Van der Waals interactions between atoms and dispersive surfaces at finite temperature

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Abstract. The long-range interactions between an atomic system in an arbitrary energy level and dispersive surfaces in thermal equilibrium at non-zero temperature are revisited within the framework of the quantum-mechanical linear response theory, using generalized susceptibilities for both atom and electromagnetic field. After defining the observables of interest, one presents a general analysis of the atomic level shift valid for any number and form of dielectric surfaces. It is shown that, at zero temperature, one recovers well-known results previously obtained in the linear response regime. The case of a plane dispersive surface is elaborated on in the non-retarded regime. Calculations are given in detail for a dielectric surface exhibiting a single polariton resonance. Theoretical predictions are presented within a physical viewpoint allowing one to discriminate between the various interaction processes: on one hand, the level shift induced by non-resonant quantum fluctuations, on the other hand, two potentially resonant atom-surface couplings. The first resonant process appears for excited-state atoms and originates in an atomic de-excitation channel resonantly coupled to the surface polariton mode. It exists also at zero temperature, and has been studied and observed previously. The second physical process, which exists at non-zero temperature only, corresponds to the reverse process in which a thermal quantum excitation of a surface polariton resonantly couples to an atomic absorption channel. This novel phenomenon is predicted as well for a ground state atom, and can turn the ordinary long-range van der Waals attraction of atoms into a surface repulsion at increasing temperatures. This opens the way to the control and engineering of the sign and amplitude of van der Waals forces via surface temperature adjustment.

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1 Introduction

Van der Waals (vW) interactions between neutral polarisable systems represent the ubiquitous force of nature, at the action across all types of material bodies. They are at the origin of the cohesion of matter. They can be described as the interaction between fluctuating electric dipoles spontaneously induced in one of the neutral bodies, and their dipolar image in the other material system. One paramount example of vW interactions is the long range dipole attraction between an atomic system and a material body. For plane wall, its $1/z_0^3$ dependence in the non-retarded regime (z_0: atom-wall separation) has been documented long ago, starting with the pioneering work of Lennard-Jones [1]. Retardation effects have been later considered by Casimir and Polder [2]. Due to their importance in atomic force microscopes [3] or in cavity QED [4],

atom-surface interactions have been the subject of a renewed interest in the recent years (for a recent review, see [5]).

Over the years, a great number of theoretical works has been devoted to the study of atom-surface interactions. The interaction of an atom ground state with metallic or dielectric walls has been analysed, as well as the behaviour of excited atomic states (energy shift, level broadening/narrowing) in front of either a perfect reflector, or metallic or dielectric surfaces. Both retarded and non-retarded regimes have been considered ([5] and references in). The case of an *excited* atom interacting with a dispersive surface has been analysed more recently from both theoretical and experimental viewpoints [6–15], in particular with respect to the possibility of a resonant coupling between an atomic de-excitation channel and surface polariton resonances, leading to an enhancement and a possible inversion of the surface forces (the vW attraction

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being turned into a vW repulsion [12,13]) and to important modifications of the atomic decay channels (surface-induced alteration of branching ratios, etc.) [13,14].

Most of the above works has been done by assuming that the interacting surface is at vanishing temperatures ($T \sim 0$) and there is no thermal excitation of the surface. The consideration of surfaces at non-zero temperatures is important with respect to the study of gas-wall thermal exchanges and the establishment of thermal equilibrium between a gas and its container, as well as the prediction of heats of atom adsorption and the dynamics of adsorption/desorption. A few previous works have considered the case of non-zero surface temperatures [10,16–19].

In this article, we revisit the problem of ground or excited atoms interacting with non-zero-temperature surfaces, with a special emphasis on the case of dispersive surfaces when surface polariton modes can be thermally excited. We will analyse the possibility of a resonant coupling between a quantum of surface excitation, and atomic electric dipole absorption, as well as the influence of this virtual energy exchange on surface forces. In Section 2, the equations of motion are established for the most general case of e.m. field propagation, with any boundary surfaces, but in this article, the detailed analysis will be subsequently restricted to the non-retarded case, leaving the full analysis of the retarded characteristics to a forthcoming publication. Section 3 is devoted to the properties of atom-surface interaction at non-zero temperature, in the particular case of a plane surface exhibiting a single surface-polariton resonance, and examines the influence of a resonant energy coupling. Two appendices present the detailed derivation of the equations describing the atom-surface interaction for $T \neq 0$ (Appendix A), and the comparison with previous works (Appendix B).

2 Atom-surface interaction at finite temperature

In this section, we calculate the dynamic Stark-shift of any internal energy-level of an atom located near a surface, this surface being supposed in thermal equilibrium with the black-body radiation (BBR) at temperature T. The question of what is measured exactly in a spectroscopy experiment, and how the experimentally measured frequency-shift can be related to our result will be discussed later on, as well as the thermodynamic nature of this frequency-shift.

First, we are looking for the correction to the "energy" of the atomic eigenstates due to the interaction with a thermal field, and, into this correction, we are interested only by the contribution of the interface between vacuum and any real (dissipative) medium.

2.1 Assumptions

What is called "field" denotes the vacuum field-modes in presence of the interface with the half-infinite dielectric (or metal) space — e.m. modes and material medium being in thermal equilibrium at temperature T. Excitations of the surface are supposed to be in equilibrium at the same temperature and are included under the label "field", which means "reservoir of oscillators". The atom is supposed to be at rest at a position $\vec{r}_0$, in a given internal state $|a\rangle$. To simplify, we suppose that $|a\rangle$ is non-degenerate. The xOy plane is chosen as the interface, and the atom-surface distance is z_0.

The eigenstates of the atomic Hamiltonian H_{at} are labelled with small letters: "$i, k, ...$", each letter representing a set of quantum numbers. Those of the field Hamiltonian H_{rad} are labelled with capital letters: "$I, K, ...$". The states of the total system without interaction are then denoted: $|I, i\rangle$.

The probability for the field to be in the "I" state is given by the canonical distribution: $p(I) = e^{-\beta E_I}/\sum_I e^{-\beta E_I}$. An eigenstate of the field is a set of modes: $\{\omega_k\}$, and the mean number of occupation of each mode by photons is supposed to depend only on its frequency and on the field-temperature:

$$\bar{N}_k = \frac{1}{e^{\beta\hbar\omega_k} - 1} \tag{2.1}$$

with $\beta = (k_B T)^{-1}$.

The interaction, in first approximation, will be described with the dipolar Hamiltonian: $H_{int} = -\vec{\mu}\cdot\vec{D}(\vec{r}_0)$, where $\vec{D}(\vec{r}_0)$ is the displacement field at the location of the atom and $\vec{\mu}$ the electric dipole moment operator of the atom. This choice of the multipolar Hamiltonian [20] allows one to find the contribution of the Coulomb field as the near-field limit of the retarded interaction, and one can have at the same time the long-range limit. One can choose the Hamiltonian $H_{rad} = -\vec{p}\cdot\vec{A}(\vec{r}_0)$ where $\vec{p}$ is the electron linear momentum and $\vec{A}(\vec{r}_0)$ the vector-potential of the transverse field. However, one thus has to add the Coulomb interaction to obtain the van der Waals part of the shift [20,21].

As the near-field contribution for *real* surfaces is coming for the major part from evanescent waves, it is necessary to introduce in the calculation evanescent waves propagating along the interface (surface-modes) as well as waves propagating into the vacuum and the bulk. Barton, for example [10], models van der Waals interaction uniquely by surface-modes. They are combined modes of the electromagnetic field and of the polarization field in the medium, and can be found by solving the Laplace equation ($\omega \to 0$). Using this method, he obtains the electrostatic part of the interaction. About these surface-polaritons, one can see for example references [22,23].

To achieve the goal to obtain the near-field limit as well as the long-range one, we will work with field-modes which are plane-waves, solutions of Maxwell equations with boundary-conditions at the material interface. The translational invariance into the z-direction is thus lost and only the wave-vector components parallel to the interface have to be real, into the vacuum as well as into the dissipative dielectric. This dielectric medium is

phenomenologically modelled by a complex dielectric constant. Maxwell equations can be solved in this geometry [24]. That gives us the $(\vec{K}, z; \omega)$ Fourier component of the linear-susceptibility of the field, $\vec{K}$ being the wave-vector component along the interface.

We have to remember that this linear susceptibility does not depend on the initial state of the field, so it will not depend on temperature.

2.2 Thermodynamical statistics: definition of the observable of interest

We will not develop here all the details of the calculation of the energy level-shift in the linear-response formalism (see Refs. [7,8]). They are also developed in [25] for an isotropic vacuum (without surfaces). We use the same notations as in a previous article devoted to the case of a birefringent medium [7,8,11].

Let us examine here the thermodynamical statistics of the perturbation.

From the quantum-mechanics point of view, the interaction Hamiltonian $H_{int} = -\vec{\mu} \cdot \vec{D}(\vec{r}_0)$ is considered as a small perturbation to the Hamiltonian $H_{at} + H_{rad}$, whose eigenstates have been defined before. The two operators, $\vec{\mu}$ and $\vec{D}$, being non-diagonal in the basis $|I, i\rangle$, the first non-zero correction to the energy-levels of the total system "atom + field" is the second order one. This correction is the interaction energy of two sub-systems, and is experienced by the atom as a z-dependent potential. This provides us with the quantum mechanical correction, as in the zero-temperature case.

