-(z) + 4\pi c_{TE}$$
$$\left[f_+(z) f_-(z') \theta(z - z') + f_+(z') f_-(z) \theta(z' - z) \right] \tag{A.3}$$

where $\theta(z > 0) = 1, \theta(z < 0) = 0, A(z'), B(z')$ are arbitrary functions of z', and

$$c_{\text{TE}} = \left[f'_+(z)f_-(z) - f_+(z)f'_-(z) \right]^{-1} \tag{A.4}$$

is a constant which does not depend on z. Here and in the whole paper $F'(z) \equiv \frac{\mathrm{d}F(z)}{\mathrm{d}z}$. The two linearly independent solutions to the homogeneous equation

$$\frac{\mathrm{d}^2 f_{\pm}(z)}{\mathrm{d}z^2} - w^2(z)f_{\pm}(z) = 0 \tag{A.5}$$

have at large positive values of z asymptotics of the form $f_+(z) \approx \mathrm{e}^{-wz}, f_-(z) \approx \mathrm{e}^{wz}, \lim_{z \to \infty} w(z) = w > 0$. The general definition (2.3) tells us that

$$\tilde{g}_{22}(z, z') = g_{22}(z, z') + \frac{2\pi}{w(z_0)} \exp[-w(z_0)|z - z'|]. \tag{A.6}$$

Also for transverse-electric waves we have

$$\tilde{D}_{ij}^{(\text{TE})}(\vec{r}, \vec{r}'; \xi_n) = \int \frac{\mathrm{d}^2\vec{q}}{4\pi^2} \mathrm{e}^{\mathrm{i}\vec{q}\cdot(\vec{\rho}-\vec{\rho}')} \left(\delta_{ij} - \frac{q_i q_j}{q^2} - n_i n_j \right) \tilde{g}_{22}(q, \xi_n; z, z') \tag{A.7}$$

where $\vec{n}(0, 0, 1)$. The tedious and bulky calculations which follow from (A.7), (2.3)–(2.6) lead to the following formula for Casimir pressure (TE mode):

$$F^{(\text{TE})}(z_0) = \frac{kT}{8\pi^2} \sum_{n=0}^{\infty}{}' I_n^{(\text{TE})}(z_0) \tag{A.8}$$

where

$$I_n^{(\text{TE})}(z_0) = \int_0^{\infty} q \left\{ \left[\frac{\partial^2}{\partial z \partial z'} - w^2(z) \right] \tilde{g}_{22}(z, z') \right\} (z = z' = z_0) \, \mathrm{d}q. \tag{A.9}$$

In the Lifshitz case, $\varepsilon(z < 0) = \varepsilon_1, \varepsilon(0 < z < L) = \varepsilon_3, \varepsilon(L < z) = \varepsilon_2$ for $z_0 \in (0, L)$, we have

$$\tilde{g}_{22}(z, z') = \frac{2\pi}{w_3 \Delta} \left(b_1(z')\mathrm{e}^{w_3 z} + b_2(z')\mathrm{e}^{-w_3 z} \right) \tag{A.10}$$

$$b_1(z') = \mathrm{e}^{-w_3 z'} + \left(\frac{w_3 + w_1}{w_3 - w_1} \right) \mathrm{e}^{w_3 z'} \tag{A.11}$$

$$b_2(z') = \mathrm{e}^{w_3 z'} + \left(\frac{w_3 + w_2}{w_3 - w_2} \right) \mathrm{e}^{-w_3 z' + 2w_3 L} \tag{A.12}$$

$$\Delta = 1 - \mathrm{e}^{2w_3 L} \frac{(w_3 + w_1)(w_3 + w_2)}{(w_3 - w_1)(w_3 - w_2)}. \tag{A.13}$$

Then equation (A.9) reduces to the TE-part of the Lifshitz formula. The result for all z_0 depends only on the thickness L but not on z_0 itself. If we denote the interaction energy per unit area by $E(L, T)$, so that $F(L, T) = \partial E(L, T)/\partial L$, we have

$$E(L, T) = \frac{kT}{2\pi} \sum_{n=0}^{\infty}{}' \int_0^{\infty} q \ln[1 - \mathrm{e}^{-2w_3 L} \Delta_1 \Delta_2] \, \mathrm{d}q \tag{A.14}$$

where

$$\Delta_1 = \frac{w_3 - w_1}{w_3 + w_1}, \qquad \Delta_2 = \frac{w_3 - w_2}{w_3 + w_2}. \tag{A.15}$$

In the Lifshitz case the result for the TM mode is the same, with the replacement in (A.15) $w_j \to \frac{\varepsilon_j}{w_j}$. Of some academic interest is the use of general formulae (A.3), (A.6), (A.9) in the case when $\varepsilon(z)$ is a continuous function of z for all $-\infty < z < \infty$. In this case in (A.3), of course, we have $A(z') = B(z') = 0$. The two solutions of equation (A.5) can be found in the frame of the WKB approximation under well-defined restrictions (see [11]). In this paper we do not explore this interesting possibility.

