Van der Waals interaction mediated by an optically uniaxial layer

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We study the van der Waals interaction between macroscopic bodies separated by a thin anisotropic film with a uniaxial permittivity tensor. We describe the effect of anisotropy of the media on the magnitude and sign of the interaction. The resulting differences in the van der Waals interaction are especially important for the stability of strongly confined liquid crystals, and nanostructures characterized by highly uniaxial macroscopic molecular arrangement, such as in self-assemblies of long organic molecules forming films, membranes, colloids, etc. We introduce an improved expression for the Hamaker constant which takes into account the uniaxial symmetry of a medium. In special cases neglecting the optical anisotropy even leads to an incorrect sign of the interaction.

I. INTRODUCTION

In the last decades van der Waals interaction was assumed to be a solved problem. However, new technological applications demand smaller and smaller systems whose stability is strongly influenced even by weak interactions such as the van der Waals interaction which, thus, should be determined as accurately as possible [1,2]. Especially intriguing are electronic devices incorporating polymers, liquid-crystalline materials, and other materials which are characterized by highly anisotropic macroscopic physical properties [3–6].

Several approaches have been employed to calculate the van der Waals interaction between macroscopic bodies. The simplest way, known as the Hamaker approach [7], is to sum all pairwise interactions between constituent molecules. In condensed media these are not independent but rather are strongly influenced by the surrounding medium; therefore, taking many-body interactions into account becomes essential. On a mesoscopic scale a many-body system can be regarded as a continuum, and can be described by macroscopic quantities such as permittivity, which take into account the screening of the surrounding molecules. The continuum approach is known as the Lifshitz approach [8]. In the nonretarded limit a dependence on the separation between two bodies can be extracted from the material properties, and the van der Waals interaction can be written in a form of an explicit separation dependence and the ''Hamaker'' constant.

Although many decades ago Kihara and Honda [9] introduced the van der Waals interaction energy for a three-slab system of uniaxial media, generally, the van der Waals force for anisotropic media such as liquid crystals is still calculated by use of isotropic yet average macroscopic physical quantities. To our knowledge the anisotropy of interacting media has been avoided in experimental studies considering anisotropic media; however, there are a few other theoretical studies [10,11]. Here the reason for neglecting the anisotropy of the permittivity tensor cannot be the insignificance of the anisotropy of relevant quantities, but rather the fact that there are no known simplified expressions to calculate the van der Waals force; however, for isotropic media there are well known Hamaker constants calculated from the Lifshitz theory (see, e.g., Ref. [12]). On the other hand, a general calculation of the van der Waals force, in the case of an anisotropic permittivity tensor, is even more complex than it is in the case of isotropic interacting media.

In this paper, we emphasize the influence of the anisotropy of the permittivity tensor of a medium on the van der Waals force through the simplest example of anisotropy—the uniaxial symmetry—and introduce the Hamaker constant for the same symmetry of the permittivity tensor. There are two reasons for choosing the uniaxial symmetry. First, as already noted above, there are many important physical and biological systems consisting of layers characterized by highly uniaxial molecular arrangements. In these, the correct dependence of the van der Waals force on the anisotropic refractive indices and static dielectric constants is needed for adequate explanations of experiments. Second, the uniaxial symmetry is the highest symmetry yielding an analytical solution for the surface electromagnetic fluctuation modes which determine the van der Waals force. An analytical solution is required for derivation of the analytic Hamaker constant.

II. CALCULATION OF THE UNIAXIAL VAN DER WAALS FORCE

The calculation is performed for a simple planar parallel geometry: two macroscopic bodies separated by a layer of a uniaxial medium. Here it should be noted that due to the anisotropy of the medium, which changes the boundary conditions for the electromagnetic field surface modes, the results of the study in the planar parallel system cannot be applied to curved geometries simply by using the standard Derjaguin procedure [13]. Using the same arguments as when choosing the uniaxial symmetry of the permittivity tensor, the optical axis of the interposed uniaxial medium is assumed to be perpendicular to the gap between the macroscopic bodies. For optical axes laying either in the plane of the gap or even in an arbitrary direction, the Hamaker constant can be calculated only numerically. Since the aim of this paper is to introduce simple analytical expressions, calculations for more general cases are omitted here.

