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Historical perspective

A review on data and predictions of water dielectric spectra for calculations of van der Waals surface forces

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ABSTRACT

Van der Waals forces are one of the important components of intermolecular, colloidal and surface forces governing many phenomena and processes. The latest examples include the colloidal interactions between hydrophobic colloids and interfaces in ambient (non-degassed) water in which dissolved gases and nanobubbles are shown to affect the van der Waals attractions significantly. The advanced computation of van der Waals forces in aqueous systems by the Lifshitz theory requires reliable data for water dielectric spectra. In this paper we review the available predictions of water dielectric spectra for calculating colloidal and surface van der Waals forces. Specifically, the available experimental data for the real and imaginary parts of the complex dielectric function of liquid water in the microwave, IR and UV regions and various corresponding predictions of the water spectra are critically reviewed. The data in the UV region are critical, but the available predictions are still based on the outdated data obtained in 1974 (for frequency only up to 25.5 eV). We also reviewed and analysed the experimental data obtained for the UV region in 2000 (for frequency up to 50 eV) and 2015 (for frequency up to 100 eV). The 1974 and 2000 data require extrapolations to higher frequencies needed for calculating the van der Waals forces but remain inaccurate. Our analysis shows that the latest data of 2015 do not require the extrapolation and can be used to reliably calculate van der Waals forces. The most recent water dielectric spectra gives the (non-retarded) Hamaker constant, $A = 5.20 \times 10^{-20} J$, for foam films of liquid water. This review provides the most updated and reliable water dielectric spectra to compute van der Waals forces in aqueous systems.

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1. Introduction

The first evidence of van der Waals forces dates back to 1873 when Johannes Diderik van der Waals [1] modified the Boyle's law [2] to describe the states of gases and liquids. In 1894, Lebedev [3] realised the connection between absorption spectra and charged-fluctuation forces with the advances in electromagnetic theories [4,5]. By the end of 1930s, three dipole interactions (Keesom [6], Debye [7] and London [8] interactions) that construct the van der Waals forces were found. Hamaker advanced the van der Waals interactions from molecules to large bodies in 1937 [9]. In 1940s, the celebrated Derjaguin-Landau-Verwey-Overbeek (DLVO) theory where the electrostatic repulsions compete with van der Waals attractions was developed [10,11]. In 1948, Casimir developed the van der Waals interactions between two parallel metal plates [12], which is now known as the theory for the retarded van der Waals interactions. Lifshitz moved the final step to replace the ideally conducting walls and intervening vacuum of previous theories with real materials [13]. Now scientists can calculate the van der Waals forces for a huge variety of materials in different shapes [14, 15] using the Lifshitz theory, which is known as the macroscopic theory for van der Waals interactions and covers both non-retarded (the Hamaker theory) and retarded (the Casimir theory) van der Waals interactions.

Surface force measurements have confirmed the DLVO theory for many cases [16,17]. However, discrepancies have also been found between measured forces and DLVO forces for many complicated systems, such as bubble-particle interactions in froth flotation. Therefore, non-DLVO forces are sometimes introduced to the extended DLVO theories [18,19]. In this case, accurate predictions of DLVO forces become crucial for the validity of the extended DLVO theories. Perhaps, the so-called hydrophobic forces between hydrophobic colloids and interfaces in ambient (non-degassed) water can be accounted for by van der Waals forces involving dissolved gases and nanobubbles [20,21].

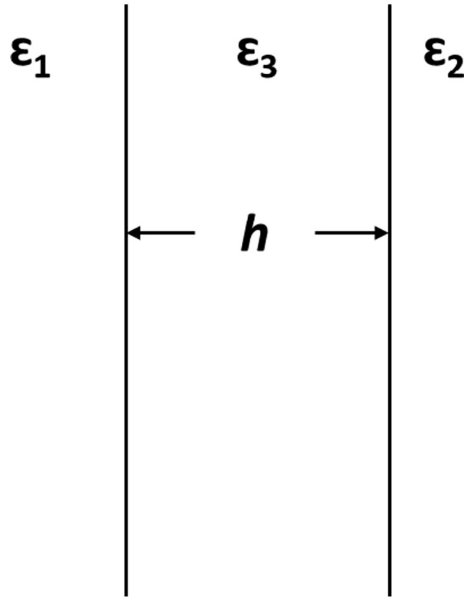

Fig. 1. Two half-spaces 1, 2 with a separation h immersed in medium 3. $\varepsilon_a(a = 1$ to 3) denotes the dielectric function of the materials.

Fig. 1 shows two half-spaces 1, 2 with a separation h immersed in medium 3. We express the van der Waals interaction between the two half-spaces in terms of an effective Hamaker coefficient A_{132}, which is a function of separation h (and, therefore, it is often called the Lifshitz-Hamaker function). In the Lifshitz theory, the magnitude of van der Waals forces depends on the differences of the dielectric responses between the interacting materials and the intervening medium. The dielectric responses are expressed as dielectric functions, $\varepsilon_a(a = 1$ to 3). We take two infinite half-spaces across a water phase (foam film) for example to demonstrate the computation of van der Waals forces using water dielectric spectra. The interaction energy E_{132} and Hamaker coefficient A_{132} between two infinite half spaces, 1 and 2 immersed in a medium 3 as a function of the separation h are as follows [13,22]:

$$E_{132}(h) = -\frac{A_{132}(h)}{12\pi h^2} \tag{1}$$

$$A_{132}(h) = -\frac{3}{2}k_BT\sum_{n=0}^{\infty}{}' \int_{x_n}^{\infty} x\ \ln[(1-y_{13}y_{23}e^{-x})(1-z_{13}z_{23}e^{-x})]dx \tag{2}$$

$$y_{a3} = \frac{x\varepsilon_a - s_a\varepsilon_3}{x\varepsilon_a + s_a\varepsilon_3} \tag{3}$$

$$z_{a3} = \frac{x - s_a}{x + s_a} \tag{4}$$

$$x_n = \frac{2h\xi_n\sqrt{\varepsilon_3}}{c} \tag{5}$$

$$s_a{}^2 = x^2 + x_n{}^2\left(\frac{\varepsilon_a}{\varepsilon_3} - 1\right) \tag{6}$$

$$\xi_n = \frac{2n\pi k_BT}{\hbar} \tag{7}$$

$$\varepsilon_a = \varepsilon_a(i\xi_n) \tag{8}$$

where x is the integration dummy (for frequency), $i = \sqrt{-1}$, c the speed of light, k_B the Boltzman constant, T the absolute temperature, $\hbar$ the Planck constant (divided by 2π) and ξ_n the Matsubara (sampling, discrete equally spaced) frequency of the dielectric function. The prime against the summation in n indicates that the zero-frequency ($n = 0$) term is divided by 2.

The Lifshitz theory as described by Eqs. (1)–(8) requires the full water dielectric spectra (with frequency up to infinity) for computing van der Waals forces in aqueous systems. Practically, the summation of Eq. (2) for computing the Hamaker function requires many thousands terms to provide accurate results (with relative errors less than

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