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.

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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

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 $\varepsilon(\omega) \rightarrow \varepsilon(\omega) + \delta\varepsilon(\omega)$. 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]

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

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, $\zeta_N = 2\pi Nk_BT/\hbar$, 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

$$\mathcal{A} = -\frac{3}{2}k_BT\sum_{N=0}^{\infty'}\mathrm{Li}_3(\overline{\Delta}_{12}^2(i\zeta_N)) = \sum_{N=0}^{\infty'}\mathcal{A}(i\zeta_N), \tag{3}$$

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 $\mathrm{Li}_v(z)$ 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 $c \rightarrow \infty$ in Eq. (2), as

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

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

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

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).

We next investigate the dependence of the terms in the above Matsubara sum on the value of the frequency. While the relative change in the dielectric response function $\delta\varepsilon(i\zeta)/\varepsilon(i\zeta)$ is a monotonic function, the factor multiplying it in Eq. (5), $\mathrm{Li}_2\left(\overline{\Delta}_{12}(i\zeta)^2\right)\left(1-\overline{\Delta}_{12}(i\zeta)^2\right)/\overline{\Delta}_{12}(i\zeta)$, is not. As a consequence, the contribution of the various terms, $\delta\mathcal{A}(i\zeta_N)$, to the total Matsubara sum has a maximum whose position depends on the exact form of $\delta\varepsilon(i\zeta)$ and $\varepsilon(i\zeta)$. This can make the connection between the variation in the dielectric spectrum and the corresponding variation in the vdW interaction free energy quite complicated.

3. Interaction free energy variation: a simple model

In order to analyze $\delta\mathcal{A}(i\zeta)$, we need a form for the frequency dependence of the dielectric function. For this we introduce a simple model that will reveal the salient features of the more realistic problem addressed later.

We assume a dielectric response $\varepsilon(\omega)$ for the two semiinfinite dielectric regions, with its imaginary part equal to $\varepsilon''(\omega)$ that we then modify to $\varepsilon(\omega) + \delta\varepsilon(\omega)$ by addition of a single narrow absorption peak, centered at the frequency ω_0 with an area under the peak equal to A, approximated as $\delta\varepsilon''(\omega) = A\delta(\omega - \omega_0)$. Therefore

$$\omega_0 = \frac{\int_0^\infty \omega\,\delta\varepsilon''(\omega)d\omega}{\int_0^\infty \delta\varepsilon''(\omega)d\omega}. \tag{7}$$

This defines our simple model. Later we will upgrade it to a realistic calculation for amorphous silica with and without the excitonic peak.

From these model assumptions, we then obtain the relevant KK transforms as

$$\varepsilon(i\zeta) = 1 + \frac{2}{\pi}\int_0^\infty \frac{\omega\varepsilon''(\omega)}{\omega^2+\zeta^2}d\omega = 1 + \tilde{\varepsilon}(i\zeta) \tag{8}$$

and

$$\delta\varepsilon(i\zeta) = \frac{2}{\pi}\int_0^\infty \frac{\omega\delta\varepsilon''(\omega)}{\omega^2+\zeta^2}d\omega = \frac{2}{\pi}\frac{A/\omega_0}{1+(\zeta/\omega_0)^2}. \tag{9}$$

Obviously the transform $\delta\varepsilon(i\zeta)$ of the dielectric response function depends on ζ/ω_0 and A/ω_0 as scaling variables.

Assuming furthermore for convenience that the medium is a vacuum, $\varepsilon_m \equiv 1$, we then have

$$\overline{\Delta}_{12}(\tilde{\varepsilon}(i\zeta)) = \frac{\tilde{\varepsilon}(i\zeta)}{2+\tilde{\varepsilon}(i\zeta)}. \tag{10}$$

What we are looking for now is the change in vdW interaction free energy as the ω_0 peak is added, *viz.* as the dielectric response changes from $\varepsilon(i\zeta) = 1 + \tilde{\varepsilon}(i\zeta)$ to $\varepsilon(i\zeta) = 1 + \tilde{\varepsilon}(i\zeta) + \delta\varepsilon(i\zeta)$.