At non-zero temperature, one has to take the statistical expectation value with the Gibbs distribution of the total system *before* coupling (energy levels: $E_I + E_i$). One obtains in this way the correction to free energy δF of the system "atom + field" due to the coupling between its two parts (cf. Landau and Lifchitz [26]). Obviously, it is possible to deduce from this δF a correction to the energy δE, or to the entropy δS, but each of them are corrections to free energy, energy, or entropy of the total system, atom and field being supposed in overall (non-constrained) equilibrium at temperature T [27].

On the opposite, we consider here the expectation value with the Gibbs distribution of the reservoir *alone* (energy levels E_I), the atom being constrained in the same quantum state $|i\rangle$. We do not take the trace over the whole system states but only over the field's states. Following the detailed analysis of Barton [28], we will identify the result of this calculation with the free-energy shift of the coupled system atom + field, the atom being constrained to stay in a given state $|i\rangle$. It represents as well the dynamical Stark shift in presence of the Black Body Radiation (BBR). Then we have identified the quantity calculated by doing statistics on quantum perturbation, taking the trace only over field states. It remains to know what is measured in an actual experiment.

Here, we are interested in the response of a dilute vapour near a surface to a probe-laser of given frequency ω_{if}. In this way, we are measuring the surface-induced frequency-shift of a given transition, $|i\rangle - |f\rangle$ (in fact a difference between the two level-shifts). What is monitored can be considered as two constrained thermal equilibriums, the atomic gas being placed in an oven maintained at temperature T.

If the experiment with the probe-laser can be considered as an *isotherm and reversible* process, then only "*work*" is given to the total system "atom + field", in order to change the atomic state from $|i\rangle$ to $|f\rangle$. This work does correspond to an increase in free-energy, as we calculate here. So we test a difference between two "free-energy"-shifts. In contrast, what we name the total "energy" of the system would have to take into account the exchange of heat with the heat-bath, through the emission or the absorption of photons by the walls.

What are the conditions on the measurement process needed to get a reversible spectroscopy experiment?

To trace only over the field-states means that we can ignore the atom-field correlation and write the density matrix of the total system as a tensor product of the atomic density matrix by the field's one. Then the shifts and transition rates can be expressed with the linear susceptibilities of each sub-system [25]. For zero temperature, it is the case if the characteristic atom-probe interaction time, τ, is very long compared to the correlation time of the vacuum field, but very short compared to the mean life-time of the excited atom (coarse-grain average). At temperature T, we assume that the atom prepared in state $|i\rangle$ has a very small probability during time τ to make a transition to level $|f\rangle$ through any type of relaxation, either BBR (in absorption or emission) or spontaneous emission. This is satisfied if the previous condition on the interaction time, τ, still applies with the vacuum field replaced by the BBR field, and the atomic lifetime taking into account absorption and stimulated emission processes. This provides the conditions to conduct a reversible experiment with a constrained thermal equilibrium.

2.3 Free-energy shift of the coupled atom-surface system, for an atom in a constrained state |i⟩

The first non-zero correction coming from the coupling is the second-order one. When one takes the trace of this contribution over all reservoir states at temperature T, one finds the correction to the free-energy of the total system "*atom in the $|i\rangle$ state + field*", due to the interaction:

$$\delta F_i = \frac{1}{\hbar} \mathsf{P} \sum_{I,K,k} p(I) \frac{D_\alpha^{IK}(\vec{r}_0) D_\beta^{KI}(\vec{r}_0) \mu_\alpha^{ik} \mu_\beta^{ki}}{(\omega_I - \omega_K) + (\omega_i - \omega_k)}$$

$$= -\frac{1}{\hbar} \mathsf{P} \sum_{I,K,k} p(I) \int_{-\infty}^{+\infty} d\omega \frac{D_\alpha^{IK}(\vec{r}_0) D_\beta^{KI}(\vec{r}_0) \mu_\alpha^{ik} \mu_\beta^{ki}}{\omega + \omega_{ki}}$$

$$\times \delta(\omega - \omega_{KI}). \tag{2.2}$$

The letters: I, K or i, k denote matrix elements of the operators Displacement Field and Dipolar Moment respectively between field-states or atom-states

$(\omega_{KI} = \omega_K - \omega_I)$. The Greek subscripts denote Cartesian components and have to be summed when they are repeated. P means principal part, excluding states giving a null denominator, and the probability $p(I)$ of the field state $|I\rangle$ has been defined above (Eq. (2.1)).

Introducing the time-dependent expansion of the delta-distribution, $\delta(\Omega) = (1/2\pi) \int_{-\infty}^{+\infty} dt\, e^{i\Omega t}$ and the time-dependent field operator, $\tilde{D}_\alpha(\vec{r}, t) = e^{iH_R t/\hbar} D_\alpha(\vec{r}) e^{-iH_R t/\hbar}$, one obtains:

$$\delta F_i = -\frac{1}{2\pi\hbar} P \sum_{I,K,k} p(I) \int_{-\infty}^{+\infty} d\omega$$
$$\times \int_{-\infty}^{+\infty} dt \frac{D_\alpha^{IK}(\vec{r}_0) D_\beta^{KI}(\vec{r}_0) \mu_\alpha^{ik} \mu_\beta^{ki}}{\omega + \omega_{ki}} e^{i\omega t} e^{-i\omega_{KI} t}$$

$$\delta F_i = -\frac{1}{2\pi\hbar} P \sum_k \mu_\alpha^{ik} \mu_\beta^{ki} \int_{-\infty}^{+\infty} d\omega$$
$$\times \int_{-\infty}^{+\infty} dt \frac{\sum_{I,K} p(I) \tilde{D}_\alpha^{IK}(\vec{r}_0, t) \tilde{D}_\beta^{KI}(\vec{r}_0, 0)}{\omega + \omega_{ki}} e^{i\omega t}. \quad (2.3)$$

We can write also the integrand's numerator as:

$$\sum_{I,K} p(I) \tilde{D}_\alpha^{IK}(\vec{r}_0, t) \tilde{D}_\beta^{KI}(\vec{r}_0, 0) =$$
$$\sum_I p(I) \langle I| \tilde{D}_\alpha^{(}\vec{r}_0, t) \left\{ \sum_K |K\rangle \langle K| \right\} \tilde{D}(\vec{r}_0, 0) |I\rangle$$
$$= \sum_I p(I) \langle I| \tilde{D}_\alpha(\vec{r}_0, t) \tilde{D}_\beta(\vec{r}_0, 0) |I\rangle$$

in order to introduce the statistical mean value on the reservoir-states of the operator: $\tilde{D}_\alpha(\vec{r}_0, t) \tilde{D}_\beta(\vec{r}_0, 0)$. We represent this mean value by an angular bracket and define the function: $\left\langle \tilde{D}_\alpha(\vec{r}_0, t) \tilde{D}_\beta(\vec{r}_0, 0) \right\rangle = g_{\alpha\beta}(t)$.

Then the correction to free-energy of the constrained equilibrium atom-field can be written:

$$\delta F_i = -\frac{1}{2\pi\hbar} P \sum_k \mu_\alpha^{ik} \mu_\beta^{ki} \int_{-\infty}^{+\infty} d\omega \frac{g_{\alpha\beta}(\omega)}{\omega + \omega_{ki}} \quad (2.4)$$

where we have used the Fourier Transform of the function $g_{\alpha\beta}(t)$:

$$g_{\alpha\beta}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt g_{\alpha\beta}(t) e^{i\omega t}.$$

Finally, the fluctuation-dissipation theorem [26] relates the F.T. of this correlation function $g_{\alpha\beta}(t)$ to the F.T. of the linear susceptibility of the field, defined by

$$G_{\alpha\beta}(\vec{r}, \vec{r}'; t) = \frac{i}{\hbar} \left\langle \left[\tilde{D}_\alpha(\vec{r}, t), \tilde{D}_\beta(\vec{r}', 0) \right] \right\rangle \theta(t). \quad (2.5)$$

$\theta(t)$ is the Heaviside step function, and vertical brackets indicate a commutator. Angular brackets denote statistical expectation value with Gibbs distribution.

This theorem leads to the form (see Appendix B in Ref. [8]):

$$\text{Im} G_{\alpha\beta}(\vec{r}, \vec{r}'; \omega) = \frac{1}{2\hbar} g_{\alpha\beta}(\vec{r}, \vec{r}'; \omega)(1 - e^{-\hbar\omega/k_B T}). \quad (2.6)$$

Therefore, it introduces the influence of temperature in the dynamic Stark shift that we are looking for

$$\delta F_i = -\frac{1}{\pi} P \sum_k \mu_\alpha^{ik} \mu_\beta^{ki} \int_{-\infty}^{+\infty} d\omega \frac{\text{Im} G_{\alpha\beta}(\vec{r}_0, \vec{r}_0; \omega)}{(\omega + \omega_{ki})(1 - e^{-\hbar\omega/k_B T})}. \quad (2.7)$$

This formula has previously been derived by Wylie and Sipe [8]. These authors deal with the zero-temperature case only, and then reduce the integral over ω to positive frequencies. They call it an "energy" shift, and that is indeed the case at zero temperature.