In the systems we are referring to, the uniaxial layer is surrounded by isotropic media, either glassy materials, liq-

uid, or air. Often, especially when talking about liquid crystals, the uniaxial order of the layer in question is obtained by inducing the order with some other uniaxially ordered material. In such a case, the system consists of two or three uniaxial media with parallel optical axes. In the following, the calculation will be performed for the general case of three uniaxial media with parallel optical axes. The transformation to the case of isotropic macroscopic bodies will be evident.

In a coordinate system with the z axis normal to the gap between two macroscopic bodies and with axes x and y in the plane of one of the interfaces, the permittivity tensor of each medium reads $\underline{\epsilon}_i^{xx}(\omega) = \underline{\epsilon}_i^{yy}(\omega) = \epsilon_{i_\perp}(\omega)$, $\underline{\epsilon}_i^{zz}(\omega) = \epsilon_{i_\parallel}(\omega)$, and $\underline{\epsilon}_i^{\mu\nu\neq\mu}(\omega) = 0$; here $i = 1, 2$, or 3 represent different media. After performing standard calculations as in Ref. [8] or Refs. [9,14], i.e., considering Maxwell's equations for the electromagnetic field in the dielectric medium and the linear response of the media, one obtains the expression for the force per unit area between two semi-infinite uniaxial bodies 1 and 3 mediated by uniaxial medium 2:

$$\Pi(d,T) = \frac{k_B T}{16\pi d^3} \frac{\epsilon_{2_\parallel}(0)}{\epsilon_{2_\perp}(0)} \int_0^\infty dx\, x^2 \frac{\Delta_{12}\Delta_{23}\exp(-x)}{1+\Delta_{12}\Delta_{23}\exp(-x)}$$

$$+ \frac{k_B T}{\pi d^3} \sum_{n=1}^\infty \left(\sqrt{\epsilon_{2_\perp}}\, d\, \frac{\xi_n}{c}\right)^3$$

$$\times \int_1^\infty dp\, p^2 \left(\frac{\Delta_{12}^R \Delta_{23}^R \exp(-2p\sqrt{\epsilon_{2_\perp}}d\xi_n/c)}{1+\Delta_{12}^R \Delta_{23}^R \exp(-2p\sqrt{\epsilon_{2_\perp}}d\xi_n/c)} \right.$$

$$+ \left. \frac{\epsilon_{2_\parallel}}{\epsilon_{2_\perp}} \frac{\bar{\Delta}_{12}^R \bar{\Delta}_{23}^R \exp(-2p\sqrt{\epsilon_{2_\perp}}d\xi_n/c)}{1+\bar{\Delta}_{12}^R \bar{\Delta}_{23}^R \exp(-2p\sqrt{\epsilon_{2_\perp}}d\xi_n/c)} \right). \quad (1)$$

Here the force is a derivative of the change of the free energy of the zero-point fluctuations of the electromagnetic field due to the presence of the bodies with respect to the separation between them. The first term corresponds to the static response of the medium, and the second term to the dynamic response of the medium, whereas $\xi_n = 2\pi n k_B T/\hbar$,

$$\Delta_{ij} = \frac{\bar{\epsilon}_i(0) - \bar{\epsilon}_j(0)}{\bar{\epsilon}_i(0) + \bar{\epsilon}_j(0)}, \quad \bar{\epsilon}_i = \sqrt{\epsilon_{i_\parallel}\epsilon_{i_\perp}},$$

$$\Delta_{ij}^R = \frac{s_i - s_j}{s_i + s_j}, \quad s_i = \sqrt{p^2 - 1 + \epsilon_{i_\perp}/\epsilon_{2_\perp}}, \quad (2)$$

$$\bar{\Delta}_{ij}^R = \frac{\bar{\epsilon}_i \bar{s}_j - \bar{\epsilon}_j \bar{s}_i}{\bar{\epsilon}_i \bar{s}_j + \bar{\epsilon}_j \bar{s}_i}, \quad \bar{s}_i = \sqrt{p^2 - 1 + \epsilon_{i_\parallel}/\epsilon_{2_\parallel}},$$