We proceed with some general observations. The expression for the KK transform Eq. (8) has the following two limits for $\zeta \to 0$ and $\zeta \to \infty$, respectively

$$\varepsilon(i\zeta) \simeq \begin{cases} 1 + \frac{2}{\pi}\int_0^\infty \omega^{-1}\varepsilon''(\omega)d\omega = 1 + \frac{2}{\pi}\mathcal{C} \\ 1 + \frac{2}{\pi}\zeta^{-2}\int_0^\infty \omega\varepsilon''(\omega)d\omega = 1 + \zeta^{-2}\frac{2}{\pi}\mathcal{C}' \end{cases}. \tag{11}$$

where we introduced

$$\mathcal{C} = \int_0^\infty \omega^{-1}\varepsilon''(\omega)d\omega = \frac{\pi}{2}(\varepsilon(0)-1)$$
$$\mathcal{C}' = \int_0^\infty \omega\varepsilon''(\omega)d\omega = \frac{\pi}{2}\omega_p^2 \tag{12}$$

These two quantities are obviously connected with the dielectric response sum rules [27]. In the first integral we recognize the static limit sum rule, with $\varepsilon(0)$ the static dielectric constant. For substances with the lowest absorption frequency in the optical (visible

and UV) region, the static dielectric constant is equal to the square of the optical refraction index. In the second integral we recognize the oscillator strength sum rule (for details see Ref. [27]), where ω_p is the plasma frequency depending on the effective number of electrons used in transitions at all energies.

The two limits in Eq. (11) then suggest a convenient approximation covering the whole range of frequencies that will allow us to analyze the corresponding vdW interaction free energy. It has the form

$$\tilde{\varepsilon}(i\zeta) \simeq \frac{(\varepsilon(0)-1)}{1+(\zeta/\omega_0)^2(\omega_0/\tilde{\omega})^2}, \tag{13}$$

with $\tilde{\omega}^2 = \mathcal{C}'/\mathcal{C}$. This approximation is, in fact, quite accurate as long as the dielectric response is given by a single band of frequencies in the optical and/or UV regimes. It becomes inadequate when there are contributions to $\varepsilon''(\omega)$ also from the IR and MW regimes. In that case, one should simply revert to the exact definition Eq. (8). From the sum rules [27], it follows that $\tilde{\omega}$ can be written explicitly as

$$\tilde{\omega}^2 = \frac{\int_0^\infty \omega\varepsilon''(\omega)d\omega}{\int_0^\infty \omega^{-1}\varepsilon''(\omega)d\omega} = \frac{\omega_p^2}{(\varepsilon(0)-1)}, \tag{14}$$

and is thus obviously equal to $\langle\omega^2\rangle$ for the spectral distribution $\omega^{-1}\varepsilon''(\omega)$. $r^2 = (\omega_0/\tilde{\omega})^2$ thus equals the square of the ratio of the position of the additional peak and the width $\langle\omega^2\rangle$ of the underlying spectrum.

We expressed the ζ dependence in terms of the dimensionless variable (ζ/ω_0) because of the assumed form of $\delta\varepsilon(i\zeta)$, Eq. (9), that depends on this dimensionless combination. Therefore $\tilde{\varepsilon}(i\zeta)$ as well as the variation in the Hamaker coefficient, Eq. (5), both depend on the static dielectric constant $\varepsilon(0) - 1$ and the ratio r.