2.4 Predicted shifts — Comparison with previous works

2.4.1 Zero temperature shifts

The integral (2.7) is only over positive frequencies in this case and the calculation can be done by making use of the complex plane to transform the integration over real frequencies into two contributions, one of them being possibly resonant. For a non-degenerate level $|a\rangle$:

$$(\delta E_a)^{surf} = \delta E_a^{QF} + \delta E_a^{res}$$
$$\delta E_a^{QF} = -\frac{1}{\pi} \sum_n \omega_{na} \mu_\alpha^{an} \mu_\beta^{na} \int_0^\infty d\xi \frac{G_{\alpha\beta}^R(\vec{r}_0, \vec{r}_0; i\xi)}{\xi^2 + \omega_{na}^2}. \quad (2.8a)$$
$$\delta E_a^{res} = -\sum_n \mu_\alpha^{an} \mu_\beta^{na} \text{Re} G_{\alpha\beta}^R(\vec{r}_o, \vec{r}_0; \omega_{na}) \theta(\omega_{an}). \quad (2.8b)$$

The quantum fluctuations part of the energy shift is present for all states and can be written as a function of the polarizability of the atom in the considered level $|a\rangle$, defined by

$$\alpha_{\alpha\beta}^a(t) = \frac{i}{\hbar} \langle a| [\mu_\alpha(t), \mu_\beta(0)]| a\rangle \theta(t)$$

and its Fourier Transform:

$$\alpha_{\alpha\beta}^a(\omega) = \int_{-\infty}^{+\infty} dt \alpha_{\alpha\beta}^a(t) e^{i\omega t}$$
$$= \lim_{\eta \to 0+} \left[\frac{2}{\hbar} \sum_n \frac{\omega_{na} \mu_\alpha^{an} \mu_\beta^{na}}{\omega_{na}^2 - (\omega + i\eta)^2} \right], \quad (2.9)$$

$$\delta E_a^{QF} = -\frac{1}{\pi}\sum_n \omega_{na}\mu_\alpha^{an}\mu_\beta^{na}\int_0^\infty d\xi \frac{G_{\alpha\beta}^R(\vec{r}_0,\vec{r}_0;i\xi)}{\xi^2+\omega_{na}^2}$$

$$= -\frac{\hbar}{2\pi}\int_0^\infty d\xi G_{\alpha\beta}^R(\vec{r}_0,\vec{r}_0;i\xi)\alpha_{\alpha\beta}^a(i\xi). \qquad (2.10)$$

The second contribution of equation (2.8) that is called resonant exists only for an excited state.

2.4.2 Surface shifts at finite temperature

The detailed calculation is given in Appendix A. The final result exhibits a kind of symmetry between the two interacting parts of the system, atom and surface, in such a way that their respective excitations contribute to the shift. We obtain:

$$\delta F_a = +\sum_{n>a}\mu_\alpha^{an}\mu_\beta^{na}\frac{1}{e^{\frac{\hbar\omega_{na}}{k_BT}}-1}\mathrm{Re}G_{\alpha\beta}(\omega_{na})\theta(\omega_{na})$$

$$-\sum_{n'<a}\mu_\alpha^{an'}\mu_\beta^{n'a}\frac{e^{\frac{\hbar\omega_{an'}}{k_BT}}}{e^{\frac{\hbar\omega_{an'}}{k_BT}}-1}\mathrm{Re}G_{\alpha\beta}(\omega_{an'})\theta(\omega_{an'})$$

$$-k_BT\sum_{k=0}^\infty {}'G_{\alpha\beta}(i\xi_k)\alpha_{\alpha\beta}^a(i\xi_k). \qquad (2.11)$$

The third term is a sum over the discrete frequencies: $\xi_k = ik2\pi k_BT/\hbar$, the prime after the sign sum meaning that one has to multiply by one half the first term $k=0$.

Formula (2.11) includes three distinct contributions:

(i) the first one can be written as:

$$\delta F_a^{abs} = +\sum_{n>a}\mu_\alpha^{an}\mu_\beta^{na}\bar{N}_{na}\mathrm{Re}G_{\alpha\beta}(\omega_{na})\theta(\omega_{na})$$

$$(2.11a)$$

with the photon thermal population factor $\bar{N}_{na}$ defined by equation (2.1), with $\omega_k = \omega_{na}$.

It corresponds to a *virtual dipole absorption* of the atom (it exists only for $\omega_n > \omega_a$), cancels at zero temperature (when $\bar{N}_{na} = 0$) and appears for $T \neq 0$. The physical process involved in this contribution can be viewed as a virtual energy exchange between a thermal excitation of the surface modes at frequency ω_{na} (proportional to $\bar{N}_{na}$) and an atomic dipole absorption. As will be seen below (Sect. 3.2), this term becomes resonant in presence of surface polaritons at frequency ω_{na} (i.e., poles of $G_{\alpha\beta}$). In the following, we will call this process a *coupling in absorption*;

(ii) the second contribution can be written as:

$$\delta F_a^{em} = -\sum_{n'<a}\mu_\alpha^{an'}\mu_\beta^{n'a}(\bar{N}_{an'}+1)\mathrm{Re}G_{\alpha\beta}(\omega_{an'})\theta(\omega_{an'}).$$

$$(2.11b)$$

It describes the contribution of *virtual atomic emission processes* (it exists for excited states only, with

$\omega_a > \omega_{n'}$), and is the exact symmetrical of the absorption term. The physical process is indeed a virtual energy exchange between an atomic dipole emission at frequency $\omega_{an'}$ and a simultaneous absorption in a surface-mode. Two terms contribute, one coming from virtual spontaneous emission processes (the only one remaining at $T = 0$), and the second one coming from emission processes stimulated by thermal photons (proportional to $\bar{N}_{an'}$). In the following, we will call this process a *coupling in emission*. Note also the sign change between absorption and emission contributions, which originates in the opposite dipole phases of the processes;

(iii) the third contribution of equation (2.11) originates in the non-resonant quantum fluctuations (QF) of the atomic dipole. This is the contribution derived long ago by McLachlan [16] for a ground state atom. McLachlan did not derive the resonant absorption term (2.11a), which comes from the contribution of the poles of the linear susceptibility located on the real axis (when one performs the integration in the complex plane — see Appendix A).

For $T \to 0$, the QF contribution can be written as the well-known integral over imaginary frequencies:

$$-k_BT\sum_{k=0}^\infty {}'G_{\alpha\beta}(i\xi_k)\alpha_{\alpha\beta}^a(i\xi_k)\xrightarrow[T\to 0\,\mathrm{K}]{}$$

$$-\frac{\hbar}{2\pi}\int_0^\infty d\xi G_{\alpha\beta}(i\xi)\alpha_{\alpha\beta}^a(i\xi). \quad (2.11c)$$

At $T = 0$, this quantity is the only one remaining along with the spontaneous emission contribution (Eqs. (2.8–2.10)).

All the formulae derived in this section apply to any number of surfaces with arbitrary forms, the remaining problem being to get the linear field susceptibility, G. In the next section, we restrict ourselves to the case of a single plane surface in the non-retarded regime.

3 Plane dielectric surface with one surface-polariton in the van der Waals regime

To illustrate the effect of finite temperature, let us consider a one surface-polariton model for a plane dielectric surface. This is the case of sapphire with its optical axis perpendicular to the surface, whose main surface-polariton at 12.2 μm is known to be resonant with a caesium transition at 12.15 μm [9,13,29]. In the case of a single surface-polariton resonance, the dielectric constant of the medium can be modelled as:

$$\varepsilon(\omega) = \eta\frac{\omega_L^2 - \omega^2 - i\omega\Gamma}{\omega_T^2 - \omega^2 - i\omega\Gamma} \qquad (3.1)$$

where ω_L and ω_T are the frequencies of the longitudinal and transverse bulk modes respectively. The frequency of the surface-polariton is then $\omega_s = \sqrt{(\eta\omega_L^2 + \omega_T^2)/(\eta+1)}$.

When we take as unit this frequency ω_s, we obtain for real frequencies:

$$\varepsilon(\omega) = \eta \frac{x_L^2 - x^2 - ix\delta}{x_T^2 - x^2 - ix\delta}, \text{ with } x = \frac{\omega}{\omega_s}, \ \delta = \frac{\Gamma}{\omega_s}.$$

For the QF contribution, we will have to use the dielectric constant along the imaginary frequency axis, taking $\omega = i\xi$, and the function $\varepsilon(i\xi)$ is then real, positive and monotonous. In the same way, we can take as unit the polariton frequency. That gives:

$$\varepsilon(i\xi) = \eta \frac{x_L^2 + y^2 + y\delta}{x_T^2 + y^2 + y\delta}, \text{ with: } y = \frac{\xi}{\omega_s}, \quad \delta = \frac{\Gamma}{\omega_s}.$$

Numerical values used in our model are given in Appendix B, where the comparison with Barton's approach [10] is done. This author works only in the electrostatic case, for a ground or excited atomic state. His result is given under the form of an integral over real frequencies. In this way, one could obtain neither the discrete sum over imaginary frequencies, nor the absorption or emission terms separately, which get important in the resonant case. However, we show that his result is the exact counterpart of the integral (2.7) in a one surface-polariton model and non-retarded case (Appendix B).