and $\epsilon_i = \epsilon_i(i\xi_n)$, unless stated otherwise. The influence of the anisotropy of the permittivity tensor on the van der Waals force enters into the problem through a change of the penetration depths of the surface fluctuation modes and via a change of the boundary conditions for the electromagnetic

field at the interface between two different media. For the uniaxial permittivity the anisotropy of interacting media 1 and 3 changes the interaction via the renormalized effective permittivity $\epsilon_i \rightarrow \sqrt{\epsilon_{i_\parallel}\epsilon_{i_\perp}}$. On the other hand, the anisotropy of medium 2, which mediates the interaction between the other two media, not only renormalizes the effective permittivity but also explicitly affects the magnitude of the interaction.

III. UNIAXIAL HAMAKER CONSTANT

In order to evaluate the integral in Eq. (1), the frequency dependence of the permittivity has to be known. The permittivity varies with the frequency in much the same way as does the atomic polarizability of an atom, and can be usually represented by a function of a form [14]

$$\epsilon(\omega) = 1 + \frac{\epsilon - n^2}{1 - i\omega/\omega_r} + \frac{n^2 - 1}{1 - \omega^2/\omega_e^2}, \quad (3)$$

where ϵ and n stand for each of the components of the corresponding tensors, $\epsilon = \epsilon(0)$ is the static dielectric constant, n is the refractive index of the medium in the visible, ω_r is the molecular rotational frequency, and ω_e is the plasma frequency. Usually, $\omega_r < 10^{13}$ s$^{-1} \ll \omega_e \sim 2\pi \times 3 \times 10^{15}$ s^{-1}. Since $\xi_1 = 2.5 \times 10^{14}$ s$^{-1} \gg \omega_r$, the dispersion relation is determined solely by the electronic absorption, i.e., $\epsilon(i\xi_n) \approx 1 + (n^2 - 1)/(1 + \xi_n^2/\omega_e^2)$. Knowing all this the force can be calculated numerically. However, our aim is to introduce an analytical expression for the van der Waals force, although it will be more approximate. In the nonretarded limit, which is valid when the bodies are in close proximity to each other, the expression in Eq. (1) reduces to $\Pi = -A/6\pi d^3$, where A is the Hamaker constant calculated from the Lifshitz theory:

$$A = -\frac{3k_B T}{4} \sum_{n=0}^{\infty'} \left(\frac{\epsilon_{2_\parallel}(i\xi_n)}{\epsilon_{2_\perp}(i\xi_n)} \right)$$

$$\times \int_0^\infty dx\, x^2 \frac{\Delta_{12}(i\xi_n)\Delta_{23}(i\xi_n)e^{-x}}{1+\Delta_{12}(i\xi_n)\Delta_{23}(i\xi_n)e^{-x}}. \quad (4)$$

Here the prime over the sum denotes that the term with $n = 0$ should be multiplied by 1/2. After performing the elementary integral in Eq. (4), neglecting the terms which correspond to "many-body" interactions (here, by analogy with the microscopic description the contributions from different orders in $\Delta_{12}\Delta_{23}$ are termed "pairwise" interaction if only the first order is taken into account, and "many-body" interaction if the complete series of orders is considered), replacing the sum over n by an integral with respect to the frequency ξ, and performing a few other simplifications, which allow us to calculate the latter integral analytically, one ends up with the final expression for the Hamaker constant for uniaxial dielectric media:

$$A = A^{\nu=0} + A^{\nu>0} = \frac{3}{4}k_B T \frac{\epsilon_{2_\parallel}}{\epsilon_{2_\perp}} \frac{\bar{\epsilon}_1 - \bar{\epsilon}_2}{\bar{\epsilon}_1 + \bar{\epsilon}_2} \frac{\bar{\epsilon}_3 - \bar{\epsilon}_2}{\bar{\epsilon}_3 + \bar{\epsilon}_2}$$

$$+ \frac{3\hbar\omega_e}{8\sqrt{2}}(\bar{n}_1^2 - \bar{n}_2^2)(\bar{n}_3^2 - \bar{n}_2^2)$$

