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Nonadditivity in van der Waals interactions within multilayers

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Working at the macroscopic continuum level, we investigate effective van der Waals interactions between two layers within a multilayer assembly. By comparing the pair interactions between two layers with effective pair interactions within an assembly we assess the significant consequences of nonadditivity of van der Waals interactions. This allows us to evaluate the best numerical estimate to date for the Hamaker coefficient of van der Waals interactions in lipid-water multilamellar systems. © 2006 American Institute of Physics. [DOI: 10.1063/1.2150825]

I. INTRODUCTION

Multilayers are ubiquitous in phospholipid assemblies¹ as well as in polymers assembled either electrostatically² or by interlayer hydrogen bonding,³ and in inorganic systems such as the intergranular films in silicon nitride structural ceramics⁴ or interfaces and grain boundaries in perovskite-based electronic ceramics.⁵ Understanding molecular interactions in these systems is an important step in controlling the assembly process. Though interactions in these assemblies are due to many different specific properties, van der Waals (vdW) interactions are a common underlying feature. Despite years of intense study the general and exact derivations of van der Waals interactions on the Lifshitz level is abstruse,⁶ unless one is satisfied with the pairwise additive formulation of van der Waals interactions in multilayer geometries.⁷

Here we will use a recent reformulation of the van der Waals–Lifshitz interactions in multilayer geometries⁸ in terms of an algebra of 2×2 matrices that will allow us to derive simple and transparent formulas for the van der Waals interactions within finely layered systems.⁹ In what follows we will analyze how the presence of other layers in a multilamellar system influences the effective pair interactions between a neighboring pair of layers. This will also allow us to obtain accurate distance dependence and magnitude of the van der Waals interactions in multilamellar systems.

We will first derive the general formulas for the van der Waals free energy of a multilayered system and then extract the effective van der Waals pair-interaction potential between two neighboring layers. We will compare this result with the standard van der Waals–Lifshitz interaction between two layers and quantify the nonpairwise additive effects, i.e., the difference between the full multilayer Lifshitz form and the corresponding expression for a two-layer case.

II. FORMALISM

Consider a symmetric periodic array, Fig. 1, between a left half-space L and a right half-space R . The periodic motif

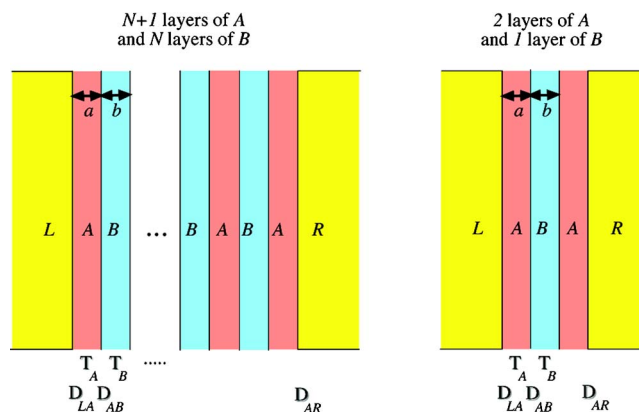


FIG. 1. Schematic description of model. Left-hand side: multilamellar system with A for lipid and B for water layers. Right-hand side: two isolated A layers interacting across a single B layer.

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is the N times repeated sequence of AB pairs between L and R , schematically $L(AB)_N AR$. For concreteness imagine layers A as lipid and all the other layers $L\dots B\dots R$ as solvent.

We recently showed^{8,9} that in the Lifshitz theory computation of the secular determinant of the electromagnetic field modes can be mapped onto an algebra of 2×2 matrices. The

secular determinant in fact follows from the 11 elements of a transfer matrix that can be simply constructed from the interaction geometry as a product of discontinuity \mathbb{D} and propagator \mathbb{T} matrices. In the case considered here, following the ‘‘mnemonic’’ introduced in Ref. 8, the transfer matrix assumes the form

$$\mathbb{M} = \mathbb{D}_{RA} \times \underbrace{\mathbb{T}_A \times \mathbb{D}_{AB} \times \mathbb{T}_B \times \mathbb{D}_{BA}}_A \times \dots \times \underbrace{\mathbb{T}_A \times \mathbb{D}_{AB} \times \mathbb{T}_B \times \mathbb{D}_{BA}}_A \times \mathbb{T}_A \times \mathbb{D}_{AL}. \quad (1)$$

N

The case of two isolated layers can be described with exactly the same formalism with $N=1$.

In the above notation the discontinuity and propagator matrices become

$$\mathbb{D}_{AB} = \begin{pmatrix} 1 & -\bar{\Delta} \\ -\bar{\Delta} & 1 \end{pmatrix} = -\mathbb{D}_{BA} \quad (2)$$

and

$$\mathbb{T}_{A,B} = \begin{pmatrix} 1 & 0 \\ 0 & e^{-2\rho_{A,B}a,b} \end{pmatrix}, \quad (3)$$

where a and b are the thicknesses of the A and B regions, and

$$\bar{\Delta} = \begin{pmatrix} \rho_A \epsilon_B - \rho_B \epsilon_A \\ \rho_A \epsilon_B + \rho_B \epsilon_A \end{pmatrix}, \quad (4)$$

with $\epsilon_A(\omega)$ and $\epsilon_B(\omega)$ the frequency-dependent dielectric functions of regions A and B ; $\rho_{A,B}^2 = Q^2 - \epsilon_{A,B}\omega^2/c^2$, where Q is the magnitude of the transverse wave vector and ω is the frequency of the corresponding em mode.

We will assume that region A corresponds to hydrocarbon, $\epsilon_A(\omega)$, and regions L , B , and R to water, $\epsilon_B(\omega)$, dielectric responses. In the computation, below, we use standard^{10,11} forms for $\epsilon_A(\omega)$ and $\epsilon_B(\omega)$, where the dielectric response of water is described with one microwave relaxation frequency, five infrared relaxation frequencies, and six ultraviolet relaxation frequencies, and that of the hydrocarbons with four ultraviolet relaxation frequencies (for details see Ref. 12). The ω dependence of $\epsilon_A(i\omega)$ and $\epsilon_B(i\omega)$ is

presented in Fig. 2. By the Kramers-Kronig relations $\epsilon_{A,B}(i\omega)$ decrease monotonically, limiting to 1 at very high frequencies $\gtrsim 10^{17} \text{ s}^{-1}$.