3.1 Non-retarded van der Waals regime at zero temperature: contribution to the surface-induced energy-shift originating in a transition such that $2\omega_{na}z_0/c \ll 1$

The linear susceptibility of the reflected field in the non-retarded van der Waals regime is well known ("electrostatic" approximation) [8]:

$$G_{xx,yy}^R(z_0, z_0; \omega) = \frac{1}{(2z_0)^3} \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} = \frac{1}{(2z_0)^3} R(\omega)$$

$$G_{zz}^R(z_0, z_0; \omega) = \frac{2}{(2z_0)^3} \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} = \frac{2}{(2z_0)^3} R(\omega) \quad (3.2)$$

where $\varepsilon(\omega)$ and $G_{\alpha\alpha}$ are complex functions of the frequency; R is the non-retarded surface response, $(\varepsilon - 1)/(\varepsilon+1)$ (i.e., static Fresnel coefficient).

From equations (2.8) and (3.2), one sees that, in the non-retarded regime, the contribution to the shift of a given transition will have the same z_0^{-3} dependence for the resonant or the non-resonant part. The reason is that we can keep the same "static" G function (3.2) to integrate over imaginary frequencies $i\xi$ when ξ is growing from zero to infinite.

In fact, into the integral (2.8a):

$$\delta E_a^{QF} = -\frac{1}{\pi} \sum_n \omega_{na} \mu_\alpha^{an} \mu_\beta^{na} \int_0^\infty d\xi \frac{G_{\alpha\beta}^R(\vec{r}_0, \vec{r}_0; i\xi)}{\xi^2 + \omega_{na}^2},$$

the factor $e^{-2\xi z_0/c}$ appearing in the retarded susceptibility $G_{\alpha\beta}^R(\vec{r}_0, \vec{r}_0; i\xi)$ — see [7,8] —, as well as the Lorentzian

form of the atomic polarizability will cut the integration over ξ at frequencies smaller than ω_{na}, where the static approximation (3.2) is valid.

For a *coupling in absorption* ($\omega_{na} > 0$) and within our one-polariton model of the surface, the non-resonant part of the shift δE_a^{QF} can be written:

$$\delta E^{QF}(na) = -\frac{(|\mu_x^{an}|^2 + |\mu_y^{an}|^2 + 2|\mu_z^{an}|^2)}{(2z_0)^3}$$

$$\times \frac{1}{\pi} \int_0^\infty du \frac{R(iux_{na})}{1 + u^2} \quad (3.3)$$

with: $u = \xi/\omega_{na}$, $x_{na} = \omega_{na}/\omega_S > 0$. So $iux_{na} = i\xi/\omega_S$ is the imaginary frequency in unit ω_S.

Splitting the contributions of the dipole-components parallel and perpendicular to the surface with $(|\mu_x^{an}|^2 + |\mu_y^{an}|^2) = |\mu_\parallel^{an}|^2$, we obtain:

$$\delta E_{\parallel,z}^{QF}(x_{na}) = -E_{\parallel,z}^{na} \left[\frac{1}{\pi} \int_0^\infty du \frac{R(iux_{na})}{1 + u^2} \right] \quad (3.4)$$

where

$$E_\parallel^{na} = \frac{|\mu_\parallel^{an}|^2}{(2z_0)^3}; \quad E_z^{na} = \frac{2|\mu_z^{an}|^2}{(2z_0)^3}. \quad (3.5)$$

These energies are of the same order of magnitude (about $2\,\text{kHz}(\mu m)^3$, for a ground state).

For a *coupling in emission* ($\omega_{an} > 0$): one obtains for the total shift, in the non-retarded regime, from equations (2.8a, 2.8b):

$$\delta E_{\parallel,z}(x_{an}) = E_{\parallel,z}^{an} \left[-\text{Re}[R(x_{an})] + \frac{1}{\pi} \int_0^\infty du \frac{R(iux_{an})}{1 + u^2} \right] \quad (3.6)$$

where we have now: $x_{an} = \omega_{an}/\omega_S > 0$.

3.2 Van der Waals regime at finite temperature: contribution to the surface-induced energy-shift coming from a transition such that $2\omega_{na}z_0/c \ll 1$

From definition (2.9), one has for imaginary frequencies:

$$\alpha_{\alpha\beta}^a(i\xi) = \frac{2}{\hbar} \sum_n \frac{\omega_{na} \mu_\alpha^{an} \mu_\beta^{na}}{\omega_{na}^2 + \xi^2}.$$

The contribution of the transition $a \to n$ ($\omega_{na} > 0$) in absorption will be then (Eq. (2.11))

$$\delta F^{abs}(\omega_{na}) = +\mu_\alpha^{an} \mu_\beta^{na} \left\{ \frac{1}{e^{\frac{\hbar\omega_{na}}{k_B T}} - 1} \text{Re} G_{\alpha\beta}(\omega_{na}) \right.$$

$$\left. -\frac{k_B T}{\hbar} \sum_{k=0}^\infty {}' G_{\alpha\beta}(i\xi_k) \frac{2\omega_{na}}{\omega_{na}^2 + \xi_k^2} \right\} \quad (3.7)$$

with $\xi_k = ik(2\pi k_B T/\hbar)$.

And for a transition $a \to n'$ $(\omega_{an'} > 0)$ in emission:

$$\delta F^{em}(\omega_{an'}) = -\mu_\alpha^{an'}\mu_\beta^{n'a}\left\{\frac{e^{\frac{\hbar\omega_{an'}}{k_B T}}}{e^{\frac{\hbar\omega_{an'}}{k_B T}}-1}\mathrm{Re}G_{\alpha\beta}(\omega_{an'})\right.$$
$$\left. -\frac{k_B T}{\hbar}\sum_{k=0}^{\infty}{}' G_{\alpha\beta}(i\xi_k)\frac{2\omega_{an'}}{\omega_{an'}^2+\xi_k^2}\right\}. \quad (3.8)$$

For a transition satisfying the condition $2\omega_{na}z_0/c \ll 1$, the real part of the linear susceptibility at real frequency will be of the form $1/z_0^3$ (3.2). However, in the discrete sum, as it was the case in the integral (2.8a), the frequency is increasing with k; then one has to consider the retarded susceptibility at imaginary frequencies, which involves the exponential factor $e^{-2\xi z_0/c}$, multiplied by a Lorentzian lineshape of width ω_{na}. The non-retarded limit can be considered as a first approximation for G at all values of ξ_k,

$$G_{xx,yy}^R(z_0,z_0;i\xi) = \frac{1}{(2z_0)^3}\frac{\varepsilon(i\xi)-1}{\varepsilon(i\xi)+1}.$$

But this is actually valid only for $z_0 \ll c/2\omega_{na}$, and then obtained only when one keeps all the k-terms in the sum.

3.2.1 Quantum fluctuations contribution

One can see that the discrete sum in equations (3.7, 3.8) lies always between two "static" limits, both in $1/z_0^3$, namely the first term $k = 0$, which is the long-range limit of the sum at non-zero temperature, expressed in function of the static value $G(0)$, and the total sum using non-retarded G. For example, for the component of the dipole parallel to the surface, the contribution to the shift of the discrete sum for one given transition obeys to:

$$\frac{k_B T}{\hbar\omega_{na}}\frac{|\mu_\parallel^{an}|^2}{(2z_0)^3}\frac{\varepsilon(0)-1}{\varepsilon(0)+1} \le \frac{k_B T}{\hbar}\sum_{k=0}^{\infty}{}' G_{xx}(i\xi_k)\frac{2\omega_{na}|\mu_\parallel^{an}|^2}{\omega_{na}^2+\xi_k^2}$$
$$\le \frac{k_B T}{\hbar\omega_{na}}\frac{|\mu_\parallel^{an}|^2}{(2z_0)^3}r[T,\omega_{na}] \quad (3.9)$$

with

$$r[T,\omega_{na}] = \sum_{k=0}^{\infty}{}' \frac{\varepsilon(i\xi_k)-1}{\varepsilon(i\xi_k)+1}\frac{2\omega_{na}^2}{\omega_{na}^2+\xi_k^2}$$

(let us remind that the prime after the sign sum means that the first $k = 0$ term is weighted by a factor $1/2$).

It is seen that if the temperature is high enough and the distance not too small, the $k = 1$ term which includes the exponential $e^{-2\frac{2\pi k_B T}{\hbar}z_0/c}$ vanishes, as well as the $k > 1$ contributions. Only the $k = 0$ term gives a significant contribution.