$$\times \left[\frac{\sqrt{2}(n_{2_\parallel}^2 - n_{2_\perp}^2)}{n_{2_\perp}(2n_{2_\perp}^2 - \bar{n}_1^2 - \bar{n}_2^2)(2n_{2_\perp}^2 - \bar{n}_3^2 - \bar{n}_2^2)} \right.$$

$$- \frac{2n_{2_\parallel}^2 - \bar{n}_1^2 - \bar{n}_2^2}{\sqrt{\bar{n}_1^2 + \bar{n}_2^2}(2n_{2_\perp}^2 - \bar{n}_1^2 - \bar{n}_2^2)(\bar{n}_1^2 - \bar{n}_3^2)}$$

$$\left. + \frac{2n_{2_\parallel}^2 - \bar{n}_3^2 - \bar{n}_2^2}{\sqrt{\bar{n}_3^2 + \bar{n}_2^2}(2n_{2_\perp}^2 - \bar{n}_3^2 - \bar{n}_2^2)(\bar{n}_1^2 - \bar{n}_3^2)} \right], \quad (5)$$

where $\bar{a}_i = \sqrt{a_{i_\parallel} a_{i_\perp}}$, and a stands for either the static dielectric constant ϵ or the refractive index in visible n. If the interacting macroscopic bodies are isotropic, the effective parameters $\bar{\epsilon}$ and $\bar{n}$ are replaced by isotropic parameters ϵ and n, respectively. If all three media are isotropic, the expression reduces to the well known formula (see, e.g., Ref. [12])

$$A = \frac{3}{4}k_B T \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \frac{\epsilon_3 - \epsilon_2}{\epsilon_3 + \epsilon_2}$$

$$+ \frac{3\hbar\omega_e}{8\sqrt{2}} \frac{(n_1^2 - n_2^2)(n_3^2 - n_2^2)}{\sqrt{n_1^2 + n_2^2}\sqrt{n_3^2 + n_2^2}(\sqrt{n_1^2 + n_2^2} + \sqrt{n_3^2 + n_2^2})}.$$

$$(6)$$

In the following, the Hamaker constant introduced for uniaxial media will first be compared to the isotropic Hamaker constant and, second, its validity with respect to the full Lifshitz theory will be discussed.

A. Uniaxial vs isotropic Hamaker constant

In the derived expressions, the difference between isotropic and uniaxial media is explicitly manifested: The relevant parameters, which determine the character of the interaction in the case of isotropic interacting media, are $\epsilon = \epsilon^{iso}$ and $n = n^{iso}$. In the case of uniaxial media the relevant parameters are not traces of the corresponding tensors, $\epsilon^{iso} = (\epsilon_\parallel + 2\epsilon_\perp)/3$ and $(n^{iso})^2 = (n_\parallel^2 + 2n_\perp^2)/3$, but rather products of their eigenvalues: $\bar{\epsilon} = \sqrt{\epsilon_\parallel \epsilon_\perp}$ and $\bar{n} = \sqrt{n_\parallel n_\perp}$. The sign of the static part of the Hamaker constant depends on the relative sequence of the introduced renormalized static dielectric constants: for $\bar{\epsilon}_2 < \bar{\epsilon}_1, \bar{\epsilon}_3$ or $\bar{\epsilon}_2 > \bar{\epsilon}_1, \bar{\epsilon}_3$ the static Hamaker constant is positive and the static part of the van der Waals interaction is attractive, whereas for $\bar{\epsilon}_1 < \bar{\epsilon}_2 < \bar{\epsilon}_3$ or $\bar{\epsilon}_1 > \bar{\epsilon}_2 > \bar{\epsilon}_3$ the static Hamaker constant is negative and the corre-