The discontinuity matrix \mathbb{D} describes the propagation of the electromagnetic modes across the dielectric boundary and the propagator matrix \mathbb{T} their propagation inside a dielectrically homogeneous region. The above equations are valid for the transverse magnetic (TM) field modes.¹³ The result for the transverse electric (TE) field modes¹³ is obtained analogously via a formal substitution

$$\bar{\Delta} = \begin{pmatrix} \rho_A \epsilon_B - \rho_B \epsilon_A \\ \rho_A \epsilon_B + \rho_B \epsilon_A \end{pmatrix} \rightarrow \Delta = \begin{pmatrix} \rho_A \mu_B - \rho_B \mu_A \\ \rho_A \mu_B + \rho_B \mu_A \end{pmatrix}, \quad (5)$$

where $\mu_{A,B}$ denote magnetic permeabilities.

The transfer matrix with elements m_{ik} can be written equivalently in the form

$$\mathbb{M} = \mathbb{D}_{RA} \times \mathbb{A}^N \times \mathbb{T}_A \times \mathbb{D}_{AL}, \quad (6)$$

where the matrix \mathbb{A} with elements a_{ik} has the form^{8,9}

$$\mathbb{A} = \mathbb{T}_A \times \mathbb{D}_{AB} \times \mathbb{T}_B \times \mathbb{D}_{BA} = \begin{pmatrix} 1 - \bar{\Delta}^2 e^{-2\rho_B b} & \bar{\Delta}(1 - e^{-2\rho_B b}) \\ -\bar{\Delta} e^{-2\rho_A a}(1 - e^{-2\rho_B b}) & e^{-2\rho_A a}(e^{-2\rho_B b} - \bar{\Delta}^2) \end{pmatrix}. \quad (7)$$

The product \mathbb{A}^N can be factored with the help of the Abelés formula for square matrices.¹⁴ This formula can be reproduced straightforwardly via induction starting from the trivial $N=2$ case¹⁵ so that

$$\mathbb{A}^N = \frac{(\det \mathbb{A})^{N/2}}{\sinh \xi} \begin{pmatrix} \sinh N\xi \frac{a_{11}}{\sqrt{\det \mathbb{A}}} - \sinh(N-1)\xi & \sinh N\xi \frac{a_{12}}{\sqrt{\det \mathbb{A}}} \\ \sinh N\xi \frac{a_{12}}{\sqrt{\det \mathbb{A}}} & \sinh N\xi \frac{a_{11}}{\sqrt{\det \mathbb{A}}} - \sinh(N-1)\xi \end{pmatrix}, \quad (8)$$

where

$$\xi \equiv \ln \frac{1}{2} \frac{\text{Tr } \mathbf{A}}{\sqrt{\det \mathbf{A}}} \left(1 + \sqrt{1 - 4 \frac{\det \mathbf{A}}{(\text{Tr } \mathbf{A})^2}} \right). \quad (9)$$

Here e^ξ and $e^{-\xi}$ are the two eigenvalues of the matrix $\mathbf{A}^* = \mathbf{A} / \sqrt{\det \mathbf{A}}$.

The em mode equation, from the secular determinant of the TM field modes, can be written as $m_{11}^{\text{TM}} = \mathcal{D}_{\text{TM}}(\omega, Q) = 0$,⁸ with an analogous equation for TE modes. The combined secular determinant thus becomes the product $\mathcal{D}(\omega, Q) = \mathcal{D}_{\text{TM}}(\omega, Q) \mathcal{D}_{\text{TE}}(\omega, Q)$. In the Lifshitz theory the fluctuation free energy is directly related to the 11 elements of the transfer matrix \mathbf{M} .⁸ For a system of N (AB) layers it can be cast⁸ into a form containing the secular determinant of the TM and TE modes

$$\begin{aligned} \mathcal{F}(N; a, b) = kT \sum_{\mathbf{Q}} \sum_{n=0}^{\infty} \ln m_{11}^{\text{TM}}(i\xi_n, Q) \\ + kT \sum_{\mathbf{Q}} \sum_{n=0}^{\infty} \ln m_{11}^{\text{TE}}(i\xi_n, Q), \end{aligned} \quad (10)$$

where ω is now explicitly the set of imaginary Matsubara frequencies $i\xi_n = i2\pi(kT/\hbar)n$ and the primed sum signifies that the $n=0$ term is taken with the weight 1/2. The sum over the transverse wave vector can be written explicitly as

$$\sum_{\mathbf{Q}} \rightarrow S \int \frac{d^2\mathbf{Q}}{(2\pi)^2} = \frac{S}{2\pi} \int_0^\infty Q dQ, \quad (11)$$

where S is the total area of the interfacial surface. In what follows we take the standard assumption that the magnetic susceptibilities of the materials, contrary to their dielectric properties, are homogeneous and everywhere equal to unity.¹²

We investigate the van der Waals interaction free energy, defined as the difference

$$\mathbb{F}(N; a, b) = \mathcal{F}(N; a, b) - \mathcal{F}(N; a, b \rightarrow \infty) \quad (12)$$

on the thickness of the solvent layer B . We can write

$$\mathbb{A}^N = (\text{Det } \mathbf{A})^{(N-1)/2} \frac{\sinh N\xi}{\sinh \xi} \begin{bmatrix} a_{11} - a^{(N)} & a_{12} \\ a_{21} & a_{22} - a^{(N)} \end{bmatrix}, \quad (13)$$

where

$$a^{(N)} = \frac{\sinh(N-1)\xi}{\sinh N\xi} \sqrt{\text{Det } \mathbf{A}}. \quad (14)$$

Obviously $a^{(N=1)} = 0$. By Eq. (6) the m_{11} element of the transfer matrix is obtained as

$$\begin{aligned} m_{11}^{(N)} = (\text{Det } \mathbf{A})^{(N-1)/2} \frac{\sinh N\xi}{\sinh \xi} (a_{11} - a_{21}\bar{\Delta} + \bar{\Delta}(a_{12} \\ - a_{22}\bar{\Delta})e^{-2\rho_A a} - a^{(N)}(1 - \bar{\Delta}^2 e^{-2\rho_B b})). \end{aligned} \quad (15)$$

