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Dielectric response variation and the strength of van der Waals interactions

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ABSTRACT

Small changes in the dielectric response of a material result in substantial variations in the Hamaker coefficient of the van der Waals interactions, as demonstrated in a simplified approximate model as well as a realistic example of amorphous silica with and without an exciton peak. Variation of the dielectric response spectra at one particular frequency influences all terms in the Matsubara summation, making the total change in the Hamaker coefficient depend on the spectral changes not only at that frequency but also at the rest of the spectrum, properly weighted. The Matsubara terms most affected by the addition of a single peak are not those close to the position of the added peak, but are distributed doubly non-locally over the entire range of frequencies. A possibility of eliminating van der Waals interactions or at least drastically reducing them by spectral variation in a narrow regime of frequencies thus seems very remote.

1. Introduction

There are important issues in the general theory of long-range (macro) molecular van der Waals (vdW) forces and its applications that are both widely misunderstood and deeply entrenched in the colloid and nano-science community. While it is clear that in the Lifshitz theory of vdW forces [1,2] the interaction free energy is a *functional* of the dielectric response function at imaginary Matsubara frequencies (itself a functional of the imaginary part of the total dielectric response function via the Kramers–Kronig relations), it is seldom appreciated exactly how this non-locality in the dielectric response acts on the properties of vdW interaction [7]. What is also often misunderstood are the actual quantitative consequences of variations in the dielectric response of the interacting media on the magnitude of vdW interactions.

There are two important contexts in which the appreciation of such issues is a *sine qua non* for the understanding of the overall features of the interaction between colloidal or nano-particles. In the first case, *refractive index matching*, changes in the dielectric response functions of the medium between the interacting dielectrics are used to modify the interparticle interactions through their vdW component [4–6,8–12]. Here one often assumes that the dielectric response is dominated by a single absorption peak in the VUV–UV–vis region of the optical spectrum, corresponding to electronic properties of the material. The strength of the vdW interaction, as codified by the Hamaker coefficient [1], then appears as a simple function of the difference between the squares of the refractive index of the medium and the interacting bodies [3]. This estimate of the Hamaker coefficient is usually referred to as the Tabor–Winterton approximation (TWA) [4]. If the zero-frequency dielectric response is small, matching the refractive index at this single absorption peak should effectively quench the long range vdW component of molecular interactions. While a tempting simplification, this can lead to gross underestimation of the overall strength of (macro) molecular interactions, possibly precluding correct interpretation of experimental data on, e.g., wetting.

Another important context for the intricacies of non-locality in the dielectric response function for the variation of the vdW interaction, and the one into which we shall delve more deeply, is the effect of *excitonic peaks* in the ultraviolet and visible (UV/Vis) and higher energy optical region of materials, such as alumina (Al_2O_3) [13], silica (SiO_2) [24], aluminum phosphate ($AlPO_4$) [14], rare gas solids such as Ne [15] and Xe [16], molecular crystals [17,18] and single-walled carbon nanotubes (SWCNTs) [19,20]. Excitons

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introduce additional peaks in the energy range below the fundamental absorption edge of the material's bandgap or slightly shift the position of some other peaks in SWCNTs. Their importance for the strength of vdW interaction in the context of SWCNTs remains less clear. Recently Hobbie and co-workers [21] used a simple empirical approach to assess the effect of the excitonic peaks on the strength of vdW interactions between SWCNTs. They concluded that in the case of semiconducting nanotubes, neglecting the three excitonic resonances in the optical regime reduces the Hamaker coefficient by roughly 5%. For metallic SWCNTs, neglect of either of these terms reduces the Hamaker coefficient by roughly 3%. In this view, excitonic effects should have a qualitatively small but possibly measurable effect, with its exact magnitude pending on more detailed calculations. It thus appears that the importance of a certain spectroscopic feature in, e.g., the optical regime does not necessarily translate directly into an equally important feature of vdW interactions. What *exactly* is the connection remains unclear.

The same problem of excitonic peaks and their influence on the overall strength of vdW interaction appears also between condensed media. In this case the theoretical method of choice to evaluate the electronic properties is the orthogonalized linear combination of atomic orbital (OLCAO) variant of density functional theory (DFT), which uses local atomic orbitals for the basis expansion rather than the plane waves [22]. This methodology formulated on a one-electron level of course precludes the inclusion of many-body excitonic corrections, as they are not compatible with the OLCAO-DFT context and may lead to concerns about the underestimation of the band gap as well as a possible rescaling of the complete spectrum. This necessarily implies modifications in the overall magnitude of the vdW interactions between the condensed media. As an example of OLCAO-DFT type of calculation, one can consider the frequency-dependent dielectric function of amorphous silica [23] that can be compared with direct experiments [24]. This comparison shows that the one-electron level OLCAO-DFT calculations cannot reproduce the measured excitonic peak. Again the question remains of how relevant this omission is for the quantitative evaluation of the corresponding strength of the vdW interaction [7].

In order to address all these issues, we will investigate in detail the effect of variation in the optical properties of the dielectric response function over an interval of frequencies on the strength of the vdW interactions as quantified by the Hamaker coefficient. We will confine ourselves to the non-retarded regime as well as to planar interaction geometry, but the analysis can be straightforwardly repeated also for, e.g., small spherical particles or, in fact, for any geometry for which there are explicit Lifshitz results [1]. We will first analyse a simple model for the variation of the dielectric response function and then apply the general theory to an actual dielectric response spectrum with/without the excitonic peak and assess the variation wrought by changes in the dielectric spectrum on the corresponding Hamaker coefficient.

