

Lifshitz theory of wetting films at three phase coexistence: The case of ice nucleation on Silver Iodide

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Abstract

Hypothesis: As a fluid approaches three phase coexistence, adsorption may take place by the successive formation of two intervening wetting films. The equilibrium thickness of these wetting layers is the result of a delicate balance of intermolecular forces, as dictated by an underlying surface potential. The van der Waals forces for the two variable adsorption layers may be formulated exactly from Dzyaloshinskii-Lifshitz-Pitaevskii theory, and analytical approximations may be derived that extend well beyond the validity of conventional Hamaker theory.

Calculations: We consider the adsorption equilibrium of water vapor on Silver Iodide where both ice and a water layers can form simultaneously and compete for the vapor as the triple point is approached. We perform numerical calculations of Lifshitz theory for this complex system and work out analytical approximations which provide quantitative agreement with the numerical results.

Findings At the three phase contact line between AgI/water/air, surface forces promote growth of ice both on the AgI/air and the water/vapor interfaces, lending support to a contact nucleation mode of AgI in the atmosphere. Our approach provides a framework for the description of adsorption at three phase coexistence, and allows for the study of ice nucleation efficiency on atmospheric aerosols.

Keywords: Adsorption, Wetting, Phase coexistence, Surface thermodynamics, Van der Waals forces, Lifshitz Theory, Hamaker constant, Heterogeneous nucleation, Ice, Silver Iodide

I. INTRODUCTION

The preferential adsorption of gases and liquids on an inert solid substrate is ubiquitous in colloidal science, and is often accompanied by the formation of thick wetting films that span from a few nanometers to several microns as two phase coexistence is approached^{1–4}. The behavior of the equilibrium layer formed can be fully characterized by an interface potential, $g(h)$, which measures the free energy as a function of the film thickness, h . For thick films, $g(h)$ is often dominated by long range van der Waals forces that can be described rigorously with the celebrated Dzyaloshinskii-Lifshitz-Pitaevskii (DLP) theory⁵.

A more complex situation arises when the adsorbed wetting film can further segregate and form a new layer between the solid substrate and the mother phase as three phase coexistence is approached^{6–12}. This can be quite generally the case for substrates in contact with multicomponent mixtures. Examples include the industrially relevant formation of clathrate hydrates from aqueous solutions of oil or carbon dioxide^{6–9}, biologically relevant aqueous solutions of Dextran and Bovine Serum Albumin¹⁰; or theoretically relevant model solutions such as ethanol/n-alkane or lutidine/water mixtures^{11,12}. The wetting problem now becomes considerably more complex, as the system can exhibit two thick layers of size, say, l and d , respectively, that are bounded by the substrate and the mother phase and can feed one from the other depending on the prevailing thermodynamic conditions.

In practice, this complex scenario can be realized for a very relevant one component test system, namely, atmospheric supercooled water vapor in close proximity to the triple point¹³. As ice nucleates on the surface of inorganic aerosols, the resulting ice / water vapor interface is exposed. This surface is actually a complex system exhibiting a thin premelted water layer, usually referred as *Quasi-Liquid Layer* (QLL). Its properties largely condition several phenomena related to ice, such as the electrification of storm clouds, frost and snowflakes formation, or ice skating^{13–16}. Hereby the surface Van der Waals forces play a crucial role in the stabilization of a thick QLL^{17,18}.

On the other hand, silver iodide may be used as a nucleus for ice formation¹⁹, with applications in cloud seeding to induce rainfall over wide areas. The conventional belief was that the capability of the AgI to influence the growth of ice was connected to their lattice match. Nonetheless, recent studies²⁰ have found substances with similar structures that do not promote nucleation. Thus they relate the faculty of the AgI to serve as ice

nucleating agent to the charge distribution in the substrate surface and to the Van der Waals forces^{21–23}. The present work aims at elucidating the role of Van der Waals forces in the ice nucleating activity of silver iodide, by describing precisely the Van der Waals interactions in the framework of the Lifshitz theory, applied to the AgI - Ice - Liquid Water - Air system (Fig. 1).

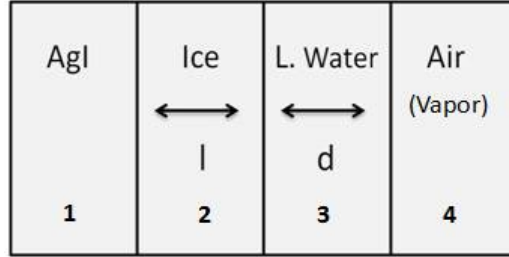


FIG. 1: Geometry of layered planar systems studied in this work. An inert substrate, AgI, in contact with water vapor (air), close to three phase coexistence can exhibit intervening phases of ice, with thickness l and water, with thickness d . Since the system is subject to material equilibrium each phase feeds from the other. The equilibrium layer thickness of l and d are dictated by the bulk free energies and the surface potential. For the sake of generality and conciseness of notation, we denote the phases AgI, ice, water, air as '1', '2', '3', '4', respectively.

The conventional view is that the van der Waals interactions between two surfaces result from the summation of forces between pairs of particles. The interaction coefficients are then added into the Hamaker coefficient, A_{Ham} , and the interaction for a layered planar system provides an energy $A_{Ham}/(12\pi h^2)$, being h the distance between the interacting media³. The Lifshitz theory of the Van der Waals forces goes beyond the pairwise summation, by treating the Van der Waals forces through continuum thermodynamic properties of the polarizable interacting media²⁴. As a particularly significant result of the detailed electromagnetic treatment, there appears a range of distances where the leading order interactions become *retarded* and decay as $1/h^3$. Accordingly, the effective interaction coefficient itself, A_{Ham} , is no longer a constant, but becomes a function of the film thickness as well. Then the generalized expression for the Van der Waals free energy becomes²⁴:

$$g_{vdW}(h) = -\frac{A_{Ham}(h)}{12\pi h^2} \quad (1)$$

In the study of ice growing at the AgI / air interface, the simple description based on inter-

actions between AgI and air across ice is not valid. Because of the existence of premelting, we also expect the formation of a fourth layer of water in between ice and air. The extension of Lifshitz theory to four media of which one is variable has been known for a long time^{24–26}. However, in the atmosphere the water layer can grow at the expense of the ice layer, depending on the prevailing conditions. Therefore both the thickness of the ice layer (l) and that of the premelted layer (d) must be taken as variables. The results for the free energy $g(l, d)$ as derived from the Lifshitz theory in the case that two of the layers are variable was anticipated recently without proof²⁷. Here we provide the full derivation in the supplementary section, discuss some of its implications and show how the apparently awkward general result may be approximated accurately in analytic form.

In the next section we formulate the problem of three phase adsorption equilibrium generally, and discuss the conditions for wetting. In Section III we concisely present the theoretical framework of van der Waals forces in the modern formulation^{28,29} and generalize the results to a system of two layers of variable thickness sandwiched between infinite bodies. We then show that the very complicated expression is amenable to an approximate but very accurate analytical representation. In Section IV we briefly discuss the parameterization of dielectric properties for AgI, water and ice that is required as input into DLP theory. In Section V we present our results. These are structured as follows: first, we test the numerical approximations performed to achieve closed analytical expressions. Secondly, the theory is exploited to describe the van der Waals forces of the complex system AgI/Ice/water/air, and their role in the ice nucleating efficiency of AgI. The conclusions of our work are presented in Section VI.

II. ADSORPTION EQUILIBRIUM AT THREE PHASE COEXISTENCE

Consider a fluid phase, say, medium '4', in contact with an inert substrate, say, medium '1'. Furthermore, consider that phase, '4', extends up to a finite but very large distance $L \rightarrow \infty$. Accordingly, '4' serves as a heat and mass reservoir that fixes the temperature and chemical potential of the full system (of course, if '4' is a multicomponent mixture, it fixes the chemical potential of each of its components). Quite generally, the density of phase '4' in the vicinity of the substrate is not that found in the bulk phase well away from the wall. Particularly, consider that phase 4 is approaching three phase coexistence, such

that two additional bulk phases '2' and '3' are slightly metastable. In a bulk system in the thermodynamic limit, slightly metastable means that these phases are not observed at all. However, close to an inert substrate, surface forces can change this situation, as one of the metastable phases could preferentially adsorb between the substrate and the mother phase '4'. By the same token, once, say, phase '2' has adsorbed preferentially in between the substrate and phase '4', the third phase '3', could adsorb preferentially in between '2' and '4', leading to a two layer system of phases '2' and '3' in between the substrate '1' and the mother phase '4'.

The question is then what sets the equilibrium film thickness of the intervening layers, '2' and '3', with thickness l and d , respectively.

Since we assume the system is at fixed temperature and chemical potential as dictated by the semi-infinite phase '4', the equilibrium states will be such that the grand free energy is a minimum³⁰. In the mood of capillarity theory, we assume the total free energy is that of infinitely large bulk systems, plus the cost to form each of the interfaces. Following Derjaguin, however, we also need to account for the effective interaction between interfaces separated by a finite distance, via a generalized surface potential $g_{1234}(l, d)$. Accordingly, the total surface free energy of the system is expressed as:

$$\omega(l, d) = -p_2l - p_3d - p_4(L - l - d) + \gamma_{12} + \gamma_{23} + \gamma_{34} + g_{1234}(l, d) \quad (2)$$

where p_i is the bulk pressure of phase i at the fixed temperature and chemical potential of phase 4, and γ_{ij} is the surface tensions between phase i and phase j . The first three terms account for the bulk free energy of the system; the next three correspond to the free energy to form the interfaces separating infinitely large bulk phases; and finally, $g_{1234}(l, d)$ accounts for the missing interactions due to the finite extent of phases 2 and 3. By this token it follows immediately that the surface potential is defined such that in the limit $l \rightarrow \infty$ and $d \rightarrow \infty$, $g_{1234} = 0$.

It is convenient to write this result as an excess over the bulk free energy of a system filled with phase 4 only, so that:

$$\Delta\omega(l, d) = -(p_2 - p_4)l - (p_3 - p_4)d + \gamma_{12} + \gamma_{23} + \gamma_{34} + g_{1234}(l, d) \quad (3)$$

This general expression corrects previous results by additive constants²⁷. Here, it rationalizes in a nutshell the adsorption equilibrium of a three phase system. In practice, this does not

change the equilibrium condition for l and d , which are obtained by equating to zero the partial derivatives of the free energy with respect to l and d . In practice, here we will be concerned with the situation where the system is exactly at bulk three phase coexistence, such that $p_2 = p_3 = p_4$. The above equation then allows us to generalize the condition for wetting at three phase coexistence.

If Eq.3 has an extremal point at small $l = l_0$ and $d \rightarrow \infty$, the system has only two interfaces with cost γ_{13} and γ_{34} , so that it must hold:

$$\lim_{d \rightarrow \infty} g(l_0, d) = \gamma_{13} - \gamma_{12} - \gamma_{23} \quad (4)$$

This provides the wetting condition for phase 2 intervening between the substrate and phase '3'. Likewise, if Eq.3 has extrema at $l \rightarrow \infty$ and finite $d = d_0$, the system forms interfaces with a cost γ_{12} and γ_{24} , and we find:

$$\lim_{l \rightarrow \infty} g(l, d_0) = \gamma_{24} - \gamma_{23} - \gamma_{34} \quad (5)$$

which provides the wetting condition for phase 3 intervening between phase 2 and 4. Finally, if Eq.3 has an extrema at finite and small $l = l_0$ and $d = d_0$ (including the case where both $l_0 = d_0 = 0$), we find:

$$g(l_0, d_0) = \gamma_{14} - \gamma_{12} - \gamma_{23} - \gamma_{34} \quad (6)$$

which corresponds to the condition of infinite adsorption layers of 2 and 3 intervening between phase 1 and phase 4.