Equivalently,

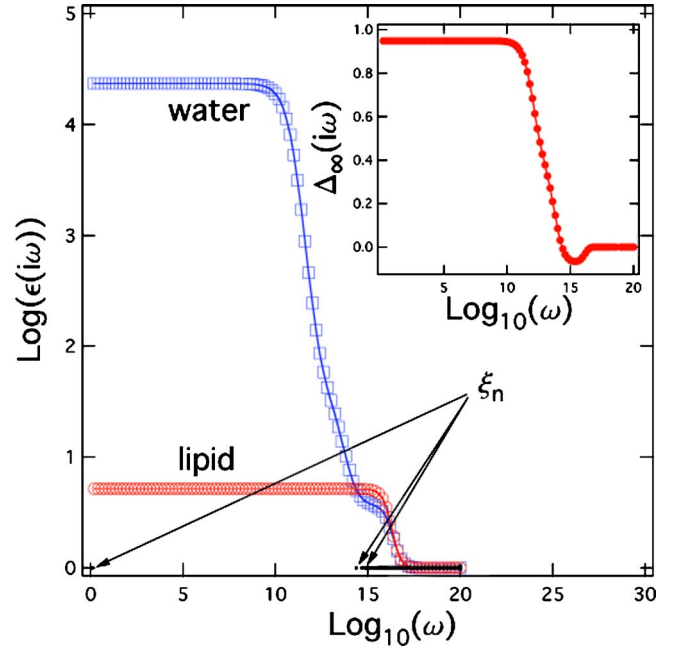


FIG. 2. Dependence of $\epsilon_A(i\omega)$ (lipid) and $\epsilon_B(i\omega)$ (water). The inset shows the dependence of the nonretarded limit Eq. (28) $\bar{\Delta}_\infty(i\omega)$. Clearly for all the Matsubara frequencies $\bar{\Delta}_\infty(i\xi_n) \ll 1$, except in the static case $n=0$ where $\bar{\Delta}_\infty(i\xi_n) \sim 1$. The bottom dots merging into a continuum after $\omega = \xi_1 \sim 10^{14} \text{ s}^{-1}$ represent the Matsubara frequencies ξ_n .

$$m_{11}^{(N)} = (\text{Det } \mathbf{A})^{(N-1)/2} \frac{\sinh N\xi}{\sinh \xi} (m_{11}^{(N=1)} - a^{(N)}(1 - \bar{\Delta}^2 e^{-2\rho_B b})). \quad (16)$$

In this way using Eq. (16) in the limit of $N=1$, the interaction of two isolated lipid layers of finite thickness a at a separation b is trivially recovered. The van der Waals free energy is proportional to the trace of the \ln of the $m_{11}^{(N)}$ element of Eq. (10).¹² If we discard all the irrelevant constants and bulk terms (which scale linearly with the total thickness of AB layers), we are left with

$$\ln m_{11}^{(N)} = \ln \frac{\sinh N\xi}{\sinh \xi} + \ln(m_{11}^{(N=1)} - a^{(N)}(1 - \bar{\Delta}^2 e^{-2\rho_B b})). \quad (17)$$

The secular determinant depends on both a and b as well as on the dielectric properties of both materials. The van der Waals free energy is defined via the \ln of the secular determinant, and thus we can extract the difference [Eq. (12)] from

$$\begin{aligned} \ln \frac{m_{11}^{(N)}(b)}{m_{11}^{(N)}(b \rightarrow \infty)} = \ln \frac{\sinh N\xi}{\sinh N\xi_\infty} - \ln \frac{\sinh \xi}{\sinh \xi_\infty} \\ + \ln \frac{(m_{11}^{(N=1)} - a^{(N)}(1 - \bar{\Delta}^2 e^{-2\rho_B b}))}{(m_{11}^{(N=1)}(b \rightarrow \infty) - a^{(N)}(b \rightarrow \infty))} \end{aligned} \quad (18)$$

and use it to evaluate the required interaction free energy.

For $N \gg 1$, the extensive part of the above interaction free energy is given by

$$\lim_{N \rightarrow \infty} \ln \frac{m_{11}^{(N)}(b)}{m_{11}^{(N)}(b \rightarrow \infty)} \cong N(\xi - \xi_\infty) + \mathcal{O}[N^{-1}]. \quad (19)$$

From Eq. (10) in the asymptotic limit of a large number of layers, the interaction free energy thus becomes

$$\begin{aligned} \mathcal{F}(N; a, b) &= kT \sum_{\mathbf{Q}} \sum_{n=0}^{\infty} ' \lim_{N \rightarrow \infty} \ln \frac{m_{11}^{(N)}(b)}{m_{11}^{(N)}(b \rightarrow \infty)} \\ &= NkT \sum_{\mathbf{Q}} \sum_{n=0}^{\infty} ' (\xi - \xi_\infty) \equiv Nf(a, b), \end{aligned} \quad (20)$$

where $f(a, b)$ can be interpreted as an effective pair interaction between two neighboring layers in the stack. This expression should be compared with the van der Waals interaction energy between two isolated layers, which can be derived from Eq. (18) for $N=1$ as

$$\begin{aligned} f_0(a, b) &= \mathcal{F}(N=1; a, b) \\ &= kT \sum_{\mathbf{Q}} \sum_{n=0}^{\infty} ' \ln \left(1 - \frac{(1 - e^{-2\rho_A a})^2 \bar{\Delta}^2 e^{-2\rho_B b}}{(1 - \bar{\Delta}^2 e^{-2\rho_A a})} \right). \end{aligned} \quad (21)$$

This form can be derived by a variety of other methods.^{11,12}

$$f(a, b) = kT \sum_{\mathbf{Q}} \sum_{n=0}^{\infty} ' \ln \left[\frac{1 - \bar{\Delta}^2 (e^{-2\rho_A a} + e^{-2\rho_B b}) + e^{-2(\rho_A a + \rho_B b)}}{(1 - \bar{\Delta}^2 e^{-2\rho_A a})} + \sqrt{\frac{\mathcal{G}(a, b, \bar{\Delta})}{(1 - \bar{\Delta}^2 e^{-2\rho_A a})^2}} \right]. \quad (25)$$

The obvious difference of the two forms—the effective pair interaction in an array [Eq. (25)] and the pair interaction of an isolated pair of layers [Eq. (21)]—is a consequence of the nonadditivity of van der Waals interactions.

One should note here that in the limit of infinitely polarizable media, $\bar{\Delta}^2 \rightarrow 1$, Eq. (25) reduces to the interaction of two metal plates. Obviously in this case, and for this case alone, there are no effects due to the nonadditivity of van der Waals interactions since the em field is ideally screened by the dielectric interfaces.