Having the explicit form of $\tilde{\varepsilon}(i\zeta)$, we can now calculate the dependence of $\delta\mathcal{A}(i\zeta)$ on the ratio ζ/ω_0 for $r = 1$ (see Fig. 1(a)). This dependence shows a maximum that depends on the values of $(\varepsilon(0) - 1)$ and the ratio r. Obviously as $(\varepsilon(0) - 1)$ grows past a fixed value, found numerically to be $\mathcal{C}_0 \simeq 4.7$ (see below) for $r = 1$, the maximum of $\delta\mathcal{A}(i\zeta)$ is displaced from $\zeta = 0$ to non-zero values. This means that the maximum contribution to the vdW interaction free energy is given by the zero frequency term for $(\varepsilon(0) - 1) < \mathcal{C}_0$ and then depends monotonically on $(\varepsilon(0) - 1)$ for larger values. In fact, indeed $Max(\delta\mathcal{A}(i\zeta))$ on $(\varepsilon(0) - 1)$ bears a striking formal resemblance to the temperature dependence of the order parameter close to a second order phase transition [29].

Fitting the calculated dependence of $Max(\delta\mathcal{A}(i\zeta))$ for $r = 1$ on $(\varepsilon(0) - 1)$, it is possible to extract the following behavior for the frequency of this maximum, ζ_{max}:

$$\zeta_{max} \sim \begin{cases} 0; & (\varepsilon(0)-1) < \mathcal{C}_0 \\ \omega_0\sqrt{(\varepsilon(0)-1)-\mathcal{C}_0}; & (\varepsilon(0)-1) \geqslant \mathcal{C}_0, \end{cases}$$

where $\mathcal{C}_0 = 4.7$ can be read off Fig. 1(a). Obviously, spectra with $(\varepsilon(0) - 1) > 4.7$ would lead to a maximum in the vdW interaction free energy variation at frequencies that scale linearly with ω_0. Furthermore, the numerical coefficient in Eq. 15 as well as $\mathcal{C}_0$ are both functions of the ratio r. The dependence of $\zeta_{max}(\varepsilon(0) - 1, r)$ is presented in Fig. 1(b). It is clear that $\mathcal{C}_0$ changes only marginally for $r > 2$ but has an important effect for $r < 1$. Apart from this, qualitatively, the functional form of ζ_{max} is very similar in the whole parameter space. It is indeed quite unexpected that the effect of addition of a lone peak to the dielectric spectrum would affect the different Matsubara terms of the vdW interaction free energy in such a non-monotonic fashion.

The relation between the spectral change and the Matsubara frequency at which there is the largest change of the vdW interaction free energy is thus quite complicated and extremely indirect. It depends on overall properties of the complete dielectric spectrum as exemplified by $(\varepsilon(0) - 1)$ and r. Though these results can
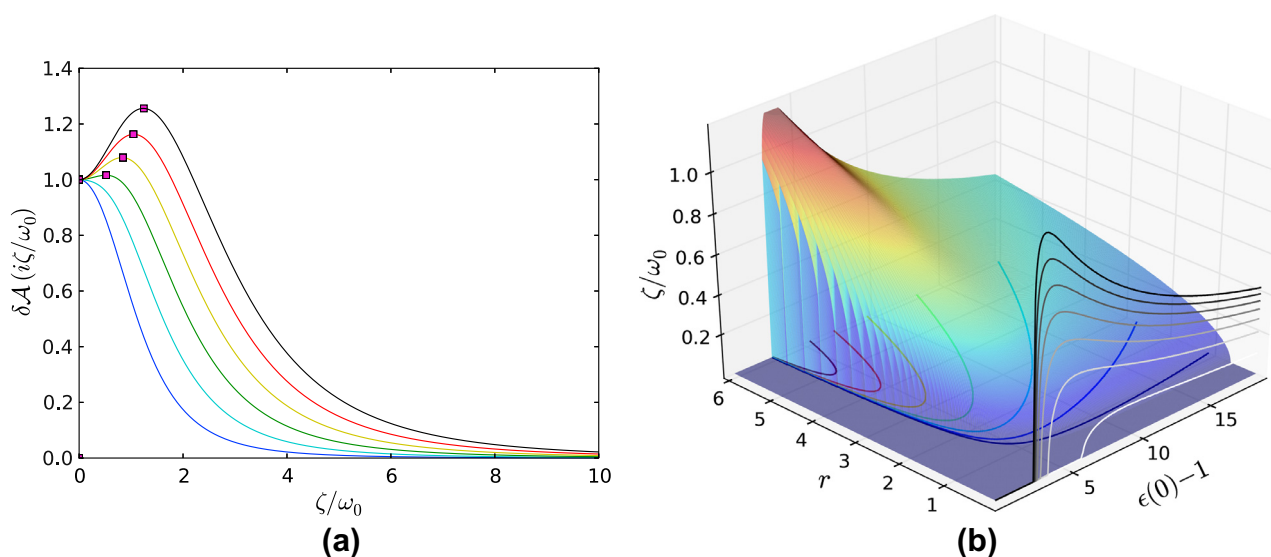
Fig. 1. (a) The function $\delta\mathcal{A}(i\zeta)$, Eq. (5), for six different values of $(\varepsilon(0) - 1)$ (from 2 to 12, top to bottom) as a function of (ζ/ω_0). With increase of $(\varepsilon(0) - 1)$ the maximum (purple squares) moves from zero frequency toward non-zero values. The inset shows the complete dependence of the maximum of $\delta\mathcal{A}(i\zeta)$, ζ_{max}, on $(\varepsilon(0) - 1)$. For this calculation, we took $r = \omega_0/\bar{\omega}_0 = 1$. (b) Contour plot of $Max(\delta\mathcal{A}(i\zeta))$ as a function of $(\varepsilon(0) - 1)$ as well as $r = \omega_0/\bar{\omega}$. The inset in (a) is obtained by cutting the contour plot (b) with a horizontal plane at $r = 1$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