At room temperature, this first term:

$$\frac{k_B T}{\hbar\omega_{na}}\frac{1}{(2z_0)^3}\frac{\varepsilon(0)-1}{\varepsilon(0)+1}$$
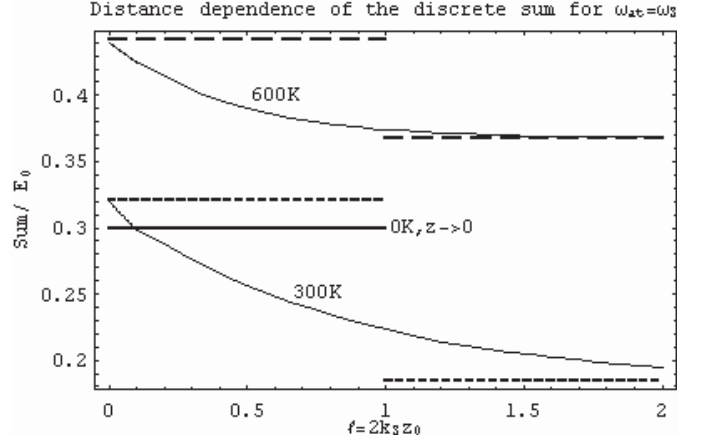
Fig. 1. Variation with the distance of the non-resonant part of the free energy-shift (QF) normalized with respect to the vdW shift of the same transition for a perfect reflector, $E_0 = |\mu^{an}|^2/(2z_0)^3$. One uses a normalized atom-surface distance, $\ell = 2k_S z_0 = (4\pi/\lambda_S)z_0$. In our single polariton model, $\ell \approx 1$ when $z_0 = 1$ μm for the sapphire surface-polariton at $\lambda_S = 12.2$ μm. The dotted horizontal lines give the asymptotic values at $z_0 \to 0$ (total electrostatic sum) and at $z_0 \to \infty$ ($k = 0$ term in Eq. (3.9)) for two different temperatures. The full curves are deduced from exact retarded susceptibilities. The full horizontal line gives the asymptotic value at $z_0 \to 0$ for $T = 0$ K.

represents for all transitions the long range limit of the discrete sum, the upper limit being the non-retarded shift (see Fig. 1).

In most of the experimental cases, one operates between 300 K and 600 K, and atoms are tested at distances of the order of 100 nm or less from the dielectric surface, for transitions which satisfy $k_B T \approx \hbar\omega_{na}$. For example, the caesium transition at 12.15 μm $(7P_{1/2}–6D_{3/2})$, resonant with a surface-mode of sapphire, is such that: $\theta = k_B T/\hbar\omega_S \approx 0.25$ at room temperature. For CaF_2 or BaF_2, the caesium $8P_{3/2}$ level has a resonant transition at 40 μm for which: $\theta \approx 1$ at room temperature [29,30] (Fig. 2).

In a first approach, for atoms very near of the surface and at usual temperatures, we can replace the discrete sum by its upper limit, easier to calculate, but one has always to add a term with the real part of G (Eq. (3.7)).

3.2.2 Total free-energy-shift

From equations (3.7, 3.8) we obtain, for a virtual coupling in absorption, *in the near-field case and at usual temperatures in spectroscopy experiments*:

$$\delta F_{xx}^{abs}(\omega_{na}) = \mu_x^{an}\mu_x^{na}\frac{1}{(2z_0)^3}\left(\frac{1}{e^{\frac{\hbar\omega_{na}}{k_B T}}-1}\mathrm{Re}\left[\frac{\varepsilon(\omega_{na})-1}{\varepsilon(\omega_{na})+1}\right]\right.$$
$$\left. -\frac{k_B T}{\hbar\omega_{na}}r[T,\omega_{na}]\right). \quad (3.10)$$

Values of $\theta = \frac{k_B T}{h \nu_S}$ for the 12μm surface-polariton of Sapphire
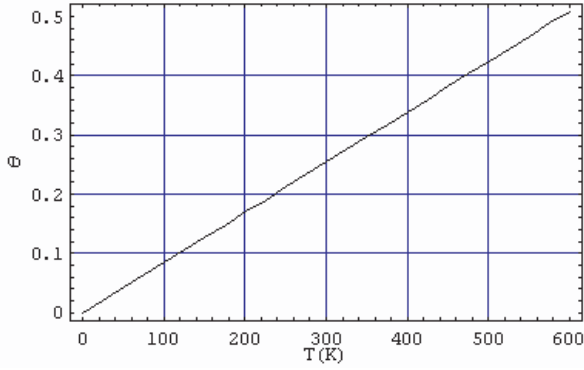
Values of $\theta = \frac{k_B T}{h \nu_S}$ for the 40μm surface-polariton of CaF$_2$
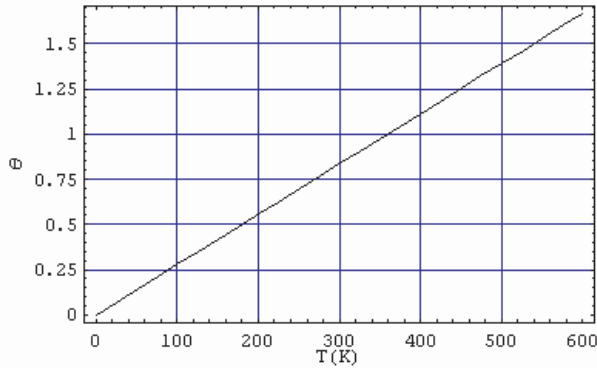
Fig. 2. Temperature dependence of parameter θ in the case of Al$_2$O$_3$ and CaF$_2$.

In the same way, for a virtual coupling in emission:

$$\delta F_{xx}^{em}(\omega_{an'}) = \mu_x^{an'} \mu_x^{n'a} \frac{1}{(2z_0)^3}$$

$$\times \left(-\frac{e^{\frac{\hbar \omega_{an'}}{k_B T}}}{e^{\frac{\hbar \omega_{an'}}{k_B T}} - 1} \mathrm{Re} \left[\frac{\varepsilon(\omega_{an'}) - 1}{\varepsilon(\omega_{an'}) + 1} \right] + \frac{k_B T}{\hbar \omega_{an'}} r[T, \omega_{an'}] \right).$$

$$(3.11)$$

In Figures 3 and 4, the variations of the atomic energy shift are represented near the resonant coupling, in the frequency domain (Fig. 3) and the temperature domain (Fig. 4). These graphs show off the importance of virtual absorption or emission resonant couplings in the amplitude and sign of surface-induced level shifts, as well as the prominent influence of surface temperature on absorption couplings.

A noteworthy prediction of this study is to pave the way to a control of the sign of vW forces, via temperature monitoring, as well as *cancelling those forces*. As shown in Figure 4, for a *resonant coupling in absorption*, when the atom resonance is located below the surface-polariton resonance frequency ($\omega_{at} = 0.99\omega_S$), the vW forces cancel and reverse for $k_B T \approx 0.3\hbar\omega_S$. Indeed, at very low temperatures ($T = 0$), there is no resonant coupling: the vW forces originate only in quantum fluctuations and are

Free-energy shift dependence on the transition frequency
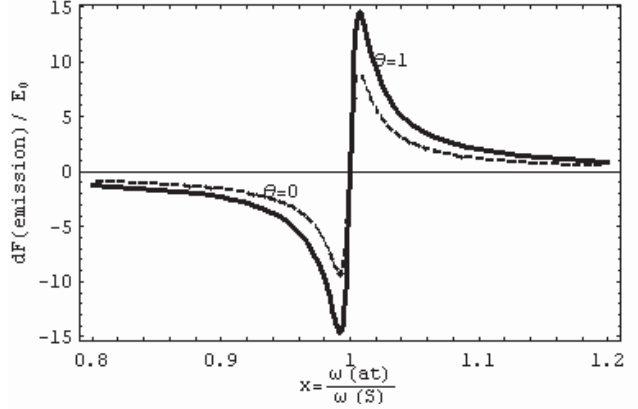
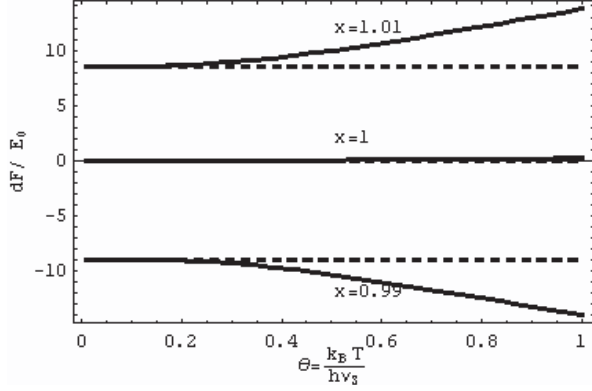Free-energy shift dependence on the transition frequency
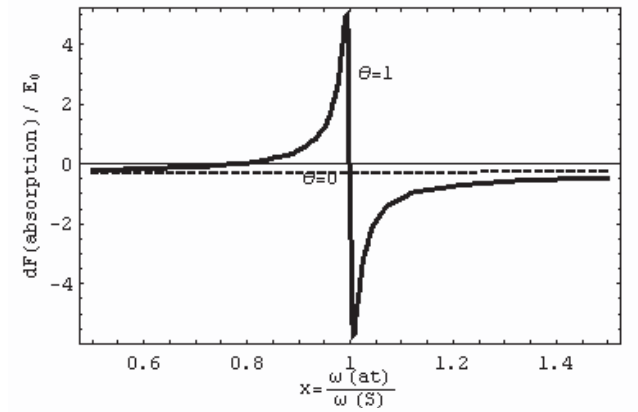
Fig. 3. Frequency dispersion characteristics of the free-energy shift for absorption or emission couplings at two different temperatures. Note that the resonance for a virtual coupling in absorption appears only for finite temperatures. The resonance sign is opposite to that of the resonance induced by virtual emission couplings.

purely attractive. For increasing temperatures, the atom-surface resonant coupling gets predominant. Since the relative phases of the atom dipole and surface polariton mode (driven by temperature excitations) are such that this resonant contribution is repulsive, the surface forces vanish for a given temperature and then get repulsive (Fig. 4; absorption couplings, $x = 0.99$).