III. RESULTS

A. The asymptotic limit, $a \ll b$

To build some intuition for nonpairwise additive effects, first consider a few limiting results. For very thin layers $a \ll b$, the effective pair interaction [Eq. (25)] goes over to

To derive a more explicit form for the effective pair interaction $f(a, b)$ [Eq. (20)] in an array, use Eq. (9),

$$\xi = \ln(u + \sqrt{u^2 - 1}) \quad \text{with} \quad (22)$$

$$u = \frac{1}{2} \frac{1 - \bar{\Delta}^2 (e^{-2\rho_A a} + e^{-2\rho_B b}) + e^{-2(\rho_A a + \rho_B b)}}{(1 - \bar{\Delta}^2)^2 e^{-(\rho_A a + \rho_B b)}},$$

or

$$\begin{aligned} \xi - \xi_\infty &= \ln \frac{1}{2} \left[\frac{1 - \bar{\Delta}^2 (e^{-2\rho_A a} + e^{-2\rho_B b}) + e^{-2(\rho_A a + \rho_B b)}}{(1 - \bar{\Delta}^2)^2 e^{-2\rho_A a}} \right. \\ &\quad \left. + \sqrt{\frac{\mathcal{G}(a, b, \bar{\Delta})}{(1 - \bar{\Delta}^2 e^{-2\rho_A a})^2}} \right]. \end{aligned} \quad (23)$$

Here

$$\begin{aligned} \mathcal{G}(a, b, \bar{\Delta}) &= (1 - e^{-2(\rho_A a + \rho_B b)})^2 - 2\bar{\Delta}^2 (e^{-2\rho_A a} + e^{-2\rho_B b}) \\ &\quad \times (1 + e^{-2(\rho_A a + \rho_B b)}) - 4e^{-2(\rho_A a + \rho_B b)} \\ &\quad + \bar{\Delta}^4 (e^{-2\rho_A a} - e^{-2\rho_B b}). \end{aligned} \quad (24)$$

This leads to the final result for the effective pair-interaction energy

$$\begin{aligned} f(a, b) &= kT \sum_{\mathbf{Q}} \sum_{n=0}^{\infty} ' \ln \left(1 - \frac{\bar{\Delta}^2 (2\rho_A a)^2 e^{-2\rho_B b}}{(1 - e^{-2\rho_B b})(1 - \bar{\Delta}^2)^2} \right) \\ &\rightarrow -kT \sum_{\mathbf{Q}} \sum_{n=0}^{\infty} ' \frac{\bar{\Delta}^2 (2\rho_A a)^2 e^{-2\rho_B b}}{(1 - e^{-2\rho_B b})(1 - \bar{\Delta}^2)^2}, \end{aligned} \quad (26)$$

while the isolated pair interaction [Eq. (21)] in the same limit takes the form

$$\begin{aligned} f_0(a, b) &= kT \sum_{\mathbf{Q}} \sum_{n=0}^{\infty} ' \ln \left(1 - \frac{\bar{\Delta}^2 (2\rho_A a)^2 e^{-2\rho_B b}}{(1 - \bar{\Delta}^2)} \right) \\ &\rightarrow -kT \sum_{\mathbf{Q}} \sum_{n=0}^{\infty} ' \frac{\bar{\Delta}^2 (2\rho_A a)^2 e^{-2\rho_B b}}{(1 - \bar{\Delta}^2)}. \end{aligned} \quad (27)$$

These expansions of the complete forms [Eqs. (25) and (21)] are valid only if the argument of the ln function is positive, which is by definition always the case in the limit $a \ll b$.

The nonretarded limit, with $c \rightarrow \infty$ and $\rho_{A,B} \rightarrow Q$,

$$\bar{\Delta}(\omega) \rightarrow \bar{\Delta}_\infty(\omega) = \left(\frac{\epsilon_B(\omega) - \epsilon_A(\omega)}{\epsilon_B(\omega) + \epsilon_A(\omega)} \right), \quad (28)$$

can be evaluated analytically. We are left with the following results for the effective pair potential:

$$f(a,b) \simeq - \frac{SkT(2a)^2 \pi^4}{2\pi(2b)^4} \sum_{n=0}^{\infty} \frac{\bar{\Delta}_\infty^2(\omega\xi_n)}{(1 - \bar{\Delta}_\infty^2(\omega\xi_n))^2} \quad (29)$$

and the isolated-pair potential:

$$f_0(a,b) \simeq \frac{SkT(2a)^2}{2\pi(2b)^4} 6 \sum_{n=0}^{\infty} \frac{\bar{\Delta}_\infty^2(\omega\xi_n)}{(1 - \bar{\Delta}_\infty^2(\omega\xi_n))}. \quad (30)$$

Above S the total area of the interacting surfaces. The effective pair interaction in an array is thus enhanced by a factor

$$E = \frac{\pi^4}{15} \sum_{n=0}^{\infty} \frac{\bar{\Delta}_\infty^2(\omega\xi_n)}{(1 - \bar{\Delta}_\infty^2(\omega\xi_n))^2} \Big/ \frac{6 \sum_{n=0}^{\infty} \frac{\bar{\Delta}_\infty^2(\omega\xi_n)}{(1 - \bar{\Delta}_\infty^2(\omega\xi_n))}. \quad (31)$$

With water and lipid dielectric responses this comes to $E = 10.637$ (by summing the first 1000 terms, the numerator equals 607.179 and the denominator equals 55.442). Nonpairwise additive effects boost the interaction by a factor of ~ 10 in this particular case, which is substantial.

In order for the expansions [Eqs. (26) and (27)] to make sense, the following two conditions have to be fulfilled:

$$(ab)^2 \sum_{n=0}^{\infty} \frac{\bar{\Delta}_\infty^2(\omega\xi_n)}{(1 - \bar{\Delta}_\infty^2(\omega\xi_n))^2} \ll 1 \text{ and} \quad (32)$$

$$(ab)^2 \sum_{n=0}^{\infty} \frac{\bar{\Delta}_\infty^2(\omega\xi_n)}{(1 - \bar{\Delta}_\infty^2(\omega\xi_n))} \ll 1.$$

Obviously the range of validity of these two conditions depends on the largest value of the dielectric discontinuity. Evaluating the first condition for the numerical case treated above (water-lipid) with $a=4$ nm, we get the value of the order of $b \geq 100$ nm for the effective pairwise case and about $\sqrt{10.637}$ times smaller value for the isolated pair case.

Should the dielectric discontinuity be very large at any frequency, $\bar{\Delta}_\infty^2(\omega\xi_n) \rightarrow 1$, the range of validity of Eqs. (29) and (30) is displaced towards very large values of the interlayer spacings b . For any finite value of b we recover the Casimir result, valid for infinitely polarizable material A.