The above results serve to illustrate the crucial significance of the surface potential $g(l, d)$. Not only it dictates the allowed equilibrium values of layer thickness, but it also embodies all allowed wetting conditions in the system. The surface potential consists of contributions of different nature. First, a structural contributions, which is short range, as it decays in the lengthscale of the bulk correlation length of a few molecular diameters, conveys information on the packing correlations between the hard core of the molecules; Second, van der Waals contributions, which are long range and result from spontaneous electromagnetic fluctuations of the media. Additionally, charged systems will also have electrostatic contributions, with a decay that is given by the Debye screening length.

In the next section we discuss the calculation of van der Waals contributions, which, in the absence of electrolytes are expected to dominate the long range behavior of the system.

III. ANALYTIC APPROXIMATION FOR SURFACE VAN DER WAALS FORCES

A. Lifshitz theory of Van der Waals forces

The starting point of this section is the general result for the surface free energy embodied between two semiinfinite planar bodies, L and R , separated by an arbitrary number of layers (m, n, \dots) due to van der Waals forces:²⁹

$$g_{Lm\dots R} = \frac{k_B T}{2\pi} \sum_{n=0}^{\infty} \int_0^{\infty} \rho \, d\rho \ln(D_{Rm\dots L}^E D_{Lm\dots R}^M) \quad (7)$$

where D^E and D^M are the dispersion relations of the standing waves of electric and magnetic modes in the system. The integral is performed over transverse components of the momentum, and the sum is performed over an infinite set of discrete Matsubara frequencies. k_B is Boltzmann's constant and we assume set temperature $T = 273.15$ K to the triple point of water.

The dispersion relations depend on the specific geometry of the system. For a layered planar system composed of two bulk bodies (say, $L=1$ and $R=3$) separated by a dielectric ($m=2$) with thickness ' h ', the result is well known:²⁹

$$D_{123}^{E,M} = 1 - \Delta_{12}^{E,M} \Delta_{32}^{E,M} e^{-2\rho_2 h} \quad (8)$$

Assuming from now on that all magnetic susceptibilities are equal to one²⁴, the Δ_{ij} functions have the form

$$\Delta_{ij}^E = \frac{\rho_j - \rho_i}{\rho_j + \rho_i} \quad \Delta_{ij}^M = \frac{\epsilon_i \rho_j - \epsilon_j \rho_i}{\epsilon_i \rho_j + \epsilon_j \rho_i} \quad (9)$$

where $\rho_i^2 = \rho^2 + \frac{\epsilon_i \xi_n^2}{c^2}$, and ϵ_i , the dielectric function of the medium $i = 1, 2, 3$ is evaluated at the corresponding Matsubara frequency

$$\xi_n = \frac{2\pi k_B T}{\hbar} n, \quad n = 0, 1, 2, \dots \quad (10)$$

with c , the velocity of light and \hbar , Planck's constant in units of angular frequency.

In this work, we deal with the Van der Waals free energy between two bulk media (AgI and air), separated by two intervening layers (ice and water), with variable thicknesses ' l ' and ' d ', respectively (Fig.1). The corresponding dispersion relation of the four media system was anticipated by Estes et al.²⁷, and is demonstrated here in the *supplementary material*

1. The result is:

$$D_{1234}^{E,M} = 1 - \Delta_{12}^{E,M} \Delta_{32}^{E,M} e^{-2\rho_2 l} - \Delta_{23}^{E,M} \Delta_{43}^{E,M} e^{-2\rho_3 d} - \Delta_{12}^{E,M} \Delta_{43}^{E,M} e^{-2\rho_2 l - 2\rho_3 d} \quad (11)$$

The subscripts 1-4 indicate, respectively, AgI, ice, liquid water and air, but we keep throughout this section this notation for the sake of generality.

The related result for the interaction between a plate coated with a layer of fixed thickness l and another plate at a variable distance h has been known for a long time (c.f.²⁴⁻²⁶). Here, Eq.7 together with Eq.11 generalize this result for the case where *both* l and d are variable. Accordingly, the layer thickness l and d stand on the same footing, and the free energy $g_{1234}(l, d)$ is now symmetrical with respect to the interchange of l and d , as expected. The result also satisfies a number of desirable physical properties, and is consistent with expectations for the limiting cases where the layers either become infinitely thick or vanish altogether.

Firstly, one notices that in the limit where both d and l tend to infinity, $D_{1234}^{E,M} \rightarrow 1$, so that the surface potential vanishes, as implied in the discussion of the previous section.

In the limiting case where $d \rightarrow \infty$, one readily finds from Eq.11 that $D_{1234}^{E,M} \rightarrow D_{123}^{E,M}$. As a result, it follows:

$$\lim_{d \rightarrow \infty} g_{1234}(l, d) = g_{123}(l) \quad (12)$$

and likewise, for $l \rightarrow \infty$,

$$\lim_{l \rightarrow \infty} g_{1234}(l, d) = g_{234}(d) \quad (13)$$

With some additional algebraic work, we also find for the opposite limit of vanishing thickness that:

$$\lim_{d \rightarrow 0} (g_{1234}(l, d) - g_{234}(d)) = g_{124}(l) \quad (14)$$

$$\lim_{l \rightarrow 0} (g_{1234}(l, d) - g_{123}(l)) = g_{134}(d) \quad (15)$$

These limiting cases serve as a check of consistency for the numerical calculation of $g_{1234}(l, d)$.

As evidenced by the above results, $g_{1234}(l, d)$ contains information on $g_{123}(l)$ and $g_{234}(d)$. This can be illustrated explicitly upon linearization of the logarithmic term in Eq.7. The resulting expression can be readily interpreted as given by:

$$g_{1234}(l, d) = g_{123}(l) + g_{234}(d) + \Delta g_{1234}(l, d) \quad (16)$$

Accordingly, $g_{1234}(l, d)$ may be given as a sum of $g_{123}(l)$ and $g_{234}(d)$, plus a correction $\Delta g_{1234}(l, d)$ which accounts for the indirect interaction of the two macroscopic bodies across the layers.

Despite this simplification, the expressions for the three media potential still remain very difficult to interpret intuitively. In the next section we derive analytical formula which allow to interpret $g_{1234}(l, d)$ easily and serve also as an accurate means to calculate the free energy efficiently.

The results extend the theory for the calculation of interface potentials for three media reported recently³¹. In order to make the derivation self contained, we first summarize the results for g_{123} from Ref.³¹ and then extend these ideas to the calculation of the correction function $\Delta g_{1234}(l, d)$.

B. Analytical approximations for the three media contributions

We start from the exact form of the 3-media contributions, $g_{123}(h)$, where 'h' now stands for the thickness of layer '2'.

$$g_{123}(h) = \frac{k_B T}{2\pi} \sum_{n=0}^{\infty} \int_0^{\infty} \rho d\rho \ln(D_{123}^E D_{123}^M) \quad (17)$$

Of course, now the dispersion relation would be that given in Eq. 8. Linearization of the logarithm as implied in Eq.16, together with the change of variables $\rho_m \rightarrow \rho$ and $x \rightarrow 2h\rho_m$, provides (*supplementary material 2*):

$$g_{123}(h) = -\frac{k_B T}{8\pi h^2} \sum_{n=0}^{\infty} \int_{r_n}^{\infty} x dx R(n, x) e^{-x} \quad (18)$$

where $R(n, x) = \Delta_{12}^E \Delta_{32}^E + \Delta_{12}^M \Delta_{32}^M$, while the lower limit of the integral is $r_n = 2h\sqrt{\epsilon_2}\xi_n/c$. Notice that the $\Delta_{ij}^{E,M}$ functions are redefined in terms of x_i instead of ρ_i , given that $x_i^2 = x^2 + (\epsilon_i - \epsilon_2)(2h\xi_n/c)^2$.

Although this expression remains rather cumbersome, it has been shown recently that very accurate analytical approximations may be obtained using problem adapted one-point Gaussian quadrature rules³¹. The one-point Gaussian quadrature (detailed in *supplementary material 3*) allows the transformation of an integral $\int f(x)w(x)dx$ without known primitive, into the product of a simple integral $\int w(x)dx$ and the function $f(x)$ evaluated at the

quadrature point, x_1 . Essentially, this corresponds to the application of the mean value theorem, with the one-point Gaussian quadrature rule exploited as a means to estimate x_1 .

1. First Gaussian Quadrature Approximation

First, let us separate the $n = 0$ contribution of the summation at 18. In this summand the value of the Matsubara frequency (equation 10) is 0, which simplifies the expressions. Hence we can solve straightforwardly the integral and state $g_{123}(h) = g_{123}^{\xi_n=0}(h) + g_{123}^{\xi_n>0}(h)$, with

$$g_{123}^{\xi_n=0}(h) = -\frac{k_B T}{16\pi h^2} \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right) \left(\frac{\epsilon_3 - \epsilon_2}{\epsilon_3 + \epsilon_2} \right) \quad (19)$$

Afterwards, we can obtain $g_{123}^{\xi_n>0}(h)$ by applying the one-point Gaussian quadrature (*supplementary material 4*) for the rest of the summation, employing $w(x) = x e^{-x}$ as a weight function and $f(x) = R^E + R^M = R(n, x)$. The results materialize in terms of r_n , with the quadrature point $x_1 = (2 + 2r_n + r_n^2)/(1 + r_n)$

$$g_{123}^{\xi_n>0}(h) = -\frac{k_B T}{8\pi h^2} \sum_{n=1}^{\infty} R(n, x_1) (1 + r_n) e^{-r_n} \quad (20)$$

We denote the result of Eq.19 and Eq.20 as the First Gaussian Quadrature Approximation (FGQA).

2. Second Gaussian Quadrature Approximation

In order to simplify further the above result, our purpose is to turn the summation of Eq. 20 into an integral. We begin by making use of the Euler-MacLaurin formula, finding out that the corrections to the integral approximation are negligible (*supplementary material 5*). Performing a change of variable to $\nu_n = \nu = \nu_T n$, with $\nu_T = 2\sqrt{\epsilon_2} \xi_T / c$ and $\xi_T = 2\pi k_B T / \hbar$, we find

$$g_{123}^{\xi_n>0}(h) = -\frac{c\hbar}{32\pi^2 h^2} \int_{\nu_T}^{\infty} \tilde{R}(\nu, x_1) (1 + h\nu) e^{-h\nu} d\nu \quad (21)$$

With $\tilde{R}(\nu, x_1) = R(\nu, x_1) \epsilon_2^{-1/2} j_2^{-1}$ and $j_2 = \left(1 + \frac{1}{2} \frac{d \ln \epsilon_2}{d \ln \xi_2}\right)$ (this factor emerges from the change of variable, as it is specified in *supplementary material 5*).

The integral at the equation 21 is dominated by an exponential decay at large h , and by the algebraic decay of $\tilde{R}(\nu, x_1)$ when h tends to zero. Unfortunately, the crossover from

algebraic to exponential decay is not amenable to analytical integration. Therefore, we introduce an auxiliary exponential function³¹, $e^{-\nu/\nu_\infty}$, with the parameter ν_∞ chosen to mimic the scale at which the algebraic decay of $\tilde{R}(\nu, x_1)$ becomes significant.

$$g_{123}^{\xi_n > 0}(h) = -\frac{c\hbar}{32\pi^2 h^2} \int_{\nu_T}^{\infty} \tilde{R} e^{\nu/\nu_\infty} [e^{-\nu/\nu_\infty} (1 + h\nu) e^{-h\nu}] d\nu \quad (22)$$

In this expression, the term in square brackets is an easily integrable weight function, which converges both at $h \rightarrow \infty$ and at $h \rightarrow 0$, as the original integrand. Accordingly, we can exploit again the mean value theorem and perform a one point Gaussian quadrature (*supplementary material 6*), with $f(\nu) = \tilde{R}(\nu, x_1) e^{\nu/\nu_\infty}$ and $w(\nu)$ equal to the term inside the brackets at 22. The outcome is the quadrature point $\nu^* = \nu_T + \nu_\infty \xi$, where ξ is an adimensional factor

$$\xi = \frac{(\nu_T h + 1)(\nu_\infty h + 1) + 2\nu_\infty h}{(\nu_\infty h + 1)^2(\nu_T h + 1) + (\nu_\infty h + 1)\nu_\infty h} \quad (23)$$

together with the approximate expression for the free energy as:

$$g_{123}^{\xi_n > 0}(h) = -\frac{c\hbar\nu_\infty}{32\pi^2 h^2} \tilde{R}_\xi^* \tilde{F} \quad (24)$$

where $\tilde{R}_\xi^* = \tilde{R}(\nu^*, x_1) e^\xi$ and

$$\tilde{F} = \frac{(\nu_T h + 1)(\nu_\infty h + 1) + \nu_\infty h}{(\nu_\infty h + 1)^2} e^{-\nu_T h} \quad (25)$$

Since \tilde{R}_ξ^* depends on h weakly, the free energy is dominated by the function \tilde{F} . Inspection of Eq.25 shows that $g_{123}^{\xi_n > 0}$ depends on the two inverse length scales, ν_∞ and ν_T . When $h \ll \nu_\infty^{-1}$, \tilde{F} becomes a constant, and $g_{123}^{\xi_n > 0} \propto h^{-2}$. This is the Hamaker limit of non-retarded interactions. For $\nu_\infty^{-1} \ll h \ll \nu_T^{-1}$, \tilde{F} falls as $1/h$, so that $g_{123}^{\xi_n > 0} \propto h^{-3}$, which corresponds to the Casimir regime of retarded interactions. Finally, when $h \gg \nu_T^{-1}$, the evolution of the interaction is dominated by the exponential $e^{-\nu_T h}$. In this regime, $g_{123}^{\xi_n > 0}$ vanishes altogether, and only the $n = 0$ term, Eq.19 of the van der Waals free energy survives.