be derived explicitly only for the very simple model explained above, the salient features revealed remain true even in more realistic cases, as we will elucidate below.

4. Interaction free energy variation: realistic spectrum variation

We now apply our general formulation of the dielectric response variation and the consequent vdW interaction free energy variation to the case of an exciton peak in amorphous silica. This is aimed at elucidating the often posed, but never properly answered, question of what exactly is the effect of addition or removal of a single sharp (exciton) peak on the vdW interaction free energy.

For the non-perturbed dielectric dispersion spectrum, we take the imaginary part of the dielectric permittivity, $\epsilon''(\omega)$, of amorphous silica, as calculated with the OLCAO-DFT methodology by Li and Ching [23]. Being a one-electron approximation, the calculated spectrum does not contain any exciton effects; the corresponding peak measured by Tan et al. [24] is missing. In order to simulate an additional excitonic peak, we next synthesize a modified spectrum by adding a Lorentz oscillator peak just below the fundamental absorption edge of the OLCAO-DFT calculated dielectric dispersion spectrum, at a frequency $\hbar\omega_0 = 8.21$ eV. The magnitude, position, and full width at half maximum (FWHM) of this Lorentz oscillator peak were determined by comparison with experimental spectra [24], so that the ratios of both the position and magnitude of the exciton peak to the first interband transition peak were the same in the experimental spectrum and our synthesized spectrum. The FWHM of the added Lorentz oscillator peak is the same as that of the exciton peak in the measured spectrum. Finally, the whole synthesized spectrum was rescaled so that the total oscillator strength of the spectrum was unchanged by the addition of the Lorentz oscillator peak and that the number of electrons does not depend on the way the spectrum is constructed: the number of electrons involved in transitions up to a certain sufficiently large energy is fixed for a given real material [27].

From Fig. 2(a) we discern that the addition of the Lorentz oscillator peak affects all or most of the imaginary part of the dielectric spectrum. The imposition of the oscillator strength sum rule has the most significant effect only in a narrow frequency interval centered around the fundamental absorption edge, showing a weak tail at larger frequencies. As expected, the corresponding KK transform of the dispersion spectrum $\varepsilon(i\zeta)$ shown in Fig. 2(b) shows the largest variation close to the static $\zeta = 0$ region but has a finite variation distributed throughout the whole range of imaginary frequencies. Obviously the non-local connection between $\varepsilon''(\omega)$ and $\varepsilon(i\zeta)$, provided by the KK transform, Eq. (1), shows up in their quite distinct dependence on the addition of an extra Lorentz oscillator peak.