Note that the b dependence for the effective and isolated pair cases remains unchanged: interactions vary identically as $f(a,b) \sim f_0(a,b) \sim b^{-4}$. The nonpairwise additive effects thus merely boost the prefactor of this dependence.

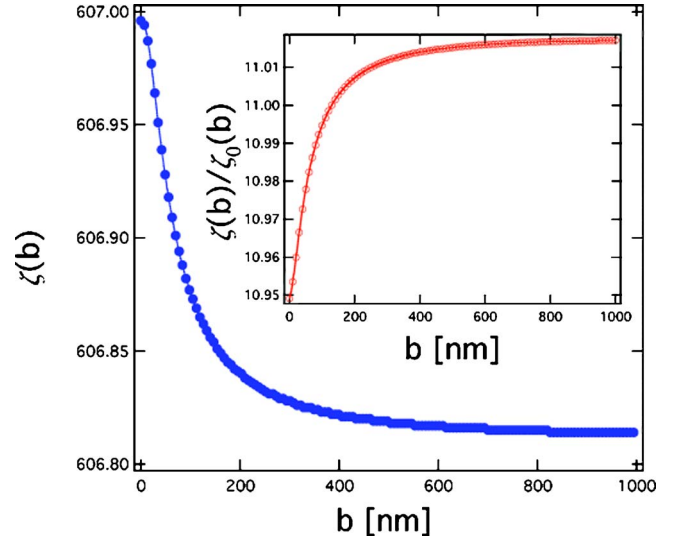


FIG. 3. Dependence of $\zeta(b)$ and the ratio $\zeta(b)/\zeta_0(b)$ from Eqs. (33) and (36) on the separation b . We see that the dependence of both functions $\zeta(b)$ and $\zeta_0(b)$ on b is weak. The nonpairwise boost remains pretty much the same as in the nonretarded limit.

To estimate retardation effects we follow the standard approach¹² and assume that the speed of light in both materials is the same and equal to the speed of light in the intervening medium (water) so that $\rho_A = \rho_B$. $\bar{\Delta}(\omega\xi_n)$ then retains its nonretarded form, $\bar{\Delta}_\infty(\omega\xi_n)$ [Eq. (28)]. This turns out to be a very good approximation to quantitatively describe the retardation effects.¹² We thus get for the effective pair potential

$$f(a,b) \simeq - \frac{SkT(2a)^2}{4\pi(2b)^4} \zeta(b), \quad (33)$$

where

$$\zeta(b) = \frac{\pi^4}{15} \frac{\bar{\Delta}_\infty^2(0)}{(1 - \bar{\Delta}_\infty^2(0))^2} + \sum_{n=1}^{\infty} \frac{4\mathcal{P}(b\alpha_n)\bar{\Delta}_\infty^2(\omega\xi_n)}{(1 - \bar{\Delta}_\infty^2(\omega\xi_n))^2} \quad (34)$$

and

$$\mathcal{P}(z) = 3 \text{Li}_4(e^{-2z}) + 6z \text{Li}_3(e^{-2z}) + 6z^2 \text{Li}_2(e^{-2z}) + 4z^3 \text{Li}_1(e^{-2z}), \quad (35)$$

with $\text{Li}_m(x)$ the standard polylog function¹⁶ and $\alpha_n = (\xi_n/c) \sqrt{\epsilon_B(\omega\xi_n)}$. Obviously the large n terms in the above sum are screened spatially with a characteristic length depending on n . For the isolated pair interaction we get an analogous formula

$$f_0(a,b) \simeq - \frac{SkT(2a)^2}{4\pi(2b)^4} \zeta_0(b), \quad (36)$$

where now

$$\zeta_0(b) = 6 \frac{\bar{\Delta}_\infty^2(0)}{(1 - \bar{\Delta}_\infty^2(0))} + \sum_{n=1}^{\infty} \frac{4\mathcal{P}_0(b\alpha_n)\bar{\Delta}_\infty^2(\iota\xi_n)}{(1 - \bar{\Delta}_\infty^2(\iota\xi_n))} \quad (37)$$

with

$$\mathcal{P}_0(z) = e^{-2z}(3 + 6z + 6z^2 + 4z^3). \quad (38)$$

Here again the large n terms in the above sum are screened spatially with a characteristic length depending on n . Obviously, every term in the expression for the effective pair potential is larger than the corresponding terms in the expression for the isolated pair potential. The same has to be true for their sums. Both formulas [Eqs. (33) and (36)] are exact in the limit of $a \ll b$.

Numerical results for $\zeta(b)$ and $\zeta_0(b)$ are presented on Fig. 3 for terms through $n=1000$. We see that the boost $\zeta(b)/\zeta_0(b)$ observed in the nonretarded limit survives retardation to an extent $\zeta(b \gg a)/\zeta_0(b \gg a) = 11.02$.

The range of validity of the asymptotic Eqs. (33) and (36) is given by the inequalities

$$(ab)^2 \zeta(b) \leq 1 \text{ and } (ab)^2 \zeta_0(b) \leq 1, \quad (39)$$

respectively. For $\zeta(b)$ as shown on Fig. 3 and $a=4$ nm the interlayer separation has to be of the order of $b \geq 100$ nm for the effective pair-interaction case and a number $\sqrt{11.02}$ smaller for the isolated pair case. It thus takes a while until the asymptotics become reliable estimates for the interaction.

B. General behavior

We now note from Fig. 2 that in the case of lipid-water systems the nonretarded form of $\bar{\Delta}$, i.e., $\bar{\Delta}_\infty(\iota\xi_n)$, can be large only for zero frequency, where $\bar{\Delta}_\infty(0) \sim 1$. At all other Matsubara frequencies the differences in dielectric responses are usually small so that $\bar{\Delta}_\infty(\iota\xi_n) \ll 1$. Our strategy will thus be to treat differently the $n=0$ and the $n \geq 1$ terms in the sum over the Matsubara frequencies. In the first case we will evaluate the complete integral in Eq. (25), whereas for all the other terms we will make the approximation $\bar{\Delta}(\iota\xi_n) \ll 1$. To estimate retardation effects we again follow the standard approach¹² and assume the equality of the speeds of light in materials A and B , thus $\rho_A = \rho_B$. For $\bar{\Delta}(\iota\xi_n)$ we thus again retain only the nonretarded form, $\bar{\Delta}_\infty(\iota\xi_n)$.