C. Analytical approximations for the four media correction

Consistent with the linearization approximation in Eq.16, the 4-media correction is given as:

$$\Delta g_{1234}(l, d) = -\frac{k_B T}{2\pi} \sum_{n=0}^{\infty} \int_0^{\infty} \rho d\rho R_{1234} e^{-2(\rho_2 l + \rho_3 d)} \quad (26)$$

where now $R_{1234}(n, \rho) = \Delta_{12}^E \Delta_{43}^E + \Delta_{12}^M \Delta_{43}^M$ and $\Delta_{ij}^{E,M}$ as defined in Eq.9.

In order to proceed, first notice from the definition of ρ_i that one can write:

$$\rho_2^2 = \rho_{1/2}^2 - \frac{1}{2} \frac{\Delta\epsilon}{c^2} \xi_n^2 \quad (27)$$

$$\rho_3^2 = \rho_{1/2}^2 + \frac{1}{2} \frac{\Delta\epsilon}{c^2} \xi_n^2 \quad (28)$$

where we have introduced $\Delta\epsilon = \epsilon_3 - \epsilon_2$, and $\rho_{1/2}^2 = \rho^2 + \frac{1}{2} \frac{(\epsilon_3 + \epsilon_2)}{c^2} \xi_n^2$. Then we assume small $\Delta\epsilon$ and apply Taylor to get

$$\rho_2 \approx \rho_{1/2} - \frac{1}{4} \frac{\xi_n^2 \Delta\epsilon}{c^2 \rho_{1/2}} \quad (29)$$

$$\rho_3 \approx \rho_{1/2} + \frac{1}{4} \frac{\xi_n^2 \Delta\epsilon}{c^2 \rho_{1/2}} \quad (30)$$

Using these results, the exponential function in Eq.26 can be now factored into two simpler exponentials:

$$e^{-2(\rho_2 l + \rho_3 d)} \approx e^{-2\rho_{1/2}(l+d)} e^{-\frac{1}{2} \frac{\xi_n^2 \Delta\epsilon}{c^2 \rho_{1/2}} (d-l)} \quad (31)$$

We call this the Similar Dielectric Function (SDF) approximation.

Replacing this result in 26, we can now express $\Delta g_{1234}(l, d)$ as

$$\Delta g_{1234}(l, d) = -\frac{k_B T}{2\pi} \sum_{n=0}^{\infty} ' \int_{\sqrt{\epsilon_{1/2}} \frac{\xi_n}{c}}^{\infty} d\rho_{1/2} \rho_{1/2} R(n, \rho_{1/2}) e^{-2\rho_{1/2}(l+d)} e^{-\frac{1}{2} \frac{\xi_n^2 \Delta\epsilon}{c^2 \rho_{1/2}} (d-l)} \quad (32)$$

Where we have switched the integration variable to $\rho_{1/2}$ and define the mean dielectric response of the intervening media as:

$$\epsilon_{1/2} = \frac{1}{2}(\epsilon_2 + \epsilon_3) \quad (33)$$

With the purpose of following an analogous path to that previously described for the three media terms, we perform a second change of variable under the definition $x = 2\rho_{1/2}(l + d)$, leading to

$$\Delta g_{1234}(l, d) = -\frac{k_B T}{8\pi(l+d)^2} \sum_{n=0}^{\infty} ' \int_{r_n}^{\infty} dx \, x \, R^e(n, x) e^{-x} \quad (34)$$

where $R^e(n, x) = R(n, x) e^{-\frac{\xi_n^2 \Delta\epsilon}{c^2 x} (d^2 - l^2)}$, and the lower integration limit is $r_n = 2(l+d) \sqrt{\epsilon_{1/2}} \frac{\xi_n}{c}$.

This result is now very similar to the three media potential of Eq.18, so we can find approximate solutions along the same lines.

1. First Gaussian Quadrature Approximation

First, we split the sum into the $n = 0$ term and the remaining contributions ($n > 0$). The former can be integrated right away and yields, in analogy with Eq.19:

$$\Delta g_{1234}^{\xi_n=0}(l+d) = -\frac{k_B T}{16\pi(l+d)^2} \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right) \left(\frac{\epsilon_4 - \epsilon_3}{\epsilon_4 + \epsilon_3} \right) \quad (35)$$

For the high frequency contributions, we proceed by performing a one-point Gaussian quadrature (again, *supplementary material 4*) under the definitions $f(x) = R^e(n, x)$ and $w(x) = e^{-x}$, and get:

$$\Delta g_{1234}^{\xi_n>0}(l, d) = -\frac{k_B T}{8\pi(l+d)^2} \sum_{n=1}^{\infty} R^e(n, x_1)(1+r_n)e^{-r_n} \quad (36)$$

where $x_1 = (2 + 2r_n + r_n^2)/(1 + r_n)$. To avoid any confusion, we highlight here that $R^e(n, x)$ depends on $(d^2 - l^2)$, meaning that the dependence of $g_{1234}^{\xi_n>0}$ on (l, d) is not as simple as $(l+d)$. The equation 36 is the First Gaussian Quadrature Approximation under the Similar Dielectric Function Approximation (SDF-FGQA), and its validity will be proved quantitatively in the results section.

2. Second Gaussian Quadrature Approximation

The same development of the previous SGQA is applied now to the equation 36. By employing the Euler-MacLaurin formula and operating the change of variable $\nu = \nu_T n = 2\sqrt{\epsilon_{1/2}}\xi_T n/c$ (*supplementary material 5*) we reach

$$\Delta g_{1234}^{\xi_n>0}(l, d) = -\frac{c\hbar}{32\pi^2(l+d)^2} \quad (37)$$

$$\int_{\nu_T}^{\infty} \tilde{R}^e(\nu, x_1)[1 + (l+d)\nu]e^{-(l+d)\nu} d\nu$$

With the definition $\tilde{R}^e(\nu, x_1) = R^e(\nu, x_1)\epsilon_{1/2}^{-3/2}j_{1/2}^{-1}$. Analogously, $j_{1/2} = \left(1 + \frac{1}{2}\frac{d\ln\epsilon_{1/2}}{d\ln\xi_n}\right)$, and recall here that $\Delta\epsilon = \epsilon_3 - \epsilon_2$, being 3 and 2 the subscripts of liquid water and ice. Then we introduce the auxiliary exponential, $e^{-\nu/\nu_\infty}$, and proceed with the one point Gaussian quadrature over ν allowing $f(\nu) = \tilde{R}^e(\nu, x_1)e^{\nu/\nu_\infty}$ and $w(\nu) = [1 + (l+d)\nu]e^{-\nu/\nu_\infty}e^{-\nu(l+d)}$ (*supplementary material 6*). This operation leads to

$$\Delta g_{1234}^{\xi_n>0}(l+d) = -\frac{c\hbar\nu_\infty}{32\pi^2(l+d)^2} \tilde{R}_\xi^{e,*} \tilde{F}(l+d) \quad (38)$$

where $\tilde{R}_\xi^{e,*} = \tilde{R}^e(\nu^*, x_1)e^\xi$ must be evaluated at the quadrature point $\nu^* = \nu_T + \nu_\infty \xi$, while the functions ξ and \tilde{F} , with $h = l + d$, are as Eq. 23 and Eq. 25, respectively.

Since the leading order behavior of Eq.38 is given by $\tilde{F}(l+d)$, the analogy of the correction term $\Delta g_{1234}(l+d)$ with the three media potential $g_{123}(h)$ is made obvious. In practice, $\Delta g_{1234}^{\xi_n > 0}$ also depends on $l - d$, by virtue of the factor:

$$R^e(\nu^*, x_1) = R(\nu^*, x_1)e^{-\frac{1}{4} \frac{\Delta \epsilon}{\epsilon_{1/2}} \frac{\nu^{*2}}{x_1} (d^2 - l^2)} \quad (39)$$

However, using the results for ν^* and x_1 , one finds that $R^e(\nu^*, x_1)$ provides only corrections of order unity to the leading order dependence provided by the function $\tilde{F}(l + d)$.

D. Summary of results and outlook

In this section we have provided analytical expressions for the van der Waals free energy of two thick plates separated by two layers of variable thickness, l and d , $g_{1234}(l, d)$. Starting from the exact Lifshitz result (Eq. 7) with the appropriate dispersion relation for our system (Eq. 6), we perform the expansion of the logarithm and show that $g_{1234}(l, d)$ can be expressed in terms of the free energies for three media, $g_{123}(l)$ and $g_{234}(d)$, together with a correction $\Delta g_{1234}(l, d)$.

The terms $g_{123}(l)$ and $g_{234}(d)$ may be treated in a general form $g_{RmL}(h)$ (Eq. 18). Their zero frequency contribution is taken independently (Eq. 19), while the rest is simplified through two Gaussian quadrature approximations and the Euler-MacLaurin formula (Eq. 24).

The four media term, $g_{1234}(l, d)$ can be worked out analogously, and yields, to leading order, exactly the same distance dependence than $g_{RmL}(h)$, with $h = d + l$.

For qualitative purposes, this means that the complicated two variable dependence of $g_{1234}(l, d)$ can be described by a sum of one single variable functions, such that:

$$g_{1234}(l, d) \approx C_{123} \frac{\tilde{F}(l)}{l^2} + C_{234} \frac{\tilde{F}(d)}{d^2} + C_{1234} \frac{\tilde{F}(l + d)}{(l + d)^2} \quad (40)$$

where the factors $C_{...}$ are material parameters of the intervening media and $\tilde{F}(h)$ is given by Eq.25. A similar relation holds also under the approximation of purely pairwise additive interactions, with the function $\tilde{F}(h)$ merely replaced by a constant factor³²⁻³⁴.

IV. DESCRIPTION OF THE DIELECTRIC RESPONSE

So far we have described the different contributions to the surface van der Waals free energy, whose computation in the framework of the Lifshitz's theory requires the knowledge of the dielectrical properties of every substance implied, essentially through the Δ_{ij} functions (Eq. 9) that appear in the dispersion relations.

In order to test our theory, we need to consider an explicit model for the dielectric properties of the system. As a simple one single component test system, we consider the adsorption of water vapor on Silver Iodide just below water's triple point. In this situation, we expect that a layer of ice of arbitrary thickness l can form, while, as the system approaches the melting line, the ice surface can premelt and form a water layer of thickness d .

Since the characterization of the dielectric properties is rather cumbersome, and the main goal of this paper is to test the theory of the previous section, we provide here just a brief description. A complete bibliographic review of the extinction index of these substances, together with detailed explanation of the resulting parameterization has been presented as a part of a Master's thesis³⁵, and will be published promptly in a forthcoming article.