The effect of peak addition on the corresponding terms in the Matsubara sum for the non-retarded Hamaker coefficient (Eq. (6)) is shown in Fig. 3. Clearly, the largest variation of about 10% is observed for lowest Matsubara terms, closest to the static limit. We are thus in the $\zeta_{max} = 0$ limit, see Fig. 1.

After summing up the Matsubara terms, the total change of the Hamaker coefficient amounts to $\delta\mathcal{A} = -5.03$ zJ and is proportional to the area between the two curves in Fig. 3. The value of the Hamaker coefficient for the original spectrum is 84.9 zJ. The relative change in the Hamaker coefficient is thus ~6%. Considering that this change is due to the presence of a single narrow Lorentzian peak in the dielectric spectrum of the interacting material, it is non-negligible. Addition of multiple peaks would simply contribute additively to the overall change of the Hamaker coefficient.

We now modify the unperturbed calculated dielectric dispersion spectrum by adding a Lorentz oscillator peak at variable frequency positions, thus avoiding the constraint that the simulated excitonic peak should be just below the fundamental absorption edge. Again the FWHM and the oscillator strength of these added Lorentz oscillator peaks were taken from experimental spectra [24], while the position was chosen arbitrarily. The background spectrum was multiplied by a scaling factor so that that the oscillator strength at 43 eV (6.88×10^{16} s^{-1}) for the original spectrum with the additional Lorentzian peak matches the oscillator strength at 43 eV from the experimental spectrum as measured in Ref. [24]. This guarantees that the effective number of electrons up to and including the energy 43 eV remains invariant.

In general the effective number of electrons up to and including the energy $\hbar\omega$ is related to the oscillator strength sum rule and is given by
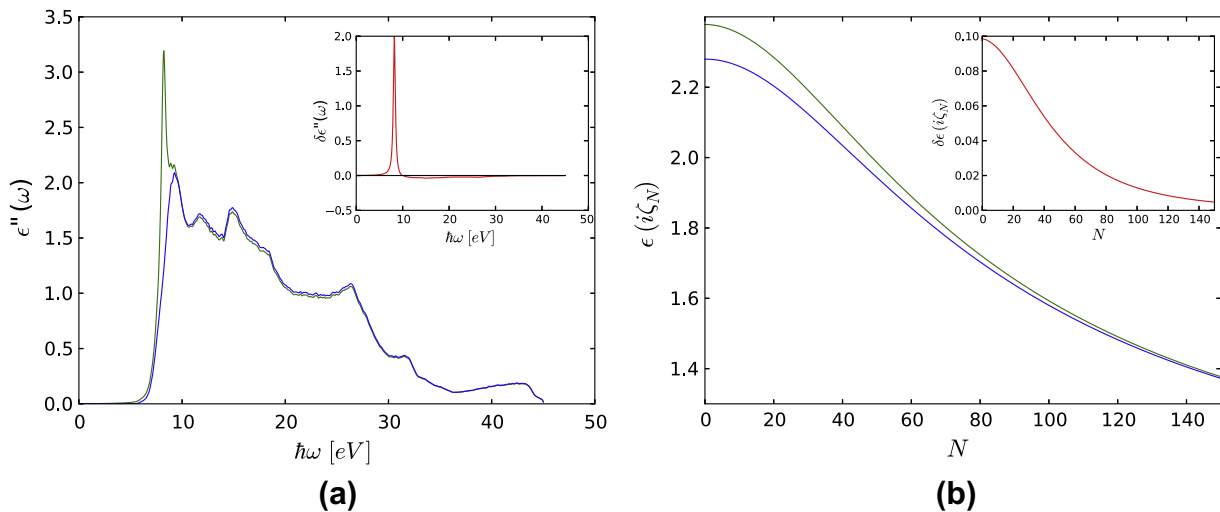
Fig. 2. (a) The dielectric dispersion spectrum $\epsilon''(\omega)$ as a function of frequency ω in eV for amorphous silica without the exciton peak (blue line) and with a simulated exciton peak (green line). The inset shows the difference between the two spectra as a function of frequency. (b) The KK transform $\epsilon(i\zeta_N)$ without (blue line) and with (green line) the exciton peak, as a function of the Matsubara index N of ζ_N. The inset again shows the difference. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
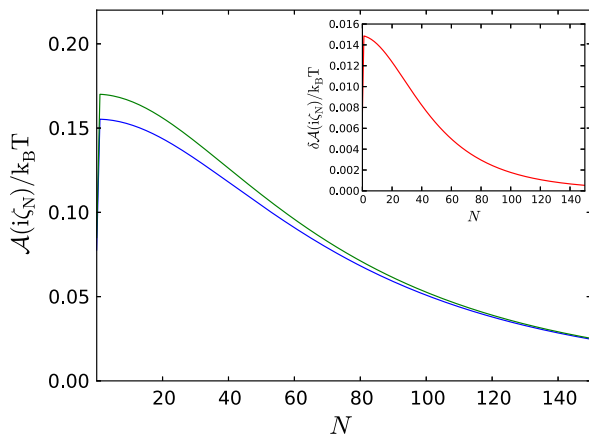