1. Small $\bar{\Delta}_\infty(\iota\xi_n)$, no retardation

We start, however, by first deriving a few approximate formulas and only then make full numerical evaluation. Start

with the nonretarded form and expand all the terms in the n sum with respect to the dielectric discontinuity $\bar{\Delta}$, assuming this to be small. To the second order in $\bar{\Delta}$ we remain with

$$f(a,b) = kT \sum_{\mathbf{Q}} \sum_{n=0}^{\infty} ' \ln \left(1 - \frac{\bar{\Delta}^2(\iota\xi_n)(1 - e^{-2\rho_A a})^2 e^{-2\rho_B b}}{(1 - e^{-2(\rho_A a + \rho_B b)})} \right) \\ \rightarrow -kT \sum_{\mathbf{Q}} \frac{(1 - e^{-2\rho_A a})^2 e^{-2\rho_B b}}{(1 - e^{-2(\rho_A a + \rho_B b)})} \sum_{n=0}^{\infty} ' \bar{\Delta}^2(\iota\xi_n) \quad (40)$$

for the effective pair interaction and

$$f_0(a,b) = kT \sum_{\mathbf{Q}} \ln(1 - \bar{\Delta}^2(\iota\xi_n)(1 - e^{-2\rho_A a})^2 e^{-2\rho_B b}) \\ \rightarrow -kT \sum_{\mathbf{Q}} (1 - e^{-2\rho_A a})^2 e^{-2\rho_B b} \sum_{n=0}^{\infty} ' \bar{\Delta}^2(\iota\xi_n) \quad (41)$$

for the isolated pair interaction. This nonretarded, small dielectric discontinuity limit then gives

$$f(a,b) \simeq - \frac{SkT}{4\pi(a+b)^2} \left(\zeta\left(2, \frac{b}{a+b}\right) - 2\zeta(2,1) \right) \\ + \zeta\left(2, \frac{b+2a}{a+b}\right) \sum_{n=0}^{\infty} ' \bar{\Delta}^2(\iota\xi_n), \quad (42)$$

where $\zeta(2,x)$ is the Riemann zeta function, and similarly,

$$f_0(a,b) \simeq - \frac{SkT}{4\pi} \left(\frac{1}{b^2} - \frac{2}{(a+b)^2} + \frac{1}{(b+2a)^2} \right) \sum_{n=0}^{\infty} ' \bar{\Delta}^2(\iota\xi_n). \quad (43)$$

Clearly the last two results reduce to Eqs. (29) and (30) in the limit $a \ll b$ and $\bar{\Delta} \ll 1$. We can numerically evaluate the two infinite sums in Eqs. (42) and (43), obtaining $\sum_{n=0}^{\infty} ' \bar{\Delta}^2(\iota\xi_n) = 0.633$ by summing the first 1000 terms. Note also that the ratio $f(a=4 \text{ nm}, b)/f_0(a=4 \text{ nm}, b)$ varies no more than between 1 and 1.082 for the whole range of b .

2. Small $\bar{\Delta}_\infty(\iota\xi_n)$, retardation

Now let us add the effects of retardation but still keep the small dielectric discontinuity approximation $\bar{\Delta} \ll 1$. Assume again that the speed of light in both materials equals the speed of light in the water regions; the retarded result comes out as

$$f(a,b) \simeq - \frac{SkT}{4\pi(a+b)^2} \left[\frac{1}{2} \left(\zeta\left(2, \frac{b}{a+b}\right) - 2\zeta(2,1) + \zeta\left(2, \frac{b+2a}{a+b}\right) \right) \bar{\Delta}^2(0) + \sum_{n=1}^{\infty} \left(\mathcal{Z}\left(2 + 2\alpha_n(a+b), \frac{b}{a+b}\right) \right. \right. \\ \left. \left. - 2\mathcal{Z}(2 + 2\alpha_n(a+b), 1) + \mathcal{Z}\left(2 + 2\alpha_n(a+b), \frac{b+2a}{a+b}\right) \right) \bar{\Delta}^2(\iota\xi_n) \right],$$

with

$$\mathcal{Z}(2+y,x) \equiv \sum_{m=0}^{\infty} \frac{e^{-(x+m)y}}{(x+m)^2} + y \sum_{m=0}^{\infty} \frac{e^{-(x+m)y}}{(x+m)}. \quad (44)$$

Obviously the function $\mathcal{Z}(2+y,x)$ is exponentially screened with y . Thus retardation acts to suppress higher-order terms in n .

What about the isolated pair interaction? In complete analogy to Eq. (44),

$$\begin{aligned} f_0(a,b) \simeq & -\frac{SkT}{4\pi} \left[\frac{1}{2} \left(\frac{1}{b^2} - \frac{2}{(a+b)^2} + \frac{1}{(b+2a)^2} \right) \bar{\Delta}^2(0) \right. \\ & + \sum_{n=1}^{\infty} \left(\frac{\mathcal{R}(2\alpha_n b)}{b^2} - \frac{2\mathcal{R}(2\alpha_n b)}{(a+b)^2} \right. \\ & \left. \left. + \frac{\mathcal{R}(2\alpha_n b)}{(b+2a)^2} \right) \bar{\Delta}^2(\iota\xi_n) \right], \quad (45) \end{aligned}$$

where

$$\mathcal{R}(y) = e^{-y}(1+y). \quad (46)$$

Equation (45) is quite similar to Eq. (44), except for the definition of the retardation function, $\mathcal{Z}(2+y,x)$ vs $\mathcal{R}(y)$. This is as much as we can evaluate analytically. Now consider the full numerical evaluation of the effective and isolated pair interactions.

3. Large $\bar{\Delta}_\infty(\iota\xi_0)$, small $\bar{\Delta}_\infty(\iota\xi_{n \geq 1})$, complete numerics

As already stated, we assume that the dielectric discontinuity is large only for the $n=0$ term. We thus retain the full form of the zero-order term; all the higher-order terms we expand to second order in $\bar{\Delta}$. To these terms we also apply the approximation that the speed of light everywhere equals that in the water medium. The $n \geq 1$ terms thus look the same as in Eqs. (44) and (45). We can use the above results except that we substitute a complete integral for the zero-order term, i.e., from Eq. (20),

$$\begin{aligned} f(a,b) \simeq & \frac{SkT}{4\pi} \int_0^\infty QdQ (\xi(Q, \omega=0) - \xi_\infty(Q, \omega=0)) \\ & - \frac{SkT}{4\pi(a+b)^2} \sum_{n=1}^{\infty} \mathcal{G}(a,b, \alpha_n) \bar{\Delta}_\infty^2(\iota\xi_n), \quad (47) \end{aligned}$$

where

$$\begin{aligned} \mathcal{G}(a,b, \alpha_n) = & \mathcal{Z} \left(2 + 2\alpha_n(a+b), \frac{b}{a+b} \right) - 2\mathcal{Z}(2 + 2\alpha_n(a \\ & + b), 1) + \mathcal{Z} \left(2 + 2\alpha_n(a+b), \frac{b+2a}{a+b} \right). \quad (48) \end{aligned}$$