Those results, obtained from equations (3.10, 3.11) for a single resonance model, would not be basically modified for a real multi-resonant dielectric surface. As a practical example, for the 12.2 μm sapphire surface-polariton at a temperature $T = 450$ K, the reduced temperature factor is $\theta \sim 0.4$, and the mode occupation number is $\bar{N}_{an'} = 0.09$, thus multiplying the dielectric image coefficient (in emission) of Cs (6D$_{3/2}$) at 12.15 μm by a factor 1.09. This yields, for the contribution of the 6D$_{3/2}$–7P$_{1/2}$ transition to the sapphire/6D$_{3/2}$ C_3 coefficient, the theoretical value of –119 kHz (μm)^3, instead of –109 at zero temperature (see Ref. [13], Tab. 1).

Contribution of virtual emission couplings near resonance

Contribution of virtual absorption couplings near resonance
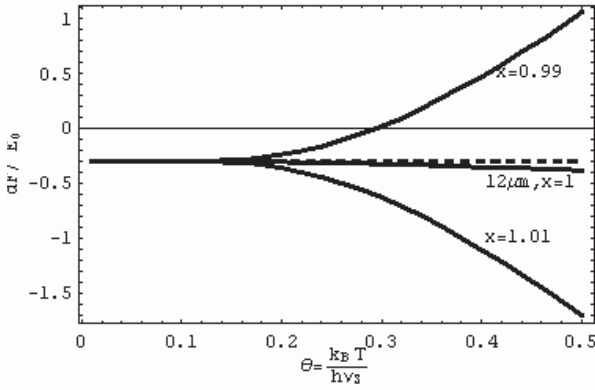
Fig. 4. Temperature-dependence of the free-energy shift for three different atomic resonances frequencies. $x = \omega_{at}/\omega_S = \nu_{at}/\nu_S$ is the transition frequency in unit of surface-polariton-frequency. $\theta = k_B T/\hbar\omega_S = k_B T/h\nu_S$ is the "temperature" in unit of polariton energy quantum. Note the change of sign between $T = 300$ K ($\theta = 0.25$) and $T = 600$ K ($\theta = 0.5$) in the case of absorption couplings with $x = 0.99$. The numerical values used in these figures correspond to the sapphire polariton at 12.2 μm.

For very high temperatures (i.e., $k_B T \gg \hbar\omega_{na}$), one can replace $r[T, \omega_{na}]$ by its first term: $[\varepsilon(0) - 1]/[\varepsilon(0) + 1]$ in equations (3.10, 3.11) and we would obtain *in the near-field case* a $1/z_0^3$ dependence, at first order in $\hbar\omega/k_B T$:

$$\delta F_{xx}^{abs}(a, \omega_{na} > 0) \approx + \mu_x^{an} \mu_x^{na} \frac{1}{(2z_0)^3} \frac{k_B T}{\hbar\omega_{na}}$$
$$\times \left[\mathrm{Re} \left[\frac{\varepsilon(\omega_{na}) - 1}{\varepsilon(\omega_{na}) + 1} \right] - \frac{\varepsilon(0) - 1}{\varepsilon(0) + 1} \right] \quad (3.12)$$

$$\delta F_{xx}^{em}(a, \omega_{na'} > 0) \approx \mu_x^{an} \mu_x^{na} \frac{1}{(2z_0)^3} \frac{k_B T}{\hbar\omega_{an'}}$$
$$\times \left[\mathrm{Re} \left[-\frac{\varepsilon(\omega_{an'}) - 1}{\varepsilon(\omega_{an'}) + 1} \right] + \frac{\varepsilon(0) - 1}{\varepsilon(0) + 1} \right]. \quad (3.13)$$

At first order in $\hbar\omega/k_B T$, it is linear on temperature, except for very low transition frequency, where one has

$$\mathrm{Re} \left[\frac{\varepsilon(\omega_{na} \approx 0) - 1}{\varepsilon(\omega_{na} \approx 0) + 1} \right] \approx \frac{\varepsilon(0) - 1}{\varepsilon(0) + 1},$$

for which this first order term vanishes. But our assumptions to have an adiabatic experiment cannot hold in this high temperature limit (see Sect. 2.2).

We can notice that *in the long-distance case at finite temperature*, there is always a $1/z_0^3$ term (coming from the term: $k = 0$) but also, coming from the real part, a $1/z_0$ or $1/z_0^2$ oscillating term depending on the observed dipole-component. This could explain the very long range interaction observed in the Sokolov experiment [31] at room temperature, at least if the metal of the slit has surface plasmon resonances in the high frequency range. This retarded interaction at finite temperature is examined in details in our next article.

4 Conclusion

In this article we have derived a general expression giving the energy shift of a quantum level of an atom interacting with material surfaces in thermal equilibrium at temperature T. This study is valid for all types and geometries of surfaces, considers any atomic energy level and takes into account field propagation effects. The case of non-retarded atom-surface interactions has been analysed here in more detail, and explicit expressions have been derived for the energy of atomic ground-state or excited states interacting with dispersive plane surfaces. In the derivation of the surface-induced energy shift, emphasis has been put on a mathematical form underlining the physical viewpoint and allowing one to discriminate between the various physical processes.

First, at vanishing temperatures, two already well-known phenomena in atom-surface interactions are discriminated, on one hand zero-point quantum fluctuation processes, and on the other hand a resonant van der Waals coupling in the case of an excited atom in resonance with surface-polariton modes. At finite temperatures, these processes are modified, in particular for the resonant atom-surface coupling which is amplified by the emergence of thermal photons stimulating virtual emission processes. In addition, our theoretical approach shows off a new type of resonant coupling process in which a thermal quantum excitation of a surface mode resonantly couples to an atomic absorption channel. This process has the noticeable property of applying to a ground state also. As any resonant coupling between two oscillators, it allows one to enhance and eventually phase-reverse the interaction potential, making repulsive the van der Waals long-range forces acting on ground-state atoms. In this way, sign and amplitude of vW forces could be precisely controlled via surface temperature monitoring. The observation of such a temperature-controlled resonant coupling would be a direct test of the quantum nature of surface

polaritons [32]. This study can also be applied to metallic surfaces exhibiting surface plasmon resonances. However, in that case, some additional features of the material should be taken into account, like the spatial dispersion of the material response (i.e., wave vector dependence of the permittivity due to non-local electronic response).

The results discussed in detail in this article are valid in the non-retarded limit, which means such conditions as $z \ll \lambda_{at}/2\pi$ (λ_{at}, characteristic atomic wavelength). These conditions represent severe restrictions to the validity range of atom-surface distances. For larger distances, retardation effects (Casimir regime) should be taken into account, as will be discussed in a forthcoming article. Retardation effects get in particular important when one considers atoms confined between two dielectric walls (dielectric nano-cavity [33]). On the other hand, for very small distances ($z < 1$ nm), the details of the surface (roughness, etc.) become prominent, as well as higher-order contributions to the vW interaction (dipole-quadrupole, etc.), and electronic cloud overlapping. The comprehension of atom-surface interactions at all distances and any temperature is central to the understanding of the nature of these fundamental forces. Every advance in this field allows one to set stronger constraints on the existence of new weak forces predicted by unification models in particle physics. They are also a key point in the operation of nanometric devices.

Appendix A: Temperature dependence of the level-shift of an atomic-state near an interface

In a second-order perturbation calculation and using the fluctuation-dissipation theorem, one finds, for the contribution of the reflected thermal field to the free-energy-shift of the a-atomic state:

$$\delta F_a = -\frac{1}{\pi}\mathsf{P}\left[\sum_n \mu_\alpha^{an}\mu_\beta^{na}\int_{-\infty}^{+\infty}d\omega\frac{G''_{\alpha\beta}(\omega)}{(1-e^{-\frac{\hbar\omega}{k_BT}})(\omega+\omega_{na})}\right].$$
(A.1)

(In this part of the calculation, we will not write the Greek subscripts — which indicate Cartesian components — for the linear susceptibility $\overleftrightarrow{G}(\omega) = \overleftrightarrow{G}'(\omega) + i\overleftrightarrow{G}''(\omega)$ of the reflected field.)

The principal part comes only from: $\omega + \omega_{na} \neq 0$. When $\omega = 0$, $G''(0) = 0$, because it is an odd function of frequency, and the integral remains finite for this value of omega. On the other hand, the poles of G'' correspond to the poles of Fresnel coefficients which give the dispersion relation of surface modes. In our model (see Appendix B),

they cannot be real when one introduces dissipation into the medium.