A. Dielectric response of AgI

The dielectric response of a substance evaluated at imaginary frequencies is a real and monotonically decreasing function that drops at the frequencies at which that material absorbs. Every valid dielectric response must fulfill the limit $\epsilon(i\xi \rightarrow \infty) = 1$, meaning that beyond the last absorption frequency only remains the dielectric response of the vacuum. The dielectric function of AgI will be described following simple model called damped oscillator³⁶, used when there are not many experimental optical properties available in the bibliography. This representation accounts for one absorption in the ultraviolet (UV) region and another in the infrared (IR), and the parameterization requires only the knowledge of the static dielectric response, $\epsilon(0)$, the refractive index before the UV absorption, n_{UV} , and the absorption frequencies ω_{UV} and ω_{IR} .

$$\epsilon(i\xi) = 1 + \frac{\epsilon(0) - n_{UV}^2}{1 + (\xi/\omega_{IR})^2} + \frac{n_{UV}^2 - 1}{1 + (\xi/\omega_{UV})^2} \quad (41)$$

The magnitudes corresponding to the characterization of the UV absorption, $\epsilon(0)$, n_{UV} and ω_{IR} , are reviewed from Bottger and Geddes³⁷. The remaining parameter, ω_{UV} , is achieved

from a calculation based on the evolution of the refractive index published by Cochrane³⁸ and the Cauchy representation^{36,39} (see *supplementary material 7*). The complete parameterization is displayed in table I.

$\epsilon(0)$	n_{UV}	ω_{IR} (eV)	ω_{UV} (eV)
7.0	2.22	0.013	4.133

TABLE I: Parameterization of the dielectric response for AgI.

B. Dielectric responses of ice and liquid water

In this work we have employed a description of the dielectric functions of liquid water and ice achieved from the numerical fit of experimental absorption spectra by means of the Drude model, also called Parsegian-Ninham model when it is employed in this framework⁴⁰. The complete bibliographic review of the extinction index of these substances, together with the resulting parameterization, has been presented as a part of a Master's thesis³⁵, and will be the subject of a forthcoming article.

For the case of water, we have selected extinction coefficients available in the literature, and choose those measured close to 0 degrees Celsius whenever possible^{41–43}. Relative to the well known parameterization by Elbaum and Schick¹⁷, our set of extinction coefficients employs measurements by Hayashi and Hiraoka which provide a complete description of the high energy band⁴⁴. The resulting parameterization is consistent with recent work which use the data of Ref.⁴⁴ together with Infra Red absorption data at ambient temperature^{18,45}.

For the dielectric response of ice, there appear to be far less recent measurements. For this reason, we have performed a parameterization largely based on the literature review by Warren⁴⁶. The resulting parameterization does not differ significantly from previous calculations by Elbaum and Schick¹⁷.

As found by Fiedler et al.¹⁸, the most significant feature in the novel parameterization with updated experimental data by Hayashi is that the dielectric constant of water remains higher than that of ice at all relevant finite frequencies. As a result, the Hamaker function for the ice/water/air system is positive for all film thicknesses below the micron.

V. RESULTS AND DISCUSSION

A. Limiting cases

First we will check the consistency of our exact solution of $g_{1234}(l, d)$ by computing the evolution of the function at the limits of $l, d \rightarrow \infty$ and $l, d \rightarrow 0$. These correspond to the cases displayed in Eq 12, 13, 14 and 15, and shown in the same order in Fig 2. The proper fulfillment of these special conditions at infinite and zero thicknesses evinces the solidity of the exact Lifshitz result and its numerical solution in the present work. The continuity property of the surface potential $g_{1234}(l, d)$ is very convenient, since layers 2 and 3 need not adsorb preferentially onto the substrate 1. Whence, in the general case where one seeks an absolute minimum of the surface potential, the case where either phase '2', phase '3' or both are not favored thermodynamically is naturally built in.

B. Numerical checks

Next we demonstrate the reliability of the First Gaussian Quadrature Approximation (FGQA) and the Second Gaussian Quadrature Approximation (SGQA) by comparing the outcomes for the three media Hamaker function (Eq. 1). The exact result is given by Eq. 7 with the dispersion relation expressed as in Eq. 8, while the FGQA calculation is performed through Eq. 20 and Eq. 19. The computation of the SGQA in Eq. 24 needs the knowledge of the ν_∞ parameter. We achieve this by requiring the approximate expression, Eq.24 to match the exact free energy in the limit of vanishing film thickness.

$$g_{123}^{SGQA}(h \rightarrow 0) = g_{123}^{exact}(h \rightarrow 0) \quad (42)$$

Essentially, this amounts to setting ν_∞ so as to match the exact Hamaker constant.

Figure 3 presents the three media Hamaker function of the systems AgI/Ice/Water, Ice/Water/Air, AgI/Ice/Air and AgI/Water/Air, and illustrates the accuracy of the analytic approximations that we have developed. The resulting Hamaker functions have been divided by $k_B T$ at this representation in order to make their values easier to handle, and offering also a ratio of their strength with respect to the thermal energy.

With $g_{AgI/Ice/Water}$ and $g_{Ice/Water/Air}$ we have the first two terms required to describe completely the free energy of the system (Eq. 16). The remaining contribution is given by

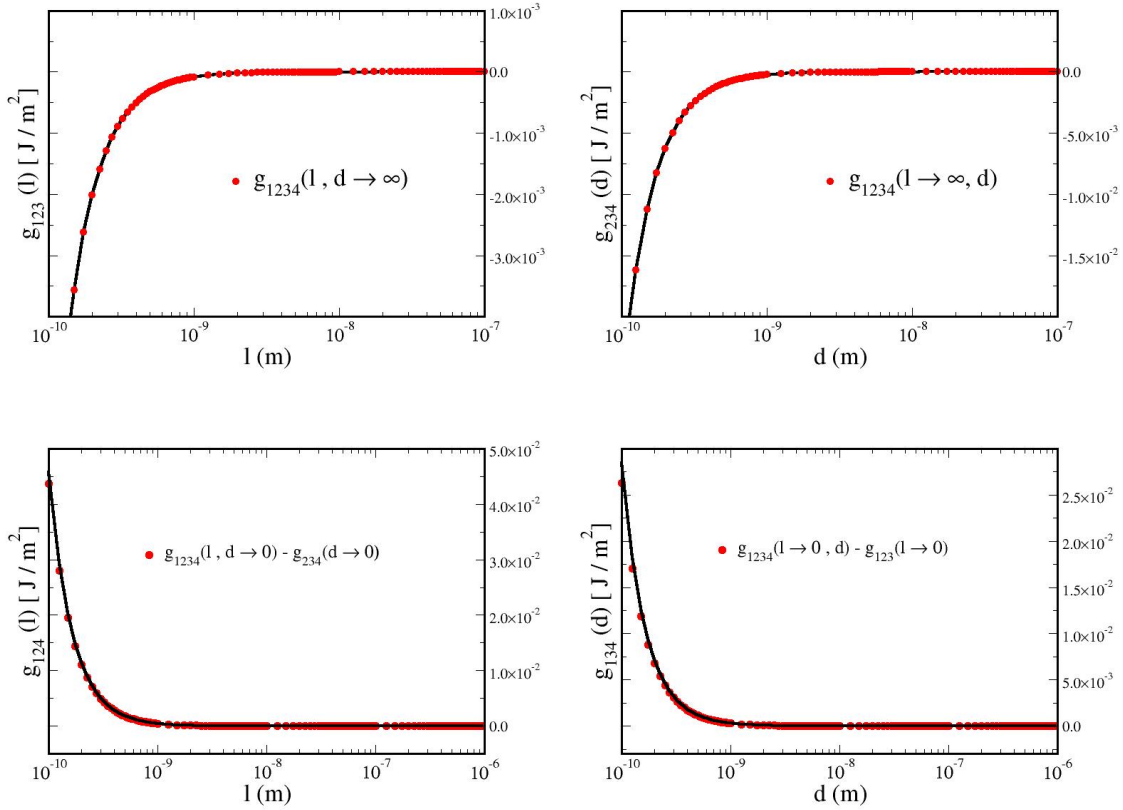


FIG. 2: Limiting cases of $g_{1234}(l, d)$ at infinite and zero thicknesses. Top left exposes the case contained in Eq. 12, top right represents Eq. 13, bottom left displays the limit in Eq. 14, and bottom right the one in Eq. 15. Black lines correspond to exact calculations of the surface potentials indicated on the y axis, while the symbols are the corresponding prediction obtained from $g_{1234}(l, d)$ as indicated in the cited equations. The labels 1, 2, 3, 4 stand for AgI, ice, water and vapor, respectively. In practice for numerical purposes the large thickness limit is evaluated at 10^{-2} m, while the vanishing thickness limit is evaluated at 10^{-12} m. All surface energies are given in J/m^2 .

$\Delta g_{1234}(l, d)$, whose values for the exact result and Second Gaussian Quadrature Approximation under the Similar Dielectric Function Approximation (SDF-SGQA) are displayed in Fig 4. Note that even if the dependence of $\Delta g_{1234}(l, d)$ on the thicknesses is more complicated than the simple $(l + d)$ that appears in Eq 38 due to the $(d^2 - l^2)$ in Eq.39, as we can express this as $(l + d)(d - l)$, it is still possible to employ the previous method to get ν_∞ for $(l + d) \rightarrow 0$. In the exact expression of $\Delta g_{1234}(l, d)$ in Eq. 26 we have to assume $l = d \rightarrow 0$, which is equivalent to the previous $(l + d) \rightarrow 0$ once we state $l = d$.

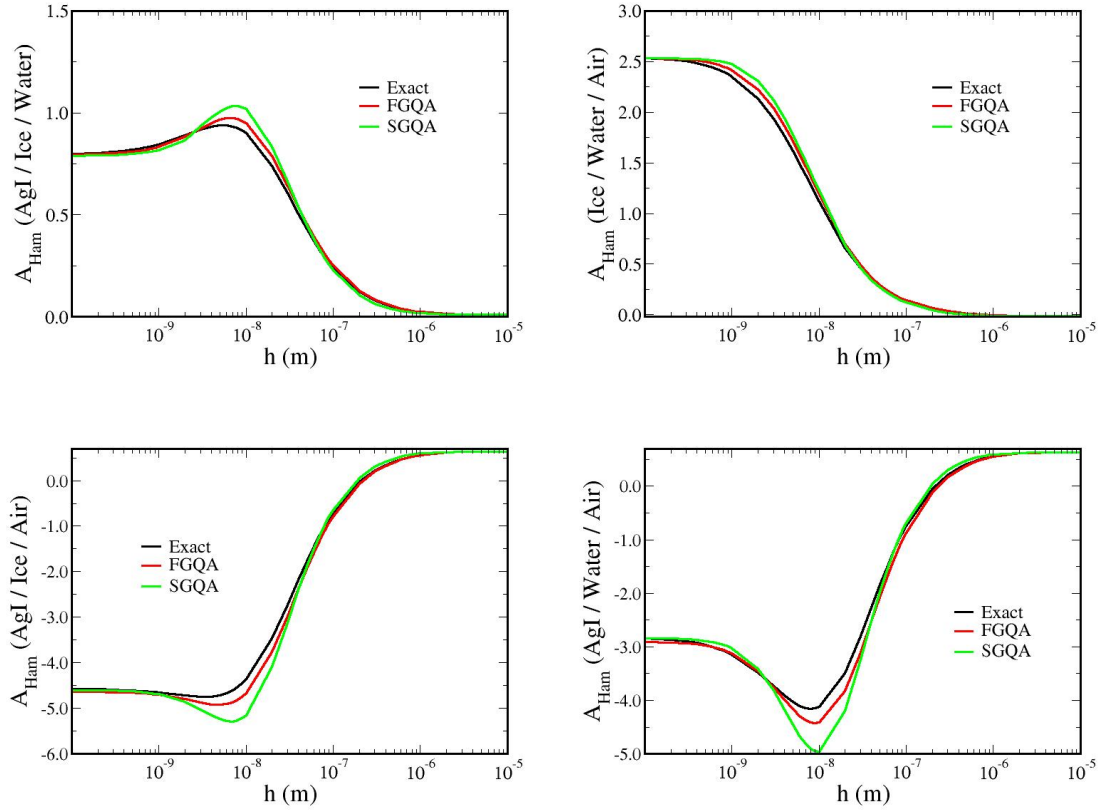


FIG. 3: Comparison of exact Hamaker functions with FGQA and from the SGQA approximations used in this work. Here we show all relevant combinations of three media formed from AgI, ice, water and vapor: AgI/Ice/Water (top, left), Ice/Water/Air (top, right), AgI/Ice/Air (bottom, left) and AgI/Water/Air (bottom, right). Results are given in units of $k_B T$.