Similarly, the appropriate form for the pairwise interaction derived from Eq. (21) is obviously

$$\begin{aligned} f_0(a,b) = & \frac{SkT}{4\pi} \int_0^\infty QdQ \ln \left(1 - \frac{(1 - e^{-2\rho_A a})^2 \bar{\Delta}^2(0) e^{-2\rho_B b}}{(1 - \bar{\Delta}^2 e^{-2\rho_A a})} \right) \\ & - \frac{SkT}{4\pi(a+b)^2} \sum_{n=1}^{\infty} \mathcal{G}_0(a,b, \alpha_n) \bar{\Delta}_\infty^2(\iota\xi_n), \quad (49) \end{aligned}$$

where

$$\begin{aligned} \mathcal{G}_0(a,b, \alpha_n) = & \mathcal{R}(2\alpha_n b) \frac{(a+b)^2}{b^2} - 2\mathcal{R}(2\alpha_n b) \\ & + \mathcal{R}(2\alpha_n b) \frac{(a+b)^2}{(b+2a)^2}. \quad (50) \end{aligned}$$

These two equations, Eqs. (47) and (49), can be evaluated numerically. For meaningful comparison define Hamaker coefficients¹² as

$$f(a,b) = \frac{SH(a,b)}{12\pi b^2} \text{ and } f_0(a,b) = \frac{SH_0(a,b)}{12\pi b^2}. \quad (51)$$

Instead of comparing the free energies of interaction we can now discuss their more compact Hamaker coefficients. We speak of Hamaker ‘‘coefficients’’ rather than Hamaker ‘‘constants,’’ because they depend in an essential way on b , see Fig. 4. Clearly, for any value of b the Hamaker coefficient of the effective pair interaction in an array is larger than the Hamaker coefficient of the isolated pair interaction, their ratio going from 1 at small b to ~ 10 at large b .

Note that the effects of nonadditivity, as quantified by the ratio $\mathcal{H}(a,b)/\mathcal{H}_0(a,b)$, are large. Asymptotically they approach the value ~ 11 , obtained already in the limit of large separation $b \gg a$, i.e., $\zeta(b \gg a)/\zeta_0(b \gg a) \sim 11$. This is a huge, an order of magnitude, boost in the interaction.

Note, however, that nonadditive effects vanish at small separations, $b \lesssim a$, where we are effectively back to isolated pair interactions which indeed can be reduced to the interaction of two semi-infinite lipid regions across water. This, of course, makes perfect sense. Our calculation gives $\mathcal{H}(a,b \sim a) = 4.3$ zJ. The standard theoretical result with no retardation effects¹² usually quoted is $\mathcal{H}(a,b \sim a) = 3.6$ zJ, while the experimental values are in the range $\mathcal{H}(a,b \sim a) \simeq 1-10$ zJ.¹⁷

IV. DISCUSSION

We have evaluated the nonpairwise additive contribution to the effective interactions between two layers in an infinite stack. As far as we are aware, this is the only complete evaluation of the nonpairwise additive effect in Lifshitz–van der Waals interactions; multilamellar geometry appears to be the only one that permits such a calculation. In the general case, the Axilrod-Teller potential gives the nonpairwise additive contributions in the case of three pointlike particles. Unfortunately there is no easy generalization of this result to the case of an arbitrary, large number of particles.

The most important lesson that follows from our calculation is that the nonpairwise additive effects can be large and persistent over a substantial regime of interlamellar spacings. In the multilamellar geometry, they become more important the larger the separation between the layers. The ratio

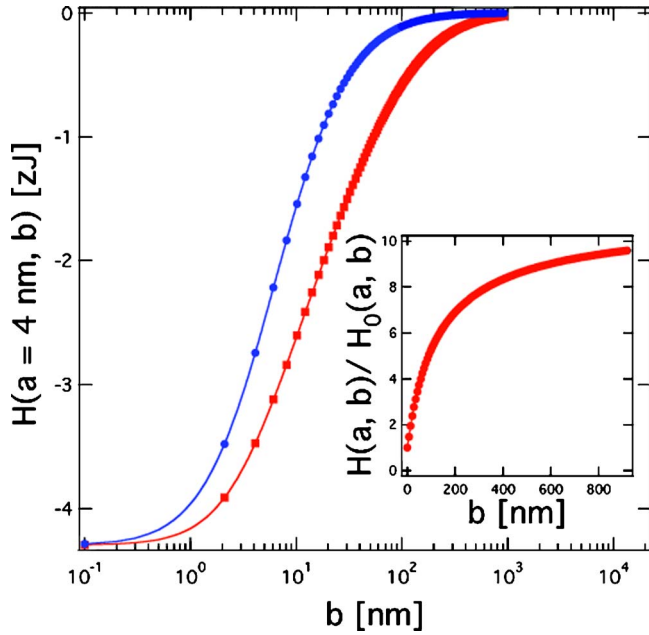


FIG. 4. Hamaker coefficients from Eq. (51) as a function of the water layer thickness b for the lipid layer thickness $a=4$ nm. The curve ● represents $\mathcal{H}(a, b)$ and ○ represents $\mathcal{H}_0(a, b)$ from Eq. (51). The inset shows the ratio of both Hamaker coefficients. The ratio approaches ~ 11 in the limit of $b \gg a$.

between the Hamaker coefficients in the nonpairwise and isolated pair interaction cases, Fig. 4, reaches the asymptotic value of ~ 10 , one order of magnitude, for large separations.