Fig. 3. The variation of the different Matsubara frequency components in the Hamaker coefficient $\mathcal{A}(i\zeta_N)$ from Eq. (3) for the two spectra from Fig. 2. The x-axis shows the index N of the Matsubara frequencies ζ_N. The biggest change is associated with the lowest frequency terms. The change in the Hamaker coefficient $\delta\mathcal{A}(i\zeta_N)$ from Eq. (6) is shown in the inset as a function of the Matsubara frequency components.

$$n_{eff}(\omega) = \frac{m_0}{2\pi^2\hbar e_0^2} \int_0^{\hbar\omega} u\,\varepsilon''(u)\,du. \qquad (15)$$

From Fig. 4(a) it is obvious that $n_{eff}(\omega)$ for a synthesized spectrum becomes effectively identical to the background spectrum without the exciton peak at energies above the added peak. Because the oscillator strength of a given dielectric response feature is dependent on the energy at which that feature occurs (hence the above integrand of $u\varepsilon''(u)$ rather than simply $\varepsilon''(u)$), the added exciton peaks vary in magnitude despite having their oscillator strength invariant, i.e., lower energy peaks are larger than high energy ones despite representing the same number of electrons involved in transitions over their given energy range.

Fig. 4(a) shows the imaginary part of the dielectric spectra for various peak positions as obtained from the aforementioned rescaling as well as their energy dependent oscillator strengths. At energies above the added Lorentzian peak the oscillator strength becomes universal. The Matsubara frequency components of the Hamaker coefficient are shown in Fig. 4(b). A broad range of

behaviors is observed for the latter, but overall one notices that the peak position at lower ω_0 leads to larger changes in the Hamaker coefficient.

Because of the rescalings implicit in the synthetic spectrum, in order to satisfy the sum rule up to the highest value of the frequency at which data are available for both spectra, the *ab initio* and the experimental results, i.e., 43 eV or 6.88×10^{16} s^{-1}, the frequency variation of the Matsubara terms in the Hamaker coefficient depends on the position of the peak. For different peak positions the corresponding relative changes in the full Hamaker coefficients are given in Table 1. We can thus conclude that the simulation of spectra with an added peak confirms the insight of the model that the addition of peaks at smaller characteristic frequency ω_0 and larger FWHM have a more pronounced effect on the Hamaker coefficient, and make it larger. In fact, one can deduce that the relative changes in the Hamaker coefficient are proportional to FWHM of the added peak and inversely proportional to its frequency ω_0.