Appendix B. Analysis of Hamaker function (4.16). Semiempirical determination of $\varepsilon(i\xi)$ for lipid and water

We will accept the following approximation for the Hamaker function (4.16):

$$A(a, T) = A_{n=0}(a, T) + A^*(a) \tag{B.1}$$

where

$$A_{n=0}(a, T) = \frac{3kT}{4}\left(1 + \frac{2a\chi_0(1 + 2\ln\chi_0 - \chi_0^2)}{(\chi_0 - 1)^2(\chi_0 + 1)}\right)\sum_{s=1}^{\infty}s^{-3}\left(\frac{\chi_0 - 1}{\chi_0 + 1}\right)^{2s} \tag{B.2}$$

$$A^*(a) = \frac{3\hbar}{4\pi}\int_0^{\infty}\mathrm{d}\xi\left(\frac{\chi - 1}{\chi + 1}\right)^2\left[1 + 2a\frac{\chi(1 + 2\ln\chi - \chi^2)}{(\chi - 1)^2(\chi + 1)}\right]. \tag{B.3}$$

B.1. Lipid–water–lipid system

This system when $a = 0$ has been studied in [13]. The dielectric permittivity of water and lipid DPPC (dipalmitoylphosphatidylcholine) are described in semiempirical approximation with formulae of the type [16]

$$\frac{\varepsilon(i\xi) - 1}{\varepsilon(i\xi) + 1} = \alpha e^{-\beta\xi}. \tag{B.4}$$

We accept for water $\alpha = 0.280$, $\beta = 1.715 \times 10^{17}$ s rad^{-1} and for lipid $\alpha = 0.363$, $\beta = 1.920 \times 10^{-17}$ s rad^{-1}. These four numbers are sufficient for calculations in (B.3), but for (B.2) we also need the dielectric permittivities at zero frequency, which are: for water $\varepsilon(0) = 80$ and for lipid $\varepsilon(0) = 2.14$. If we accept the notations

$$B_{1,3} = \alpha_{1,3}\exp[-\beta_{1,3}\xi] \tag{B.5}$$

the function

$$\chi(\xi) - 1 = 2(B_3 - B_1)\sum_{n=0}^{\infty}(B_3 - B_1 + B_1B_3)^n \tag{B.6}$$

will be represented by a power series of the form

$$\chi - 1 = 2(B_3 - B_1) + 2(B_3 - B_1)^2 + 2(B_3 - B_1)(B_3^2 + B_1^2 - B_1B_3) + \cdots \tag{B.7}$$

neglecting fourth order terms ($\alpha_1^4, \alpha_2^4, \alpha_1\alpha_2^3, \alpha_1^3\alpha_2, \alpha_1^2\alpha_2^2$), which is valid under the condition that $\alpha_{1,2} < 1$, $\beta_1 \approx \beta_2$. Then formula (B.3) will be given by the following approximate expression:

$$\frac{4\pi}{3\hbar}A^*(a) = (1 - 2a)\int_0^{\infty}\mathrm{d}\xi\left(B_3^2 + B_1^2 - 2B_1B_3\right)$$
$$- 2a\int_0^{\infty}\mathrm{d}\xi\left[\tfrac{1}{3}B_3^3 - B_1B_3^2 + B_1^2B_3 - \tfrac{1}{3}B_1^3\right] \tag{B.8}$$

$$A^*(0) = A_{33} + A_{11} - 2A_{13}, \qquad A_{ij} \equiv \frac{3\hbar}{4\pi}\frac{\alpha_i\alpha_j}{\beta_i + \beta_j} \tag{B.9}$$

is the macroscopic analogue of the compound Hamaker constant obtained from pair-wise summation of additive dispersion molecular interactions [13, 16]. The cubic terms which appear in the second integral in (B.8) correspond to a non-additivity correction due to the nonhomogeneity of the system ($a \neq 0$). Using the values given after formula (B.4) we obtain for the dispersion-only contribution

$$A^*(a) = 0.31(1 + 0.17a) \times 10^{-20}\ \mathrm{J} \tag{B.10}$$

and for the zero-frequency term (B.2) at $kT = 0.404 \times 10^{-20}$ J

$$A_{n=0} = [0.31\text{--}0.63a] \times 10^{-20} \text{ J}. \tag{B.11}$$

The sum of (B.10) and (B.11) gives the first estimation for the lwl system given in formula (4.17).

B.2. Water/lipid/water system

For the *water/lipid/water* system the calculations are similar to the derivations leading to (B.10) and (B.11) but now the coefficients before a are different:

$$A^*(a) = (0.31\text{--}1.3a) \times 10^{-20} \text{ J}, \qquad A_{n=0} = (0.31\text{--}0.95a) \times 10^{-20} \text{ J}. \tag{B.12}$$

A comparison with the simple result (B.9) clearly shows that pair-wise summation is not justified in systems with continuously varying dielectric functions.

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