Let us calculate first the integral:

$$\mathsf{P}\int_{-\infty}^{+\infty}d\omega\frac{G''(\omega)}{(1-e^{-\frac{\hbar\omega}{KT}})(\omega+\omega_{na})} =$$

$$\lim_{\eta\to 0+}\int_{-\infty}^{+\infty}d\omega\frac{G''(\omega)}{(1-e^{-\frac{\hbar\omega}{k_BT}})(\omega+\omega_{na}+i\eta)} + i\pi\frac{G''(-\omega_{na})}{1-e^{\frac{\hbar\omega_{na}}{k_BT}}}$$

which is the sum of two terms I and J:

$$I(\omega_{na}) = \lim_{\eta\to 0+}\int_{-\infty}^{+\infty}d\omega\frac{G''(\omega)}{(1-e^{-\frac{\hbar\omega}{k_BT}})(\omega+\omega_{na}+i\eta)}$$

$$= \lim_{\eta\to 0+}I(\omega_{na}+i\eta)$$

$$J(\omega_{na}) = i\pi\frac{G''(-\omega_{na})}{1-e^{\frac{\hbar\omega_{na}}{k_BT}}} = -\pi\frac{iG''(\omega_{na})}{1-e^{\frac{\hbar\omega_{na}}{k_BT}}}$$

G'' is an odd function of frequency and $\omega_{na} = (E_n - E_a)/\hbar$ can be either >0 or <0, (if state $|a\rangle$ is an excited state).

In the following, we write: $\Omega_{na} = \omega_{na} + i\eta$, ($\eta$ being positive), and we introduce functions of defined parity, using:

$$\frac{1}{1-e^{-x}} = \frac{1}{2}\left(1 + \coth\frac{x}{2}\right),$$
$$\frac{1}{\omega+\Omega_{na}} = \frac{\Omega_{na}}{\Omega_{na}^2 - \omega^2} - \frac{\omega}{\Omega_{na}^2 - \omega^2},$$

and the parity-properties of the field-susceptibility: $G(\omega) = G'(\omega) + iG''(\omega)$, G' even and G'' odd, to write: $G''(\omega) = [G(\omega) - G(-\omega)]/2i$.

We obtain:

$$I(\Omega_{na}) = \int_{-\infty}^{+\infty}d\omega\frac{G''(\omega)}{(1-e^{-\frac{\hbar\omega}{k_BT}})(\omega+\Omega_{na})}$$

$$= \frac{1}{2}\int_{-\infty}^{+\infty}d\omega\frac{G''(\omega)}{(\omega+\Omega_{na})} + \frac{1}{2}\int_{-\infty}^{+\infty}d\omega\frac{G''(\omega)}{(\omega+\Omega_{na})}$$

$$\times \coth\frac{\hbar\omega}{2k_BT}$$

$$I(\Omega_{na}) = I_1(\Omega_{na}) + I_2(\Omega_{na})$$

$$I_1(\Omega_{na}) = \frac{1}{4i} \int\limits_{-\infty}^{+\infty} d\omega \frac{G(\omega)}{\omega + \Omega_{na}} - \frac{1}{4i} \int\limits_{-\infty}^{+\infty} d\omega \frac{G(-\omega)}{\omega + \Omega_{na}}$$

$$= \frac{1}{4i} \int\limits_{-\infty}^{+\infty} d\omega \frac{G(\omega)}{\omega + \Omega_{na}} - \frac{1}{4i} \int\limits_{-\infty}^{+\infty} d\omega' \frac{G(\omega')}{-\omega' + \Omega_{na}}$$

$$I_1(\Omega_{na}) = \frac{1}{4i} \int\limits_{-\infty}^{+\infty} d\omega G(\omega) \left(\frac{1}{\omega + \Omega_{na}} + \frac{1}{\omega - \Omega_{na}} \right)$$

$$= \frac{2i\pi}{4i} G(\Omega_{na}) = \frac{\pi}{2} G(\Omega_{na}). \tag{A.2}$$

To get (A.2), we close the integral in the upper ω-complex plane (see Fig. 5). The only pole inside the integral contour is $\omega = \Omega_{na} = \omega_{na} + i\eta$. G also can have poles, but only in the lower plane, as we will see when the dissipation into the dielectric is introduced via an imaginary part of the dielectric constant.

Keeping only the even part of the integrand in I_2, we can write:

$$I_2(\Omega_{na}) = \frac{1}{2} \int\limits_{-\infty}^{+\infty} d\omega \frac{G''(\omega)}{\omega + \Omega_{na}} \coth \frac{\hbar\omega}{2k_BT}$$

$$= \frac{1}{2} \int\limits_{-\infty}^{+\infty} d\omega \frac{\Omega_{na}}{\Omega_{na}^2 - \omega^2} G''(\omega) \coth \frac{\hbar\omega}{2k_BT}$$

$$I_2(\Omega_{na}) = \frac{1}{4i} \int\limits_{-\infty}^{+\infty} d\omega \frac{\Omega_{na}}{\Omega_{na}^2 - \omega^2} G(\omega) \coth \frac{\hbar\omega}{2k_BT}$$

$$- \frac{1}{4i} \int\limits_{-\infty}^{+\infty} d\omega \frac{\Omega_{na}}{\Omega_{na}^2 - \omega^2} G(-\omega) \coth \frac{\hbar\omega}{2k_BT}$$

$$I_2(\Omega_{na}) = \frac{1}{2i} \int\limits_{-\infty}^{+\infty} d\omega \frac{\Omega_{na}}{\Omega_{na}^2 - \omega^2} G(\omega) \coth \frac{\hbar\omega}{2k_BT}$$

$$I_2(\Omega_{na}) = -\frac{\pi}{2} G(\Omega_{na}) \coth \frac{\hbar\Omega_{na}}{2k_BT}$$

$$+ \pi \sum_{k=0}^{\infty} {}' \frac{2k_BT}{\hbar} G(i\xi_k) \frac{\Omega_{na}}{\Omega_{na}^2 + \xi_k^2}. \tag{A.3}$$

The last formula is obtained after integration in the complex-plane on the same contour as for $I_1(\Omega_{na})$ (Fig. 5), but now, the integrand has several poles: $+\Omega_{na}$, near the real axis, and $\omega_k = i\xi_k = ik(2\pi k_BT/\hbar)$, on the imaginary axis. The prime after the sign sum is for taking a factor $1/2$ for $k = 0$.
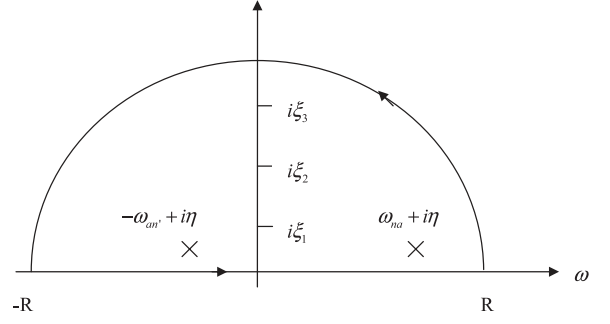
Fig. 5. Integration scheme in the ω-complex plane. The integration over the closed contour is the sum of an integral over real frequencies which gives the integral of equation (A.2) when $R \to \infty$, and of an integral over the half-circle which tends to zero when $R \to \infty$.

Finally:

$$I(\Omega_{na}) = I_1(\Omega_{na}) + I_2(\Omega_{na})$$

$$= \pi \left[-\frac{1}{2} G(\Omega_{na}) \coth \frac{\hbar\Omega_{na}}{2k_BT} \right.$$

$$\left. + \sum_{k=0}^{\infty} {}' \frac{2k_BT}{\hbar} G(i\xi_k) \frac{\Omega_{na}}{\Omega_{na}^2 + \xi_k^2} \right] + \frac{\pi}{2} G(\Omega_{na}) \tag{A.4}$$

at temperature T.

(Now, we write again the subscripts α, β, to be summed over when repeated)

$$\delta F_a = -\frac{1}{\pi} \sum_n \mu_\alpha^{an} \mu_\beta^{na} [I_{1\alpha\beta}(\omega_{na}) + I_{2\alpha\beta}(\omega_{na}) + J_{\alpha\beta}(\omega_{na})].$$

Taking the limit $\eta \to 0+$ in (A.2, A.3), one obtains:

$$I_{1\alpha\beta}(\omega_{na}) = \frac{\pi}{2} G_{\alpha\beta}(\omega_{na})$$

$$I_{2\alpha\beta}(\omega_{na}) = -\frac{\pi}{2} G_{\alpha\beta}(\omega_{na}) \coth \frac{\hbar\omega_{na}}{2k_BT}$$

$$+ \pi \sum_{k=0}^{\infty} {}' \frac{2k_BT}{\hbar} G_{\alpha\beta}(i\xi_k) \frac{\omega_{na}}{\omega_{na}^2 + \xi_k^2}$$

$$J_{\alpha\beta}(\omega_{na}) = i\pi \frac{G''_{\alpha\beta}(-\omega_{na})}{1 - e^{\frac{\hbar\omega_{na}}{KT}}} = -\frac{iG''_{\alpha\beta}(\omega_{na})}{1 - e^{\frac{\hbar\omega_{na}}{k_BT}}}$$

$$= -[G_{\alpha\beta}(\omega_{na}) - G'_{\alpha\beta}(\omega_{na})] \frac{\pi}{2}$$

$$\times \left(1 - \coth \frac{\hbar\omega_{na}}{2k_BT} \right)$$

$$\delta F_a = -\sum_n \mu_\alpha^{an} \mu_\beta^{na} \left[\frac{G'_{\alpha\beta}(\omega_{na})}{1 - e^{\frac{\hbar\omega_{na}}{k_BT}}} \right.$$

$$\left. + \sum_{k=0}^{\infty} {}' \frac{2k_BT}{\hbar} G_{\alpha\beta}(i\xi_k) \frac{\omega_{na}}{\omega_{na}^2 + \xi_k^2} \right]. \tag{A.5}$$