4.1. Discussion

Because the vdW interaction free energy is a functional of the KK transform, itself a functional of the imaginary part of the dielectric function, the relationship between the characteristics of an added peak in the $\varepsilon''(\omega)$ and the Matsubara frequency components of the Hamaker coefficient closest to that frequency is not direct. In fact, the Matsubara frequency component at which the largest change to the Hamaker coefficient occurs varies non-linearly with the frequency of the added peak and depends in a complicated way on the properties of the original spectrum. The overall variation in the Hamaker coefficient is then proportional to the full width at half maximum of the added peak and inversely proportional to its frequency. Its total relative change spans values from a few and up to ~10%, depending on the characteristics of the added peak. In the case of more complicated variations of the dielectric response, corresponding to addition of several peaks, the total variation equals the sum of variations for individual peaks and can be quite large.

In order to estimate quantitatively the effect of a single peak addition we synthesized a modified spectrum of amorphous silica by adding a Lorentz oscillator peak just below the fundamental
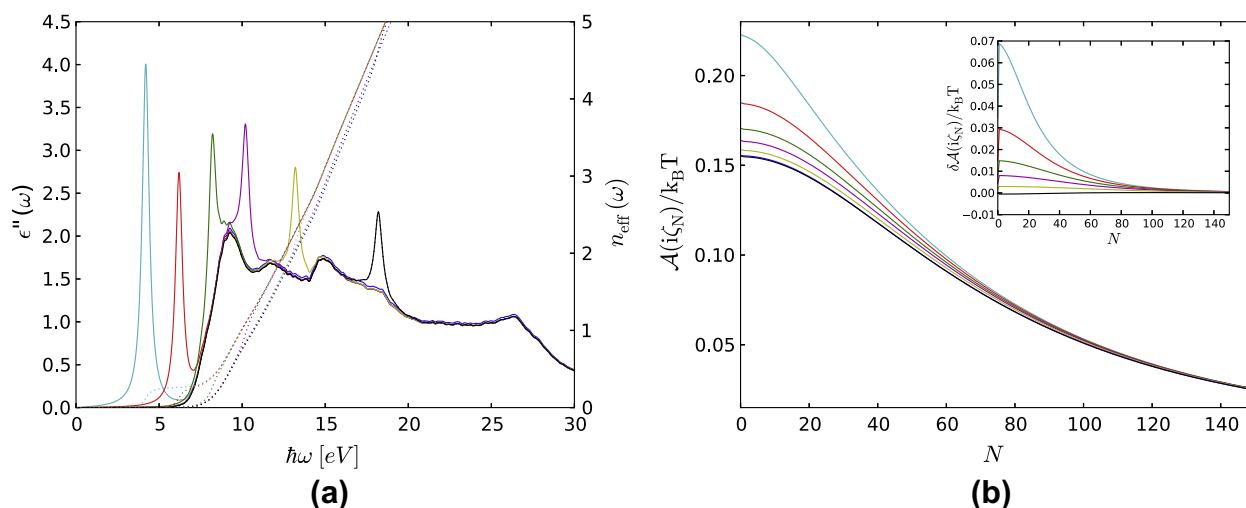
Fig. 4. (a) The background dielectric dispersion spectrum $\epsilon''(\omega)$ of amorphous silica without the exciton peak in the frequency interval 5–30 eV, (black line), and the synthesized spectrum with an added (exciton) Lorentzian peak at various frequencies in units of eV. The dashed curves represent $n_{eff}(\omega)$ as a function of frequency for each spectrum. (b) Different Matsubara frequency components as well as their change (inset), as in Fig. 3, both as a function of the Matsubara frequency index. The biggest change is associated with the low frequency terms and peak position at lower frequencies. Lower energy peaks are larger than high-energy ones despite representing the same number of electrons involved in transitions over their given energy range (see main text).

Table 1
Position of the added (excitonic) peak, index of refraction, $n_{vis} = \sqrt{\varepsilon'(\omega_{vis})}$, at $\hbar\omega_{vis} = 2$ eV, and the corresponding relative change of the Hamaker coefficient. The index of refraction for the background dispersion spectrum is 1.5222.