sponding interaction is repulsive. Similar conditions can be determined for the dynamic part of the Hamaker constant. It can be shown that the part in the square brackets in Eq. (5) is positive definite; thus the sign of the dynamic part of the Hamaker constant depends solely on the sign of the product $(\bar{n}_1^2 - \bar{n}_2^2)(\bar{n}_3^2 - \bar{n}_2^2)$. For $\bar{n}_2 < \bar{n}_1, \bar{n}_3$ or $\bar{n}_2 > \bar{n}_1, \bar{n}_3$ the dynamic Hamaker constant is positive and the dynamic part of the van der Waals interaction is attractive, whereas for $\bar{n}_1 < \bar{n}_2 < \bar{n}_3$ or $\bar{n}_1 > \bar{n}_2 > \bar{n}_3$ the dynamic Hamaker constant is negative and the corresponding interaction is repulsive. The sign of the isotropic Hamaker constant has the same sequence dependence as the uniaxial Hamaker constant, but with isotropic parameters ϵ^{iso} and n^{iso} instead of effective $\bar{\epsilon}$ and $\bar{n}$, respectively.

As already noted, up to now in experimental studies concerning uniaxial layers the van der Waals interaction was calculated by use of the isotropic Hamaker constant and isotropic parameters. There are two sources of mistakes when doing this. First, even if the effective parameters are very close to the isotropic parameters, the magnitude of obtained Hamaker constant differs from the uniaxial one because the anisotropies $\epsilon_{2_a} = \epsilon_{2_\parallel} - \epsilon_{2_\perp}$ and $\Delta n_2 = n_{2_\parallel} - n_{2_\perp}$ are neglected. (The static part is always smaller, whereas the dynamic part can be either smaller or larger.) In the static part, the neglected dependence is easily recognized in the ratio $\epsilon_{2_\parallel}/\epsilon_{2_\perp}$, whereas in the difference of the dynamic parts the dependence on the anisotropy is not that clear. Second, the difference between the isotropic and uniaxial Hamaker constants can be even more profound if the sequences of isotropic and effective parameters are different. In this case, the isotropic expression yields the wrong sign of the interaction. A change of sequences is very easily obtained for static dielectric constants, whereas the optical anisotropies are usually small. Since the static Hamaker constant is about an order of magnitude smaller than its dynamic part, the effect is not very common in experimental setups. We believe that one of the reasons why the problem of a possible wrong sign of the Hamaker constant, in systems consisting of uniaxial media, has not been recognized before is the narrowness of possible combination of materials that satisfy the described conditions (see Fig. 1). However, it can be expected that the effect has already been observed but not recognized and/or understood. The explained change of the attractive or repulsive character of the van der Waals interaction to the repulsive or attractive character due to the increased optical anisotropy can also be one of the reasons for the change in the stability of thin layers when crossing the (dis)ordering transition. As an example, we have calculated the Hamaker constant for a system which is often a part of the experimental setup: a thin liquid-crystalline film deposited on a solid substrate and in contact with air on the other side. For a liquid crystal, e.g., for 5CB ($\epsilon_\parallel = 18.5$, $\epsilon_\perp = 7$, $n_\parallel = 1.702$, and $n_\perp = 1.539$) on silica ($\epsilon = 14$ and $n = 1.5$) the van der Waals interaction is attractive in both uniaxial and isotropic phases; for the same liquid crystal on mica ($\epsilon = 11$ and $n = 1.6$) the interaction is repulsive in the isotropic and attractive in the uniaxial phase.
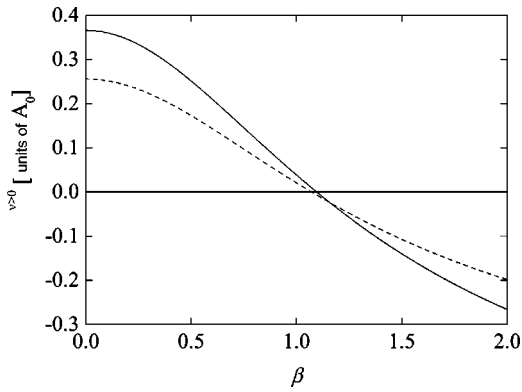
FIG. 1. Dynamic part of the Hamaker constant as a function of $\beta = n_1/n_{2_\perp}$. The solid line corresponds to the uniaxial Hamaker constant, and the dashed line to the isotropic Hamaker constant in units of $A_0 = 3\hbar\omega_e n_{2_\perp}/8\sqrt{2}$. Here $n_{2_\parallel}/n_{2_\perp} = 1.2$ and $n_3/n_{2_\perp} = 0.67$.