The asymptotic, large b , regime of the interaction is reached only for very large values of b , on the order of a few 100 nm. In that regime, Fig. 5, the interaction decays as the fourth power of the interlamellar separation and remains again approximately ten times stronger than in the isolated pair case. The start of the asymptotic regime depends cru-

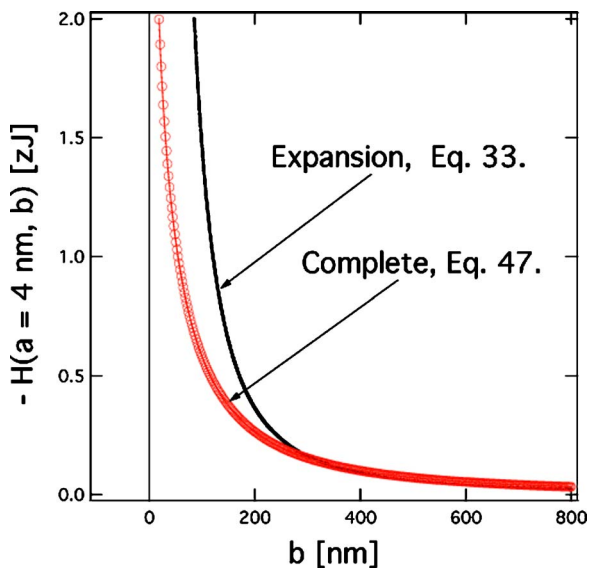


FIG. 5. Comparison between Hamaker coefficients of the exact evaluation [Eq. (47)] and large b expansion [Eq. (33)], where the Hamaker coefficient is defined as $\mathcal{H}(a, b) = \frac{3}{4}kT(a/b)^2\zeta(b)$. Consistent with analytic estimates the asymptotic expansion, Eq. (33), scales as b^{-4} and becomes valid for $b \geq 300$ nm.

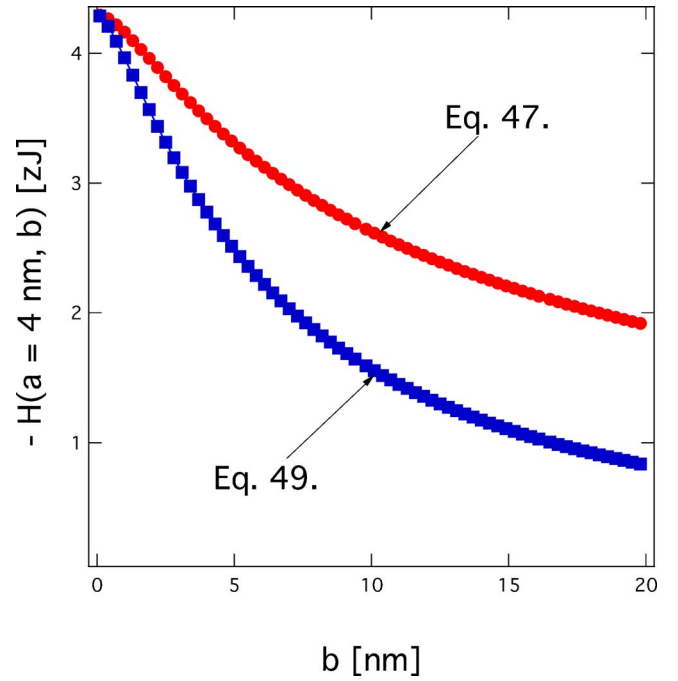


FIG. 6. Behavior of the Hamaker coefficients defined in Eq. (51) for small values of the interlamellar spacing, $0 \leq b \leq 20$ nm. The upper circles denote the values obtained from the effective pairwise expression [Eq. (47)] and lower squares from the isolated pair expression [Eq. (49)]. The approximate forms [Eqs. (52) and (53)] work only for small values of b .

cially on the largest dielectric discontinuity in the system, usually given by the static value of $\overline{\Delta_\infty(0)}$. The larger the discontinuity, the farther away the entry point into the asymptotic regime. In the limit of infinitely polarizable (metal) interfaces, the asymptotic regime is never reached and the system remains in the Casimir limit all the time. In this case because of the infinite polarizability, many-body effects are nonexistent. The interaction decomposes *exactly* into a sum of Casimir terms.

For small separation we are, in general, back to the result for two semi-infinite half-spaces (see Fig. 6). Both the effective pairwise interaction as well as the isolated pair interaction tend then to the same limit in this case. For not-too-large interlamellar spacings, $b \leq 5$ nm and $a \approx 4$ nm, the isolated pair interaction can be approximated by the nonretarded small dielectric discontinuity form [Eq. (43)],

$$f_0(a, b) \simeq -\frac{S\mathcal{H}_0(a, b \sim a)}{12\pi b^2} \left(1 - \frac{2b^2}{(a+b)^2} + \frac{b^2}{(b+2a)^2} \right) = -\frac{S\mathcal{H}_0^{\text{eff}}(a, b)}{12\pi b^2}, \quad (52)$$

except that the value of the Hamaker coefficient is given by the complete, not just the nonretarded, value valid in the limit of small interlamellar spacings as $\mathcal{H}_0(a=4 \text{ nm}, b \sim a) = 4.3$ zJ. This form [Eq. (52)] is usually used in experimental determination of the Hamaker coefficient in the case of small interlamellar spacings. There \mathcal{H}_0 usually comes out in the range of 2.87–9.19 zJ (Ref. 17) for dimyristoyl phosphatidylcholine (DMPC) and dipalmitoyl phosphatidylcholine (DPPC) multilayers. The effective pairwise result with the same philosophy would follow from Eq. (42) as

$$f(a,b) \approx -\frac{S\mathcal{H}(a,b \sim a)}{12\pi(a+b)^2} \left(\zeta\left(2, \frac{b}{a+b}\right) - 2\zeta(2,1) \right) + \zeta\left(2, \frac{b+2a}{a+b}\right) = -\frac{S\mathcal{H}^{\text{eff}}(a,b)}{12\pi(a+b)^2}. \quad (53)$$

Again this fit to the effective pairwise Hamaker constant works only for small values of the spacing with the limiting value of $\mathcal{H}(a=4 \text{ nm}, b \sim a)=4.3 \text{ zJ}$. For an extended range in b the complete formulas [Eqs. (47) and (49)] are preferable.

We have given the best estimate of the effective pair interactions between lipid layers in a multilamellar stack, where the solvent is water, that takes into account nonpairwise additive terms to all orders in a resummed version of the van der Waals interaction energy. We evaluated the effective Hamaker coefficient, $\sim 4.3 \text{ zJ}$ for small values of the spacing. This value coincides exactly with the estimate for two semi-infinite half-spaces. For larger values of interlamellar spacing the effective van der Waals interaction free energy between a pair of layers in the stack and the corresponding Hamaker coefficient turn out to be much larger, up to an order of magnitude, than in the case of the isolated pair interaction. This order-of-magnitude boost in the van der Waals interactions is something one should seriously consider in other contexts where nonpairwise additive effects have not yet been seriously contemplated.

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