2. Interaction free energy variation: general

Assume that the spectral response of two interacting planar dielectric surfaces is changed from $\varepsilon(\omega) \to \varepsilon(\omega) + \delta\varepsilon(\omega)$. The Kramers–Kronig (KK) transform that enters the vdW interaction free energy is defined as [27]

$$\varepsilon(i\zeta) = 1 + \frac{2}{\pi}\int_0^\infty \frac{\omega\varepsilon''(\omega)}{\omega^2+\zeta^2}d\omega, \tag{1}$$

with $\varepsilon''(\omega)$ the imaginary part of $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$. Quite generally $\varepsilon(i\zeta)$ is a real, monotonically decreasing function of its argument ζ. It follows from the Lifshitz theory of vdW interactions [25] that the corresponding interaction free energy change is then defined as $\delta\mathcal{G} = \mathcal{G}[\varepsilon(i\zeta) + \delta\varepsilon(i\zeta)] - \mathcal{G}[\varepsilon(i\zeta)]$. For the planar case of vdW interaction between two semi-infinite layers, one obtains to the lowest (linear) order in the dielectric response change $\delta\varepsilon$ the simple result [25]

$$\begin{aligned}\delta\mathcal{G} &= -\frac{k_BT}{4\pi}\sum_{N=0}^{\infty\prime}\zeta_N^2\left(\mathrm{Tr}\int_{(V)}\mathcal{D}_{ik}(i\zeta_N,\mathbf{r},\mathbf{r})d^3\mathbf{r}\right)\delta\varepsilon(i\zeta_N)\\ &= -\frac{k_BT}{4\pi}S\sum_{N=0}^{\infty\prime}\zeta_N^2\left(\mathrm{Tr}\int_{(z)}\mathcal{D}_{ik}(i\zeta_N,z,z)dz\right)\delta\varepsilon(i\zeta_N),\end{aligned} \tag{2}$$

where the last identity in the above equation stems from the presumed planar geometry with surface area S of the interacting interfaces. $\mathcal{D}_{ik}(\omega,\mathbf{r},\mathbf{r}')$ is the retarded frequency domain dyadic Green's function of the electromagnetic field. The sum is over the Matsubara frequencies, $\zeta_N = 2\pi N k_B T/\hbar$, where N is an integer, and the $N = 0$ term is counted with a weight $1/2$. At room temperature the thermal Matsubara frequencies are a multiple of $2.4 \times 10^{14}\ \mathrm{s}^{-1}$ and/or 0.025 eV and thus cover the whole frequency regime rather unevenly. While only a single ζ_N, i.e. ζ_0, corresponds to the static response, several for the IR frequencies and a whole band of Matsubara frequencies fall within the optical and UV regimes, it is inadmissible to conclude from this that the optical and UV regimes therefore typically dominate the properties of the vdW interaction. This interaction is a functional of $\varepsilon(i\zeta_N)$ and not $\varepsilon(\zeta_N)$. Because of this non-locality, variation in the spectral properties of the interacting media at a certain frequency is not directly related to the corresponding frequency term variation in the Matsubara summation over N.

Limiting ourselves to the non-retarded case of planar parallel interfaces between two semi-infinite media separated by distance D with dielectric response function $\varepsilon(\omega)$ and an intervening medium of $\varepsilon_m(\omega)$, the vdW interaction free energy $\mathcal{G}(D)$ per unit surface area S in the non-retarded limit is given by

$$\frac{\mathcal{G}(D)}{S} = -\frac{\mathcal{A}}{(12\pi D^2)}$$

where $\mathcal{A}$, the *Hamaker coefficient*, is defined as

$$\mathcal{A} = -\frac{3}{2}k_BT\sum_{N=0}^{\infty\prime}Li_3(\overline{\Delta}_{12}^2(i\zeta_N)) = \sum_{N=0}^{\infty\prime}\mathcal{A}(i\zeta_N), \tag{3}$$

with the dielectric contrast given by

$$\overline{\Delta}_{12}(i\zeta_N) = \left(\frac{\varepsilon(i\zeta_N) - \varepsilon_m(i\zeta_N)}{\varepsilon(i\zeta_N) + \varepsilon_m(i\zeta_N)}\right). \tag{4}$$

The polylog function $\mathrm{Li}_\nu(z)$ is defined in a standard way [26] and the KK transforms $\varepsilon(i\zeta)$ as well as $\varepsilon_m(i\zeta)$ have been introduced in Eq. (1). The variation of this interaction free energy corresponding to a small variation in the dielectric response functions of the interacting bodies can then be obtained formally from the limit $c \to \infty$ in Eq. (2), as

$$\delta\left(\frac{\mathcal{G}(D)}{S}\right) = -\frac{k_BT}{8\pi D^2}\sum_{N=0}^{\infty\prime}\mathrm{Li}_2\left(\overline{\Delta}_{12}(i\zeta_N)^2\right)\frac{\left(1-\overline{\Delta}_{12}(i\zeta_N)^2\right)}{\overline{\Delta}_{12}(i\zeta_N)}\frac{\delta\varepsilon(i\zeta_N)}{\epsilon(i\zeta_N)} = -\frac{\delta\mathcal{A}}{12\pi D^2}, \tag{5}$$

where $\mathrm{Li}_2(x)$ is the dilogarithm function and the variation of the Hamaker coefficient is given by

$$\delta\mathcal{A} = \frac{3}{2}k_BT\sum_{N=0}^{\infty\prime}\delta\mathcal{A}(i\zeta_N). \tag{6}$$

Above $\delta\mathcal{A}(i\zeta_N)$ is the partial contribution to the full Hamaker coefficient at the Matsubara frequency ζ_N whose definition is obvious from comparison with Eq. (5).