The numerical solution of the exact formula (Eq. 7) with the dispersion relation of Eq. 11 is presented in Fig. 5, left. The range is fixed from 0.3 nm to 30 nm, which is approximately the expected range of lengths of relevance of the Van der Waals forces, but the behavior is quite monotonous for wider thicknesses. This result is then taken as a reference to compare with energy curves emerging from the employment of the First Gaussian Quadrature under the Similar Dielectric Function approximation (Fig. 5, right), whose results arise from solving equations 19, 20 and 36. The outcome never exceeds a relative error of 3% with respect to the exact result. Since we have proved how good this approximation works, we can now take advantage of its drastically lower computation time to perform a more exhaustive calculation of $g_{1234}(l, d)$, using now a finer mesh that otherwise would require a

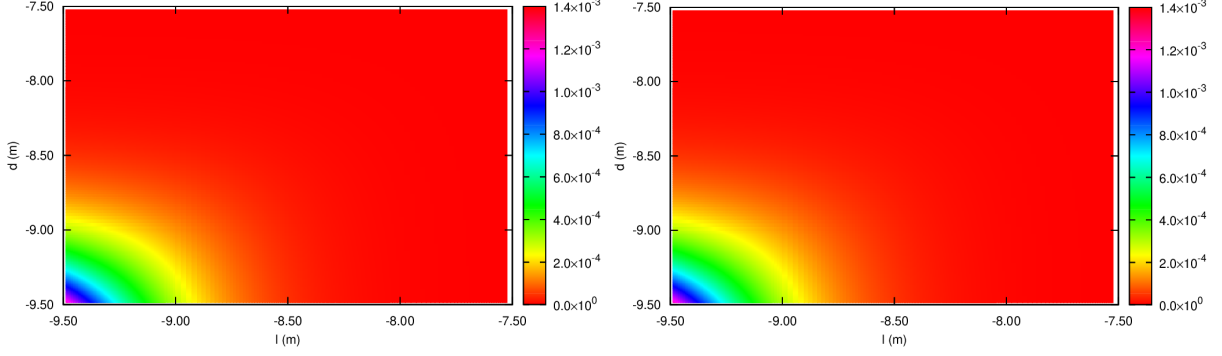


FIG. 4: Correction $\Delta g_{1234}(l, d)$ obtained from the exact expression (left) and from the SDF-SGQA (right). It supplies a repulsive contribution when both thicknesses ('l' for ice and 'd' for liquid water) are low, preventing the total $g_{1234}(l, d)$ to present an absolute minimum when both the liquid water layer and the ice layer disappear. Here the thicknesses are displayed in decimal logarithmic scale and surface energies are given in J/m^2 .

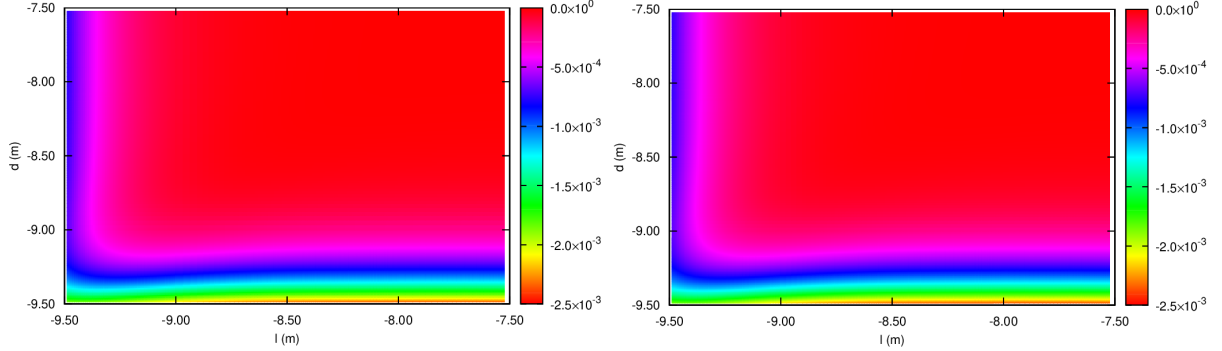


FIG. 5: Comparison of the full surface potential from numerical results with theoretical calculations. Exact $g_{1234}(l, d)$ (left), obtained from the Eq. 7 with the dispersion relation of Eq. 11. FGQA of $g_{1234}(l, d)$ (right) under the SDF approximation. In both cases, the axes 'l' and 'd' are the thicknesses of the ice and the liquid water layers represented in decimal logarithmic scale, while surface free energies are given in J/m^2 .

huge amount of time to be completed.

The FGQA approximation has also the advantage of being quite easier to compute in terms of complexity of the algorithm. The computation of the SGQA is even faster, but requires the calculation of the ν_∞ parameter.

C. Van der Waals forces of Water and ice adsorbed on AgI

1. Three media systems

In this section, we discuss the implications of every three media - Hamaker function displayed in Fig. 3.

Recall that from Eq. 1, the $A_{Ham}(h)$ has opposite sign to $g_{123}(h)$. Thus the AgI/Ice/Water and Ice/Water/Air functions (top in Fig. 3) provide a negative surface free energy, with absolute minima at vanishing film thickness. This means that van der Waals forces do not favor the growth of ice at the AgI/water interface, and do not favor the growth of a premelting film of water at the ice/air interface either.

On the other hand, both the AgI/Ice/Air and AgI/Water/Air systems (Fig. 3, bottom) present negative values of the Hamaker function, which implies positive and monotonous decreasing surface free energies. Accordingly, van der Waals forces favor the growth of both ice and water thick films at the AgI/air interface.

In practice, the ultimate behavior of growing films on the AgI surface is dictated by a balance of short range structural forces and long range van der Waals forces. Since the ice/air interface is known to exhibit a significant amount of premelting¹⁵, and van der Waals forces appear to inhibit growth of a liquid film, we conclude that the existence of premelting on ice is the result of short range structural forces, in agreement with recent findings from computer simulation⁴⁷⁻⁴⁹.

2. AgI/Ice/Water/Air

Once again, recall that according to Eq. 16, the four media Van der Waals free energy, $g_{1234}(l, d)$, is given as the sum of two three-media contributions and $\Delta g_{1234}(l, d)$. The results for the four media surface free energy, displayed in the Fig. 5 (either left or right), illustrate how as 'l' (the ice width) increases, the Van der Waals free energy in the Eq. 16 is completely governed by $g_{234}(d)$, and analogously, if 'd' (water layer thickness) becomes very large, the system behaves as if the air was not there, and the whole dispersive interaction comes now by the hand of $g_{123}(l)$. When 'l' and 'd' are negligible, the $\Delta g_{1234}(l, d)$ term in Eq. 16 contributes with a positive energy, so that the total $g_{1234}(l, d)$ of the system does not have an absolute minimum at $l = d = 0$.

Looking closely figure 5 at this scale, we appreciate how the lower set of minima appears for extremely low 'd' ($d \rightarrow 0$, liquid water almost disappear) and for several - increasing values of ice width. Indeed, the Lifshitz theory extended to four media supports and confirms an intuitive result from the comparison between the Hamaker functions of three media systems in the previous section: the Van der Waals interactions favor the growth of either ice or water at the AgI/air interface only if the thickness of the other substance (water or ice) remains close to zero.

This is confirmed by noticing that $g_{1234}(l, d) < 0$ at the bottom left corner of Fig.5. According to Eq.6 this implies that the surface tension $\gamma_{AgI/air}$ is smaller than the sum of $\gamma_{AgI/ice}$, $\gamma_{ice/water}$ and $\gamma_{water/air}$, implying that the adsorption of large ice and water films in between the AgI/air interface is unfavorable.

3. *AgI/Water/Ice/Air*

We have assumed all along that the nucleation occurs with the arrangement AgI/Ice/Water/Air. Nevertheless, this is not necessarily true, and it worth to check the behavior of the system AgI/Water/Ice/Air. For this purpose we solve numerically the exact Eq. 7 with the dispersion relation of Eq. 11, but this time with the following meaning of the indices: 1 = AgI, 2 = Liquid Water, 3 = Ice, 4 = Air. The result is presented in Fig. 6, The resulting surface potential is a positive (and therefore repulsive) energy, whose zeros (minima) are placed at large values of both thicknesses, meaning that the system will try to lower its energy by increasing the amount of both substances. Therefore, it appears that diverging layers of condensed water can grow on AgI if water is first adsorbed onto AgI and ice grows in between water and air. On the contrary, growth of ice in between AgI and water is not favored. The origin of this difference can be traced to the larger propensity of ice to grow in between water and air than that of water to form in between ice and air. This can be checked by looking at Fig. 6 along the axis of large water thickness, where it is seen that the free energy decreases by letting ice grow. This corresponds to the phenomenon of surface freezing, which here is seen to be favored by van der Waals forces, consistent with recent calculations¹⁸.

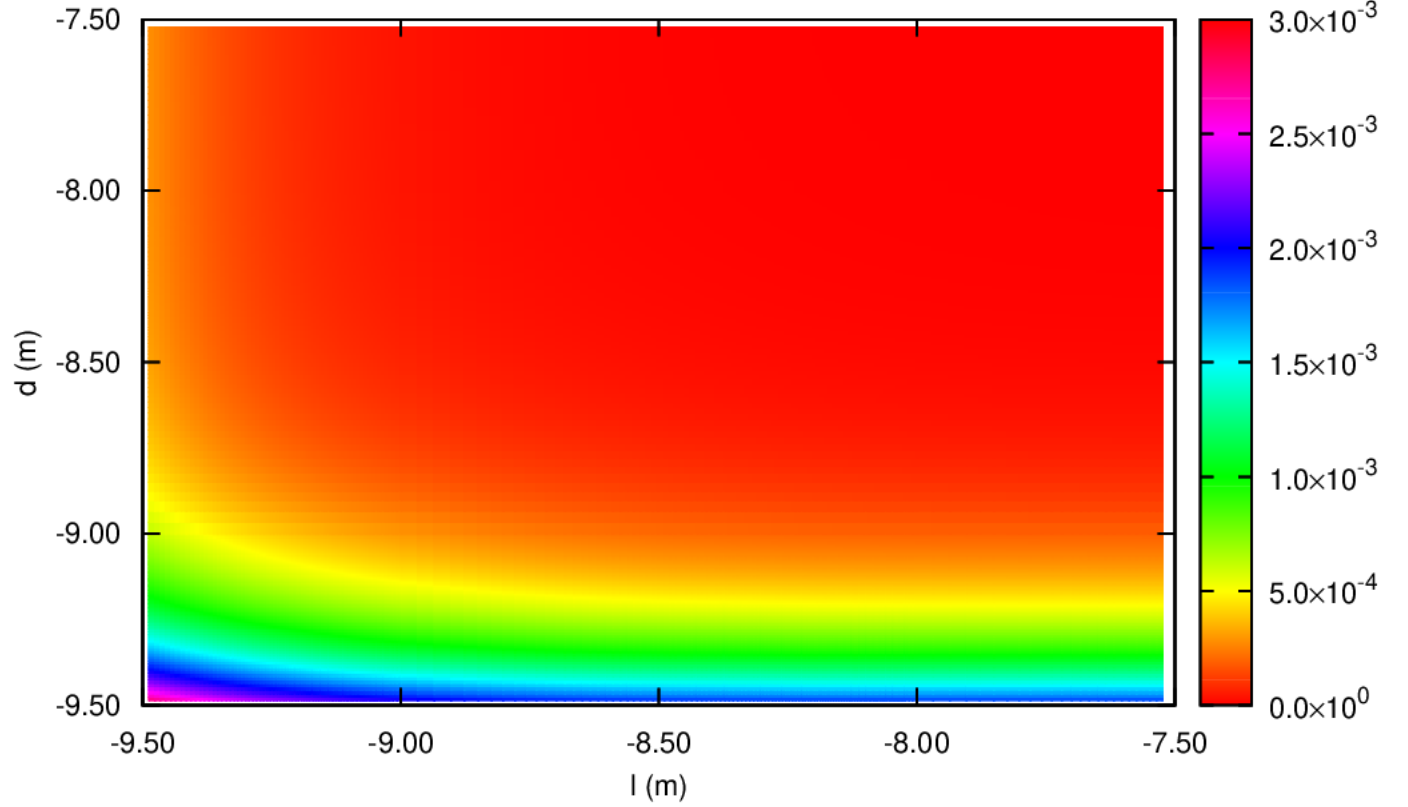


FIG. 6: Surface free energy for $g_{1234}(l, d)$ and the layer order AgI/Water/Ice/Air. The axes 'l' and 'd' are now the thicknesses of the liquid water and the ice layers, in decimal logarithmic scale. Surface free energies in J/m^2 .