ω_0 (eV)	4.2	6.2	8.2	10.2	13.2	18.2
ω_0 ($\times 10^{-16}$ s^{-1})	0.638	0.942	1.245	1.549	2.005	2.764
n_{vis}	1.7065	1.5926	1.5566	1.5404	1.5289	1.5209
$\delta\mathcal{A}/\mathcal{A}$ (%)	16.2	9.4	5.9	3.8	1.8	−1

absorption edge of the OLCAO-DFT calculated dielectric dispersion spectrum. For the added exciton peak at 8.21 eV the calculated change in the Hamaker coefficient was established accurately to be 6%. The spectrum was synthesized in such a way that the total oscillator strength $n_{eff}(\omega)$ up to 43 eV is held invariant for each spectrum at 12.173 electrons per formula unit of SiO_2. An added peak sweeps up 0.2814 electrons per formula unit from across the whole spectrum into the vicinity of that peak, relocating 2.31% of the total oscillator strength of the material. Therefore the change in Hamaker coefficient of 6% is quite significant, not only because this change is seen despite oscillator strength being held invariant, but doubly so because of how little oscillator strength was actually relocated into this added excitonic peak.

A secondary effect of adding features to the $\varepsilon''(\omega)$ spectrum is a change in the visible range index of refraction, n_{vis}. This follows directly from the KK transform which links the real and imaginary parts of any physical variable that obeys causality. Table 1 shows the effect on $n_{vis} = \sqrt{\varepsilon'(\omega_{vis})}$ evaluated at $\hbar\omega_{vis} = 2$ eV from the addition of each peak. Because the dispersive and absorptive optical properties of a given system are inextricably linked in this manner, any change in the index of refraction (or, equivalently, $\varepsilon'(\omega)$) of a material necessarily results in a change of the $\varepsilon''(\omega)$ spectrum as well, and thus a change in the Hamaker coefficient for a given system. In this manner the index-matching approach to eliminating vdW forces in a system is not totally misguided; however, the implied mechanism is erroneous and the results are imprecise.

Previous results have shown that, in real materials, it is necessary to include transitions up to approximately 20 eV in order to make a reasonable estimate of the Hamaker coefficient for that system [28]. Neglecting features at these higher energies has the consequence of significantly underestimating the strength of vdW-Ld interactions. This further highlights the danger of index-matching approaches that extrapolate results from low-energy data: without sufficient knowledge of high-energy spectral features in a material, it is not possible to calculate Hamaker coefficients with any accuracy.

4.2. Conclusions

Our calculations of a simplified approximate model as well as of a realistic example of amorphous silica spectrum with and without an exciton peak indicate that even small changes in the dielectric response can show up as substantial variations in the Hamaker coefficient of the vdW interactions. However, caution needs to be exercised in making estimates of these variations. VdW interactions are non-local in the frequency response: first through the summation over the Matsubara frequencies in the Lifshitz theory, and then through the imaginary part of the total dielectric response function via the KK relations. This means that a variation of the dielectric absorption spectrum at one particular frequency influences all the terms in the Matsubara summation of the vdW interaction energy, making the total change in the Hamaker coefficient depend not only on the spectral changes at that frequency, but also at the rest of the spectrum properly weighted. For example, the Tabor–Winterton approximation would suggest that matching the refractive index at a single absorption peak should effectively quench the long range vdW component of molecular interactions. Our detailed calculations prove that this is certainly not the case.

While it is true that addition of a single peak in the dielectric absorption spectrum can induce a substantial change in the magnitude of vdW interactions, the Matsubara terms that are most affected are not those close to the position of the added peak but are distributed over the whole interval of frequencies and can show a maximum whose position is not directly related to the position of the added peak. A possibility of eliminating vdW interactions or at least drastically reducing them by spectral variation in a narrow regime of frequencies thus seems very remote.

Some care is therefore necessary when estimating and/or predicting changes in the vdW interactions wrought by changes in the dielectric spectrum. There is no linear correspondence between

the interaction free energy variation and the spectral properties of the interacting media.

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