B. Hamaker approximation vs Lifshitz theory

After a comparison between the isotropic and uniaxial Hamaker constants the validity of the approximations that lead us from the full Lifshitz theory to the Hamaker constant should be discussed. By comparing the Hamaker constants, in which we take into account either ''many-body'' interactions [Eq. (4)] or just ''pairwise'' interactions [Eq. (5)], it can be seen that in the nonretarded limit neglecting the higher orders does not considerably alter the magnitude of the interaction. Nevertheless, one should bear in mind that a screening of the surrounding molecules decreases the interaction, though, for realistic parameters only by $\sim 5\%$ at the most. As already known, the main defect of the introduced ''Hamaker'' procedure is not in neglecting ''many-body'' interactions but in neglecting the retardation. The latter becomes important when the time it takes for the electromagnetic field of one atom to reach the second one and to return becomes comparable to the period of the fluctuating dipole. Usually, this happens when the interacting atoms are about 10 nm apart. In Fig. 2 we present the van der Waals force for the two systems considered above. The van der Waals force as calculated from the full Lifshitz theory for uniaxial media is compared to the forces in the nonretarded limit, either taking into account or neglecting the anisotropy. Although, strictly speaking, the approximation of no retardation is valid only when the interacting bodies are in close proximity to each other, one should keep in mind that the retardation does not change the character of the interaction but only decreases its magnitude when the separation between the bodies is increased. If there is another, stronger interaction, which acts in the system, and the van der Waals interaction contributes only a correction to the primary interaction or if the van der Waals interaction is itself the primary interaction, one can be satisfied with an approximate analytical expression which is far easier to calculate and gives better insight into the effect
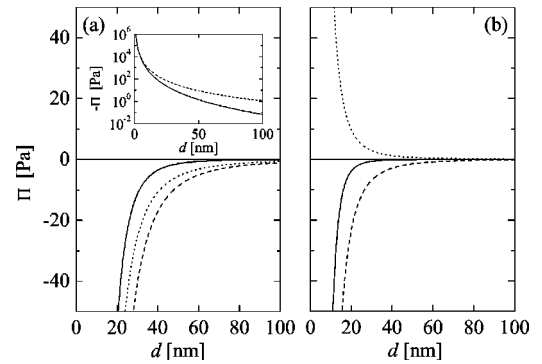

FIG. 2. Van der Waals force per unit area in the layer of nematic liquid crystal in contact with a solid substrate—(a) silica ($\epsilon = 14$, $n = 1.5$) and (b) mica ($\epsilon = 11$, $n = 1.6$)—and air. Solid curves correspond to full Lifshitz theory for uniaxial media, dashed curves are the van der Waals force per unit area calculated with uniaxial Hamaker constant, and dotted lines are calculated with the Hamaker constant for isotropic media. Inset: logarithmic plot of uniaxial pressures.

of dielectric and optical properties of constituent media on the van der Waals interaction. Here is the opportunity for the analytical expression we have derived. Especially lately, in studies which aim to explain experiments on the spinodal dewetting of thin soft organic materials usually characterized by uniaxial dielectric permittivity and refractive index, a correct determination of at least the character of van der Waals interaction is very important [15,16].

IV. CONCLUSION

In conclusion, we have derived an improved analytical expression for the van der Waals interaction between macroscopic bodies, characterized by a uniaxial permittivity tensor. We have shown that neglecting the anisotropy of static dielectric constants and refractive indices can yield the wrong character of the interaction, leading to an incorrect interpretation or prediction of the stability of thin uniaxial depositions. Taking into account the anisotropy of dielectric and optical properties of the media is especially important when the anisotropy is significant and if the optical properties of constituting media are alike. The uniaxial van der Waals interaction also yields a correction to the structural interaction in heterophase nematic and smectic systems [17,18] resulting in a correction to the equilibrium thickness of partially ordered surface nematic and smectic layers close to ordering substrates.

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