4. Mechanism of ice nucleation

We will use this last part of the discussion to summarize some conclusions and considerations about the role of AgI as an ice nucleator.

Our results show that van der Waals forces promote the condensation of both ice and water on the AgI/air interface, a result which appears to be quite in agreement with the known nucleation efficiency of AgI²⁰. In fact, we find that the Hamaker constant of the AgI/ice/air system is larger (in absolute value) than that of AgI/water/air. This means that van der Waals forces actually promote the freezing of water vapor over the condensation of liquid water onto AgI. This expectation from the Hamaker constants is confirmed by inspection of Fig.5, which shows that indeed, the free energies along the $d \rightarrow 0$ axis of vanishing water thickness are more negative than those found along the $l \rightarrow 0$ axis of vanishing ice thickness.

On the contrary, it is found that van der Waals forces do not promote ice growth at the AgI/water surface. This can be read off from Fig.5, by looking at the free energy along the $d \rightarrow \infty$ axis, or merely, by inspection of the Hamaker function of the AgI/ice/water system, Fig.3.

From these observations, we can conclude that van der Waals forces actually favor a deposition mode of ice nucleation from the vapor phase. Of course, this is quite at odds with experimental findings, which show that AgI can nucleate ice both from vapor or water at a similar undercooling of about 4 °C⁵⁰.

The reason for this apparent discrepancy is that the ultimate behavior of the system is dictated by a balance of both structural and van der Waals forces. Since an undercooling of at least 4 °C is required for ice to grow from supercooled water vapor, there must be short range structural forces which oppose mildly to ice growth. Otherwise, in the absence of short range forces, van der Waals forces would favor nucleation of ice from the vapor without any undercooling. This is very much consistent with computer simulations by Shevkunov, which indicate that a one monolayer thick ice film can form at ice vapor saturation, but further growth is mildly activated⁵¹.

On the contrary, van der Waals forces do not promote ice growth for AgI immersed in water, but simulations consistently show that Ag⁺ exposed surfaces readily nucleate ice at mild supercooling²¹⁻²³. This means that short range structural forces do favor ice growth at the AgI/water surface, and a small activation is required because of the unfavorable van der Waals interactions.

Interestingly, it has been suggested that AgI is actually most efficient in the contact mode, whereby ice nucleation is promoted for AgI particles in contact with condensed water droplets²⁰. An explanation for this effect can be provided by assuming that nucleation actually occurs at the three phase contact line formed between AgI, water and air⁵², but this requires a favorable line tension. Our results lend support to such favorable phenomenon. Indeed, we find that van der Waals forces promote growth of a thin ice layer on AgI in contact with water vapor. Such growth is ultimately very slow, because of the low vapor pressure of ice. However, if such thin ice layer is formed at the contact line of an AgI particle with the air/water interface, a large reservoir of undercooled bulk water would be made available for the thin ice layer to continue growing at the water/air interface, where, as we have seen, van der Waals forces promote surface freezing.

VI. CONCLUSIONS

In this study we work out the exact Lifshitz theory of van der Waals forces for a substrate in the neighborhood of three phase coexistence, where two adsorbed layers of variable thickness can form on the substrate. The theory goes well beyond a Hamaker theory of pairwise additive forces, and naturally builds in the role of polarization of the condensed phases. By this token, it provides the Hamaker regime for small layer thicknesses, but also incorporates the Casimir regime of retarded interactions.

Accurate analytical approximations are provided which improve conventional treatments of non-retarded van der Waals forces³ and apply also to the regime of retarded interactions. This extends the validity of the calculations from film thicknesses barely decades of nanometers to arbitrary large values. Unlike the Gregory equation advocated by Israelachvili³, this is achieved without any ad-hoc parameter⁵³. By this token, we find one can now accurately evaluate the free energy in the Hamaker and Casimir regimes with the same data that is required to estimate Hamaker constants^{3,36,39,54}. The proper account of retardation does not only provide better accuracy. It is a major qualitative improvement, as the crossover from non-retarded to retarded interactions is often accompanied by a sign reversal of the van der Waals forces.

Our results are applied to the study of water vapor adsorption on AgI, where both layers of ice and water can form close to the triple point. Previous studies on the ice nucleation efficiency of AgI have provided insight into the short range interactions of either undercooled water or vapor with the AgI surface^{21–23,51}. However, in the atmosphere both ice and water compete simultaneously for the vapor phase and it is very difficult to assess the relative stability of thick water and ice films from simulation. Our results indicate that van der Waals forces stabilize the growth of ice films at the AgI/air interface, but on the contrary, inhibit the growth of ice in the immersion mode. Importantly, van der Waals forces also promote growth of thick ice films at the air/water interface. This explains the intriguing observation of sub-surface nucleation in experiments and computer simulations^{55,56}, but also helps understand how the water/AgI/air contact line could promote ice nucleation⁵². The AgI/vapor surface provides the site for stabilized ice layers that serve as embryos for the growth of a stable ice film at the water/vapor interface, thus lending support to contact mode freezing of AgI particles found in experiments²⁰.

Our results provide a general framework to gauge the role of van der Waals forces in the colloidal sciences, where multicomponent solutions display multiphase coexistence ubiquitously, and provide a solid background to assess how long range forces condition the ice nucleation efficiency of atmospheric aerosols.

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AUTHORS CONTRIBUTIONS

Juan Luengo: Methodology, Formal analysis, Visualization, Software, Investigation, Writing-Original Draft; Luis G. MacDowell: Validation, Conceptualization, Methodology, Writing-Review and Editing.

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- ¹ B. Derjaguin, *Langmuir* **3**, 601 (1987).
 - ² P. G. de Gennes, F. Brochard-Wyart, and D. Quéré, *Capillarity and Wetting Phenomena* (Springer, New York, 2004) pp. 1–292.
 - ³ J. N. Israelachvili, *Intermolecular and Surfaces Forces*, 3rd ed. (Academic Press, London, 1991) pp. 1–674.
 - ⁴ M. Schick, in *Liquids at Interfaces*, Les Houches Lecture Notes (Elsevier, Amsterdam, 1990) pp. 1–89.
 - ⁵ I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, *Soviet Physics Uspekhi* **4**, 153.175 (1961).
 - ⁶ S. Takeya and R. Ohmura, *J. Chem. Eng. Data* **51**, 1880 (2006).
 - ⁷ G. Aspenes, L. Dieker, Z. Aman, S. Hiland, A. Sum, C. Koh, and E. Sloan, *J. Colloid. Interface Sci.* **343**, 529 (2010).
 - ⁸ R. Nakane, E. Gima, R. Ohmura, I. Senaha, and K. Yasuda, *J. Chem. Thermodyn.* **130**, 192 (2019).

- ⁹ M. Boström, R. W. Corkery, E. R. A. Lima, O. I. Malyi, S. Y. Buhmann, C. Persson, I. Brevik, D. F. Parsons, and F. Johannes, *ACS Earth and Space Chem.* **3**, 1014 (2019).
- ¹⁰ Y. Antonov and B. A. Wolf, *Langmuir* **30**, 6508 (2014).
- ¹¹ S. Rafai, D. Bonn, and J. Meunier, *Physica. A* **386**, 31 (2007).
- ¹² C. Hertlein, L. Helden, A. Gambassi, S. Dietrich, and C. Bechinger, *Nature* **451**, 172 (2008).
- ¹³ J. G. Dash, A. W. Rempel, and J. S. Wettlaufer, *Rev. Mod. Phys.* **78**, 695 (2006).
- ¹⁴ R. Rosenberg, *Phys. Today* **58**, 50 (2005).
- ¹⁵ B. Slater and A. Michaelides, *Nat. Rev. Chem* **3**, 172 (2019).
- ¹⁶ Y. Nagata, T. Hama, E. H. G. Backus, M. Mezger, D. Bonn, M. Bonn, and G. Sazaki, *Acc. Chem. Res.* **52**, 1006 (2019).
- ¹⁷ M. Elbaum and M. Schick, *Phys. Rev. Lett.* **66**, 1713 (1991).
- ¹⁸ J. Fiedler, M. Boström, C. Persson, I. Brevik, R. Corkery, S. Y. Buhmann, and D. F. Parsons, *J. Phys. Chem. B* **124**, 3103 (2020), pMID: 32208624, <https://doi.org/10.1021/acs.jpccb.0c00410>.
- ¹⁹ B. Vonnegut, *Journal of applied physics* **18**, 593 (1947).
- ²⁰ C. Marcolli, B. Nagare, A. Welti, and U. Lohmann, *Atmospheric Chemistry and Physics* **16**, 8915 (2016).
- ²¹ G. Fraux and J. P. K. Doye, *J. Chem. Phys.* **141**, 216101 (2014), <https://doi.org/10.1063/1.4902382>.
- ²² S. A. Zielke, A. K. Bertram, and G. N. Patey, *J. Phys. Chem. B* **19**, 9049 (2015).
- ²³ B. Glatz and S. Sarupria, *J. Chem. Phys.* **145**, 211924 (2016), <https://doi.org/10.1063/1.4966018>.
- ²⁴ V. A. Parsegian, *Van der Waals Forces* (Cambridge University Press, Cambridge, 2005) pp. 1–311.
- ²⁵ B. W. Ninham and V. A. Parsegian, *J. Chem. Phys.* **53**, 3398 (1970), <https://doi.org/10.1063/1.1674507>.
- ²⁶ R. Podgornik, P. L. Hansen, and V. A. Parsegian, *J. Chem. Phys.* **119**, 1070 (2003), <https://doi.org/10.1063/1.1578613>.
- ²⁷ V. Estes, S. Carretero-Palacios, L. G. MacDowell, J. Fiedler, D. F. Parsons, F. Spallek, H. Míguez, C. Persson, S. Y. Buhmann, I. Brevik, and M. Boström, *Phys. Chem. Chem. Phys.* **22**, 11362 (2020).
- ²⁸ N. G. van Kampen, B. R. A. Nijboer, and S. K., *Phys. Lett.* **26A**, 307 (1968).

- ²⁹ B. W. Ninham, V. A. Parsegian, and G. H. Weiss, *J. Stat. Phys.* **2**, 323 (1970).
- ³⁰ H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (John Wiley & Sons, New York, 1985).
- ³¹ L. G. MacDowell, *J. Chem. Phys.* **150**, 081101 (2019).
- ³² M. Müller, L. G. MacDowell, P. Müller-Buschbaum, O. Wunnicke, and M. Stamm, *J. Chem. Phys.* **115**, 9960 (2001).
- ³³ P. Loskill, H. Hähl, T. Faidt, S. Grandthyll, F. Müller, and K. Jacobs, *Adv. Colloid Interface Sci.* **179-182**, 107 (2012), interfaces, Wettability, Surface Forces and Applications: Special Issue in honour of the 65th Birthday of John Ralston.
- ³⁴ D. N. Simavilla, W. Huang, C. Housmans, M. Sferrazza, and S. Napolitano, *ACS Cent. Sci* **4**, 755 (2018).
- ³⁵ J. Luengo and L. MacDowell, *Van der Waals Forces at Ice Surfaces with Atmospheric Interest*, Master's thesis, Facultad de Ciencias (2020).
- ³⁶ D. B. Hough and L. R. White, *Adv. Colloid Interface Sci.* **14**, 3 (1980).
- ³⁷ G. Bottger and A. Geddes, *The Journal of Chemical Physics* **46**, 3000 (1967).
- ³⁸ G. Cochran, *Journal of Physics D: Applied Physics* **7**, 748 (1974).
- ³⁹ L. Bergström, *Adv. Colloid Interface Sci.* **70**, 125 (1997).
- ⁴⁰ V. Parsegian and B. Ninham, *Nature* **224**, 1197 (1969).
- ⁴¹ H. R. Zelsmann, *Journal of molecular structure* **350**, 95 (1995).
- ⁴² D. J. Segelstein, *The complex refractive index of water*, Ph.D. thesis, University of Missouri–Kansas City (1981).
- ⁴³ D. M. Wieliczka, S. Weng, and M. R. Querry, *Applied optics* **28**, 1714 (1989).
- ⁴⁴ H. Hayashi and N. Hiraoka, *The Journal of Physical Chemistry B* **119**, 5609 (2015).
- ⁴⁵ J. Wang and A. V. Nguyen, *Adv. Colloid Interface Sci.* **250**, 54 (2017).
- ⁴⁶ S. G. Warren and R. E. Brandt, *J. Geophys. Research* **113**, D14220 (2008).
- ⁴⁷ D. T. Limmer and D. Chandler, *J. Chem. Phys.* **141**, 18C505 (2014).
- ⁴⁸ J. Benet, P. Llombart, E. Sanz, and L. G. MacDowell, *Mol. Phys.* **117**, 2846 (2019).
- ⁴⁹ P. Llombart, E. G. Noya, D. N. Sibley, A. J. Archer, and L. G. MacDowell, *Phys. Rev. Lett.* **124**, 065702 (2020).
- ⁵⁰ H. R. Pruppacher and J. D. Klett, *Microphysics of Clouds and Precipitation* (Springer, Heidelberg, 2010).

- ⁵¹ S. V. Shevkunov, Colloid J. **67**, 497508 (2005).
- ⁵² Y. S. Djikaev and E. Ruckenstein, J. Phys. Chem. A **112**, 11677 (2008), pMID: 18925734, <https://doi.org/10.1021/jp803155f>.
- ⁵³ J. Gregory, J. Colloid. Interface Sci. **83**, 138 (1981).
- ⁵⁴ H.-J. Butt and M. Kappl, *Surface and Interfacial Forces* (Wiley-VCH, Weinheim, 2010).
- ⁵⁵ A. J. Durant and R. A. Shaw, Geo. Phys. Res. Lett. **32** (2005), 10.1029/2005GL024175, <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2005GL024175>.
- ⁵⁶ A. Haji-Akbari and P. G. Debenedetti, Proc. Natl. Acad. Sci. U.S.A. **114**, 3316 (2017).

1. Derivation of the dispersion relation of the exact Lifshitz formula

The dispersion relation of the system is an expression that all electromagnetic waves across the system must hold. These waves have an electric, $\vec{E}(t)$, and magnetic, $\vec{H}(t)$, field function of time, t , with the form

$$\vec{E}(t) = \text{Re} \left(\sum_{\omega} \vec{E}_{\omega} e^{-i\omega t} \right) \quad (43)$$

$$\vec{H}(t) = \text{Re} \left(\sum_{\omega} \vec{H}_{\omega} e^{-i\omega t} \right) \quad (44)$$

Being i the imaginary unit, ω the frequency, and \vec{E}_{ω} , \vec{H}_{ω} the amplitudes of every field at that frequency. Each must respect a certain wave equation

$$\nabla^2 \vec{E} = \frac{\epsilon\mu}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} \quad (45)$$

$$\nabla^2 \vec{H} = \frac{\epsilon\mu}{c^2} \frac{\partial^2 \vec{H}}{\partial t^2} \quad (46)$$

With ϵ and μ the dielectric and magnetic permeability and c the velocity of light. We can turn Eq. 45 and 46 into differential equations of the components of the position solving the partial derivative with time from Eq. 43 and 44, respectively. In our system, the vectors \vec{E} and \vec{H} have periodic x, y components with the general form $f_k(z)e^{i(ux+vy)}$. Then solve the derivatives in the resulting differential equation to get the general $f''(z) = \rho_k^2 f(z)$, with

$$\rho_k^2 = u^2 + v^2 - \frac{\epsilon_k \mu_k \omega^2}{c^2} \quad (47)$$

Where we define later $\rho = u^2 + v^2$. The general solution yields $f_{k,\alpha}(z) = A_{k,\alpha} e^{\rho_k z} + B_{k,\alpha} e^{-\rho_k z}$, with $\alpha = x, y, z$ for every substance k at the system, here we name the layers generally as L/m/n/R. Finally, we impose $\nabla \cdot \vec{E} = 0$ and $\nabla \cdot \vec{H} = 0$ to reach that

$$A_z = -\frac{i}{\rho}(uA_x + vA_y) \quad (48)$$

$$B_z = \frac{i}{\rho}(uB_x + vB_y) \quad (49)$$

Which is true separately at every substance L, m, n, R. Next let us apply the boundary conditions at every interface, setting the z axis perpendicular to the interfaces and the $z = 0$ point at the interface L/m. Now the thickness of m will be 'l' and that of the substance n

will be 'd'.

- $z = 0$, interface L/m. Here $B_{x,y,z}^L$ must be zero so that f^L does not go to infinite when z tends to $-\infty$. Then we impose the conditions $E_x^L = E_x^m$ and $E_y^L = E_y^m$, sum the resulting equations and use Eq. 48 and 49 to get

$$-\rho_L A_z^L + \rho_m A_z^m - \rho_m B_z^m = 0 \quad (50)$$

On the other hand, it must also be true that $\epsilon_L E_z^L = \epsilon_m E_z^m$, that is

$$\epsilon_L A_z^L = \epsilon_m A_z^m + \epsilon_m B_z^m \quad (51)$$

- $z = l$, interface m/n. Here we apply basically the same procedure. Notice that now the exponentials do not vanish, so we reach from $E_x^m = E_x^n$ and $E_y^m = E_y^n$

$$-\rho_m A_z^m e^{\rho_m l} + \rho_m B_z^m e^{-\rho_m l} + \rho_n A_z^n e^{\rho_n l} - \rho_n B_z^n e^{-\rho_n l} = 0 \quad (52)$$

And from the condition $\epsilon_m E_z^m = \epsilon_n E_z^n$

$$\epsilon_m A_z^m e^{\rho_m l} + \epsilon_m B_z^m e^{-\rho_m l} = \epsilon_n A_z^n e^{\rho_n l} + \epsilon_n B_z^n e^{-\rho_n l} \quad (53)$$

- $z = l + d$, interface n/R. Here $A_{x,y,z}^R$ must be zero so that f^R does not go to infinite as z tends to ∞ . From $E_x^n = E_x^R$ and $E_y^n = E_y^R$ now we have

$$-\rho_n A_z^n e^{\rho_n(l+d)} + \rho_n B_z^n e^{-\rho_n(l+d)} - \rho_R B_z^R e^{-\rho_R(l+d)} = 0 \quad (54)$$

And finally, from $\epsilon_n E_z^n = \epsilon_R E_z^R$ we get

$$\epsilon_n A_z^n e^{\rho_n(l+d)} + \epsilon_n B_z^n e^{-\rho_n(l+d)} = \epsilon_R B_z^R e^{-\rho_R(l+d)} \quad (55)$$

So far we have used the boundaries for the electric fields. Solving the system of equations formed by Eq. 50, 51, 52, 53, 54 and 55 for the six variables $\{A_i\}$, $\{B_i\}$, leads to the dispersion relation $D_M = 0$, where D_M is the determinant:

$$\begin{vmatrix} -\rho_L & \rho_m & -\rho_m & 0 & 0 & 0 \\ \epsilon_L & -\epsilon_m & -\epsilon_m & 0 & 0 & 0 \\ 0 & -\rho_m e^{\rho_m l} & \rho_m e^{-\rho_m l} & \rho_n e^{\rho_n l} & -\rho_n e^{-\rho_n l} & 0 \\ 0 & \epsilon_m e^{\rho_m l} & \epsilon_m e^{-\rho_m l} & -\epsilon_n e^{\rho_n l} & -\epsilon_n e^{-\rho_n l} & 0 \\ 0 & 0 & 0 & -\rho_n e^{\rho_n(l+d)} & \rho_n e^{-\rho_n(l+d)} & -\rho_R e^{-\rho_R(l+d)} \\ 0 & 0 & 0 & \epsilon_n e^{\rho_n(l+d)} & \epsilon_n e^{-\rho_n(l+d)} & -\epsilon_R e^{-\rho_R(l+d)} \end{vmatrix} = D_M$$

Solving for the determinant explicitly gives a sum of 32 terms which is not particularly insightful. However, one notices that products of two matrix elements of the form $d_{ij}d_{kl}$ have common factors with terms $d_{il}d_{kj}$, or alternatively, terms of the form $\rho_i\epsilon_j$ share common factors with $\rho_j\epsilon_i$. Therefore, we organize the 32 terms as:

$$\begin{aligned} D_M = & (\rho_L\epsilon_m - \rho_m\epsilon_L) [(\rho_R\epsilon_n - \rho_n\epsilon_R)(\rho_m\epsilon_n + \rho_n\epsilon_m)\alpha^{-1}\beta\gamma^{-1} + (\rho_R\epsilon_n + \rho_n\epsilon_R)(\rho_n\epsilon_m - \rho_m\epsilon_n)\alpha^{-1}\beta^{-1}\gamma] \delta^{-1} \\ & + \\ & (\rho_m\epsilon_L + \rho_L\epsilon_m) [(\rho_m\epsilon_n - \rho_n\epsilon_m)(\rho_n\epsilon_R - \rho_R\epsilon_n)\alpha\beta\gamma^{-1} - (\rho_n\epsilon_m + \rho_m\epsilon_n)(\rho_R\epsilon_n + \rho_n\epsilon_R)\alpha\beta^{-1}\gamma] \delta^{-1} \end{aligned} \quad (56)$$

where we have introduced the symbols $\alpha = e^{\rho_m l}$, $\beta = e^{\rho_n l}$, $\gamma = e^{\rho_n(l+d)}$ and $\delta = e^{\rho_R(l+d)}$, for short.

Notice now that the determinant is a product of elements $(\rho_i\epsilon_j + \rho_j\epsilon_i)$, which correspond to denominators of the function Δ_{ij}^M in the main text (see also below, Eq.58); and elements $(\rho_i\epsilon_j - \rho_j\epsilon_i)$ which correspond to numerators of Δ_{ij}^M . Since, from the dispersion relation, this determinant must vanish, we can now multiply and divide by constants without changing the result. Therefore, we divide by factors of the form $(\rho_i\epsilon_j + \rho_j\epsilon_i)$, and further divide by $\alpha\beta^{-1}\gamma\delta^{-1}$ to get:

$$D_M = 1 - \Delta_{Lm}^M \Delta_{nm}^M e^{-2\rho_m l} - \Delta_{mn}^M \Delta_{Rn}^M e^{-2\rho_n d} - \Delta_{Lm}^M \Delta_{Rn}^M e^{-2\rho_m l} e^{-2\rho_n d} \quad (57)$$

$$\Delta_{ij}^M = \frac{\rho_j\epsilon_i - \rho_i\epsilon_j}{\rho_j\epsilon_i + \rho_i\epsilon_j} \quad (58)$$

which is the sought result. Notice that here D_M is symmetrical with respect to the interchange of l and d .

The result for a system of one single medium between two plates, with one plate coated by a layer of fixed thickness, d , can be obtained from this expression readily. In that situation

the physical requirement is that $D_M \rightarrow 1$, as $l \rightarrow \infty$ at fixed d . From Eq.57, we find instead:

$$\lim_{l \rightarrow \infty} D_M = 1 - \Delta_{mn}^M \Delta_{Rn}^M e^{-2\rho_n d} \quad (59)$$

Therefore, a new dispersion relation, consistent with the mentioned physical requirement can be obtained simply dividing D_M by $\lim_{l \rightarrow \infty} D_M$. This yields:

$$D'_M = 1 - \frac{\Delta_{Lm}^M \Delta_{nm}^M + \Delta_{Lm}^M \Delta_{Rn}^M e^{-2\rho_m d}}{1 - \Delta_{mn}^M \Delta_{Rn}^M e^{-2\rho_n d}} e^{-2\rho_m l} \quad (60)$$

which is the well known dispersion relation used for systems with one coated layer of fixed size. Because of the choice of normalization condition, the dispersion relation is no longer symmetrical with respect to the interchange of l and d , since they now stand on a different footing.

Notice that in practice, this normalization of the dispersion relation amounts to subtracting $g_{mnR}(d)$ to $g_{LmnR}(l, d)$ as discussed in Eq.14-15 of the main text for the particular choice $d \rightarrow 0$.

The calculation of D_E arises from a similar analysis of the boundaries for the magnetic fields. The full dispersion relation emerges by setting $D = D_M D_E$, with $D = 0$.

2. Change of variable to 'x'

Our purpose here is to develop explicitly the route from the three media exact surface free energy to the equation over which the First Gaussian Quadrature Approximation is performed. Then we start from the generalized form

$$g_{LmR}(h) = \frac{k_B T}{2\pi} \sum_{n=0}^{\infty} \int_0^{\infty} \rho d\rho \ln(D_{LmR}^E D_{LmR}^M) \quad (61)$$

With $D_{LmR}^{E,M} = 1 - \Delta_{Lm}^{E,M} \Delta_{Rm}^{E,M} e^{-2\rho_m h}$, being h here the thickness of the medium 'm'. Next we assume that the term after the 1 at $D_{LmR}^{E,M}$ is small, and we expand the logarithm as $\ln(1 - x) \approx -x$. At the same time, let us change the variable to $\rho_m^2 = \rho^2 + \frac{\epsilon_m \xi_n^2}{c^2}$. We perform this transformation simply through $\rho_m d\rho_m = \rho d\rho$, and the lower limit of the integral now is $\rho_m(\rho = 0) = \sqrt{\frac{\epsilon_m \xi_n^2}{c^2}}$

$$g_{LmR}(h) = -\frac{k_B T}{2\pi} \sum_{n=0}^{\infty} \int_{\sqrt{\frac{\epsilon_m \xi_n^2}{c^2}}}^{\infty} \rho_m d\rho_m (\Delta_{Lm}^M \Delta_{Rm}^M + \Delta_{Lm}^E \Delta_{Rm}^E) e^{-2\rho_m h} \quad (62)$$

Being Δ_{ij}^M defined as it is presented at the Eq. 58 and Δ_{ij}^E

$$\Delta_{ij}^E = \frac{\rho_j - \rho_i}{\rho_j + \rho_i} \quad (63)$$

In the last step we perform a second change of variables to $x = 2\rho_m h$, so that $x dx = 4h^2 \rho_m d\rho_m$. Moreover, the lower limit is transformed again to $2\rho \sqrt{\frac{\epsilon_m \xi_n^2}{c^2}}$, which we define as r_n

$$g_{LmR}(h) = -\frac{k_B T}{8\pi h^2} \sum_{n=0}^{\infty} \int_{r_n}^{\infty} x dx (\Delta_{Lm}^M \Delta_{Rm}^M + \Delta_{Lm}^E \Delta_{Rm}^E) e^{-x} \quad (64)$$

Both Δ_{ij}^M and Δ_{ij}^E may be expressed in terms of $x_i = \sqrt{x^2 + (\epsilon_i - \epsilon_m)(2h\xi_n/c)^2}$ instead of ρ_i , through the straightforward substitution $x_i = 2\rho_i h$. The Eq. 64 corresponds to the stage immediately before the FGQA at the main part of the work, and is the result to which we wanted to arrive here.

3. Gaussian Quadrature

The gaussian quadrature is an integration method where the integrand is separated between a well shaped function, $f(x)$, and a weight function, $w(x)$. The generalized N points gaussian quadrature reads

$$\int_a^b f(x) w(x) dx = \sum_{i=1}^N f(x_i) m_i \quad (65)$$

With $f(x)$ evaluated at the nodes x_i (also called quadrature points). The knowledge of the sets of $\{x_i\}$ and $\{m_i\}$ requires the capability of solving from the $j = 0$ up to the $2N - 1$ integral of the kind

$$I_j = \int_a^b x^j w(x) dx = \sum_{i=1}^N x_i^j m_i \quad (66)$$

That leads to a system of $2N$ equations whose solution provides the quadrature points and all $\{m_i\}$. In this work we have used the one point gaussian quadrature ($N=1$), so the integrals that we have to solve are

$$I_0 = \int_a^b w(x) dx \quad (67)$$

$$I_1 = \int_a^b x w(x) dx \quad (68)$$

Thus we have $m_1 = I_0$, and $x_1 = I_1/I_0$.

4. One point gaussian quadrature applied to the FGQA

We wish to specify here the quadrature performed over

$$g^{\xi_n > 0}(h) = -\frac{k_B T}{8\pi h^2} \sum_{n=1}^{\infty} \int_{r_n}^{\infty} x dx R(n, x) e^{-x} \quad (69)$$

Where we have generalized for both $g_{LmR}(h)$ and $\Delta g_{1234}(l, d)$. In the last case just consider that $h = (l + d)$, and employ $R^e(n, x)$ instead of $R(n, x)$. We state then $f(x) = R(n, x)$, and $w(x) = x e^{-x}$. These are straightforward integrals of the form

$$I_0 = \int_{r_n}^{\infty} x e^{-x} dx = e^{-r_n} (1 + r_n) \quad (70)$$

$$I_1 = \int_{r_n}^{\infty} x^2 e^{-x} dx = e^{-r_n} (2 + 2r_n + r_n^2) \quad (71)$$

5. Euler - MacLaurin formula

The Euler-MacLaurin formula allows the transformation of a summatory into an integral through an approximation, and reads

$$\sum_{n=a}^b f(n) = \int_a^b f(n) dn + \frac{1}{2} (f(a) + f(b)) + \sum_{k=1}^{\infty} \frac{B_{2k}}{2k!} (f^{(2k-1)}(b) - f^{(2k-1)}(a)) \quad (72)$$

Being $\{B_i\}$ the Bernoulli coefficients and f^m the m -th derivative of f . From now on we will apply it up to the first corrective order, $k = 1$.

We start again from the generalization presented in the previous section. We have after the

FGQA the expression

$$g^{\xi_n > 0}(h) = -\frac{k_B T}{8\pi h^2} \sum_{n=1}^{\infty} R(n, x_1)(1 + r_n)e^{-r_n} \quad (73)$$

And now we evaluate the corrective term of the Eq. 72, considering that $R(n, x_1)$ is essentially constant with n compared to the exponential dependence. This is also true for the $\Delta g_{1234}(l, d)$ particularization, since even if the exponential in $R^e(n, x_1)$ contains a n^2 factor, the value of $\Delta\epsilon$ is extremelly close to zero for large n , and the value of $(d^2 - l^2)$ is quite small as well. These features make that exponential factor very close to one

$$\Delta g^{\xi_n > 0} = -\frac{k_B T}{8\pi h^2} \left[\frac{1}{2} R(1, x_1)(1 + r_T)e^{-r_T} + \frac{1}{12} R(1, x_1)r_T^2 e^{-r_T} \right] \quad (74)$$

Where $r_T = r_{n=1}$. This term is negligible for $h \ll 1$, so we can state simply

$$g^{\xi_n > 0}(h) = -\frac{k_B T}{8\pi h^2} \int_1^{\infty} R(n, x_1)(1 + r_n)e^{-r_n} dn \quad (75)$$

The following step is to change the variable to $\nu = (4\pi k_B T \epsilon_m^{1/2} n)/(c\hbar)$. Realize that ϵ_m is also a function of n , so we change the variable through

$$d\nu = \frac{4\pi k_B T}{c\hbar} \epsilon_m^{1/2} dn \left[1 + \frac{1}{2} \frac{d \ln \epsilon_m}{d \ln \xi_n} \right] \quad (76)$$

The term inside the brackets is defined to be j_m , and its value is approximately 1. Then once the variable is changed we achieve

$$g^{\xi_n > 0}(h) = -\frac{c\hbar}{32\pi^2 h^2} \int_{\nu_T}^{\infty} \tilde{R}(\nu, x_1)(1 + h\nu)e^{-h\nu} d\nu \quad (77)$$

Where $\tilde{R}(\nu, x_1) = \epsilon_m^{-1/2} j_m^{-1} R(\nu, x_1)$.

6. One point gaussian quadrature applied to the SGQA

Beginning at the Eq. 77, we multiply by $e^{\nu/\nu_\infty} e^{-\nu/\nu_\infty}$ and perform the one point gaussian quadrature approximation with $f(\nu) = \tilde{R}(\nu, x_1)e^{\nu/\nu_\infty}$, and $w(\nu) = e^{-\nu/\nu_\infty}(1 + h\nu)e^{-h\nu}$. We solve then I_0 and I_1 by parts

$$I_0 = \int_{\nu_T}^{\infty} e^{-\nu/\nu_\infty} (1 + h\nu)e^{-h\nu} d\nu \quad (78)$$

$$I_0 = \nu_\infty \frac{(\nu_T h + 1)(\nu_\infty h + 1) + \nu_\infty h}{(\nu_\infty h + 1)^2} e^{-\nu_T h - \frac{\nu_T}{\nu_\infty}} \quad (79)$$

$$I_1 = \int_{\nu_T}^{\infty} \nu e^{-\nu/\nu_\infty} (1 + h\nu)e^{-h\nu} d\nu \quad (80)$$

$$I_1 = \nu_\infty \frac{(\nu_T h + 1)(\nu_\infty h + 1)^2 \nu_T + (2\nu_T h + 1)(\nu_\infty h + 1)\nu_\infty + 2\nu_\infty^2 h}{(\nu_\infty h + 1)^3} e^{-\nu_T h - \frac{\nu_T}{\nu_\infty}} \quad (81)$$

7. Parameterization of the damped oscillator model for AgI

The damped oscillator model employed for the AgI describes the dielectric function at imaginary frequencies as

$$\epsilon(i\xi) = 1 + \frac{\epsilon(0) - n_{UV}^2}{1 + (\xi/\omega_{IR})^2} + \frac{n_{UV}^2 - 1}{1 + (\xi/\omega_{UV})^2} \quad (82)$$

Notice here that it is constructed precisely to fulfill the properties associated to any valid dielectric function: positive and decreasing function, at infinite frequencies it reaches the response of the vacuum ($\epsilon(i\xi \rightarrow \infty) = 1$) and at zero frequencies it reaches the value of the static contribution ($\epsilon(i\xi \rightarrow 0) = \epsilon(0)$). Considering only the UV absorption, we can get the parameters ω_{UV} and $C_{UV} = n_{UV}^2 - 1$ from the Cauchy's representation

$$n^2 - 1 = (n^2 - 1) \frac{\omega^2}{\omega_{UV}^2} + C_{UV} \quad (83)$$

Using fot that a linear fit with experimental data of the evolution of the refractive index at those frequencies. The other magnitudes to complete the parameterization of the Eq. 82 were directly available in the bibliography.