We can introduce the polarizability of state $|a\rangle$ at imaginary frequency:

$$\alpha_{\alpha\beta}^a(i\xi) = \frac{2}{\hbar}\sum_n \frac{\omega_{na}\mu_\alpha^{an}\mu_\beta^{na}}{\omega_{na}^2 + \xi^2},$$

to obtain finally:

$$\delta F_a = -\sum_n \mu_\alpha^{an}\mu_\beta^{na}\frac{G'_{\alpha\beta}(\omega_{na})}{1 - e^{\frac{\hbar\omega_{na}}{k_B T}}}$$
$$- k_B T \sum_{k=0}^{\infty}{}' G_{\alpha\beta}(i\xi_k)\alpha_{\alpha\beta}^a(i\xi_k). \quad \text{(A.6)}$$

To introduce positive frequencies only and then numbers of occupation of the field modes, we re-write it in separating the couplings in emission ($n' < a$) from those in absorption ($n > a$):

$$\delta F_a = +\sum_{n>a}\mu_\alpha^{an}\mu_\beta^{na}\frac{1}{e^{\frac{\hbar\omega_{na}}{k_B T}} - 1}\mathrm{Re}G_{\alpha\beta}(\omega_{na})\theta(\omega_{na})$$
$$- \sum_{n'<a}\mu_\alpha^{an'}\mu_\beta^{n'a}\frac{e^{\frac{\hbar\omega_{an'}}{k_B T}}}{e^{\frac{\hbar\omega_{an'}}{k_B T}} - 1}\mathrm{Re}G_{\alpha\beta}(\omega_{an'})\theta(\omega_{an'})$$
$$- k_B T \sum_{k=0}^{\infty}{}' G_{\alpha\beta}(i\xi_k)\alpha_{\alpha\beta}^a(i\xi_k). \quad \text{(A.7)}$$

In the limit of low temperature, if the two functions G and α do not vary too much on the interval, $d\xi = 2\pi k_B T/\hbar$, we recover the formula for zero temperature:

With:

$$\omega_k = i\xi_k = ik\frac{2\pi k_B T}{\hbar},$$

$$d\xi = \xi_1 - \xi_0 = \xi_1 = \xi_{k+1} - \xi_k = \frac{2\pi k_B T}{\hbar}$$

$$- k_B T \sum_{k=0}^{\infty}{}' G_{\alpha\beta}(i\xi_k)\alpha_{\alpha\beta}^a(i\xi_k) \xrightarrow[T\to 0\,\mathrm{K}]{}$$
$$- \frac{\hbar}{2\pi}\int_0^{\infty}d\xi G_{\alpha\beta}(i\xi)\alpha_{\alpha\beta}^a(i\xi).$$

Here we have to recall that, in all these cases, the term in $G(i\xi)$ which dominates the variation of G with ξ is exponential: $e^{-\frac{2\xi z_0}{c}}$, where z_0 is the distance of the atom to the surface ($2z_0$, distance between the atom and its image in the static limit). This exponential term will not vary too much on a frequency-interval $2\pi k_B T/\hbar$ if the condition: $k_B T \ll \hbar c/4\pi z_0$ holds.

On the other hand, the polarizability (of Lorentzian form: $\omega_{na}/(\xi^2 + \omega_{na}^2)$) will not vary too much on the same interval if the condition $k_B T \ll \hbar\omega_{na}$ is verified for every positive frequency of transition of the atom $\omega_{an'}$ or ω_{na}.

If the two conditions hold, one can use the low-temperature formula and then we have a dependence in $1/z_0^3$ or a $1/z_0^4$ for the contribution of a given transition

to the shift, depending on: $c/2z_0 \gg \omega_{na}$ (near field limit), or $c/2z_0 \ll \omega_{na}$ (far field limit).

For example, in the case of an atomic transition at 40 μm and a temperature of 400 K, for distances of 100 nm, we are in the case $k_B T \approx \hbar\omega_{an}$, so one has: $\hbar c/4\pi z_0 \gg k_B T \approx \hbar\omega_{an} \approx \hbar 2\pi c/\lambda_{na}$ if $z_0 \ll \lambda_{na}/8\pi^2 \approx 0.5$ μm, which will be a condition more restrictive than: $c/2z_0 \gg \omega_{na} = 2\pi c/\lambda_{na}$ if $z_0 \ll \lambda_{na}/4\pi \approx 3$ μm.

Even if one can consider being in the near-field limit, one needs to take the finite T formula to express the free-energy shift for an experiment at 600 K.

Appendix B: Comparison with the Barton's work [10] in the electrostatic limit

Barton gives, for the increase of the free-energy shift (relatively to the $T = 0$ case) of any atomic level "a", in the case of an isotropic medium ([10], Eq. (7.19)):

$$\delta F_a^B(T) = -\frac{\sigma^2}{8z^3}\sum_n \left(2\left|\mu_z^{na}\right|^2 + \left|\mu_\parallel^{na}\right|^2\right)$$
$$\times \int_0^{\infty}d\omega\left(\frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}\right)\frac{\omega_{na}\omega}{\omega_{na}^2 - \omega^2}g(\omega,\omega_s) \quad \text{(B.1)}$$

where:

$$g(\omega,\omega_s) = \frac{(2\Gamma/\pi)\omega_s^2}{(\omega_s^2 - \omega^2)^2 + \omega^2\Gamma^2} \quad \text{(B.2)}$$

and:

$$\sigma^2 = \frac{\varepsilon(0) - 1}{\varepsilon(0) + 1} - \frac{\varepsilon(\infty) - 1}{\varepsilon(\infty) + 1}. \quad \text{(B.3)}$$

This makes use of a one surface-polariton model with a dielectric constant satisfying (Eq. (3.1)):

$$\varepsilon(\omega) = \eta\frac{\omega_L^2 - \omega^2 - i\omega\Gamma}{\omega_T^2 - \omega^2 - i\omega\Gamma}. \quad \text{(B.4)}$$

The frequency of the surface-polariton being then:

$$\omega_s = \sqrt{\frac{\eta\omega_L^2 + \omega_T^2}{\eta + 1}}.$$

We want to make a link with the formula (2.7):

$$\delta F_a(T) = -\frac{1}{\pi}\mathsf{P}\left[\sum_n \mu_\alpha^{an}\mu_\beta^{na}\int_{-\infty}^{+\infty}d\omega\frac{G''_{\alpha\beta}(\omega)}{(1 - e^{-\frac{\hbar\omega}{k_B T}})(\omega + \omega_{na})}\right]$$
$$\text{(B.5)}$$

the principal part P being taken at: $\omega + \omega_{na} = 0$.

In the electrostatic limit, and for an isotropic medium, the linear susceptibility can be written (Eq. (3.2)):

$$G_{xx}(\omega) = G_{yy}(\omega) = \frac{1}{2}G_{zz}(\omega) = \frac{1}{8z^3}\frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1},$$
$$G_{\alpha\beta} = 0 \text{ if } \alpha \neq \beta.$$

That gives for the imaginary part of G:

$$G''_{xx}(\omega) = G''_{yy}(\omega) = \frac{1}{2}G''_{zz}(\omega) = \frac{1}{8z^3}\mathrm{Im}\frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1}.$$

In our one-polariton model, one has:

$$\mathrm{Im}\frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} = \sigma^2\frac{\omega_s^2\omega\Gamma}{(\omega_s^2 - \omega^2)^2 + \omega^2\Gamma^2}$$

$$G''_{xx}(\omega) = G''_{yy}(\omega) = \frac{1}{2}G''_{zz}(\omega) = \frac{\sigma^2}{8z^3}\frac{\omega_s^2\omega\Gamma}{(\omega_s^2 - \omega^2)^2 + \omega^2\Gamma^2}. \tag{B.6}$$

With our notations, Equation (B.1) can also be written:

$$\delta F_a^B(T) = -\frac{1}{\pi}\mathsf{P}\left[\sum_n |\mu_\alpha^{na}|^2 \right.$$
$$\left. \times \int_0^\infty d\omega\frac{2}{e^{\frac{\hbar\omega}{k_BT}} - 1}\frac{\omega_{na}}{\omega_{na}^2 - \omega^2}G''_{\alpha\alpha}(\omega)\right], \quad (\text{B.7})$$

the principal part is for $\omega \neq \omega_{na}$ ($\omega_{na} > 0$) or else for $\omega \neq -\omega_{n'a}$ ($\omega_{n'a} < 0$).

So we have to compare (B.5) with (B.7), or else:

$$\int_{-\infty}^{+\infty} d\omega\frac{1}{(1 - e^{-\frac{\hbar\omega}{k_BT}})(\omega + \omega_{na})}G''_{\alpha\alpha}(\omega)$$

with:

$$\int_0^\infty d\omega\left(\frac{1}{e^{\frac{\hbar\omega}{k_BT}} - 1}\right)\frac{2\omega_{na}}{\omega_{na}^2 - \omega^2}G''_{\alpha\alpha}(\omega)$$

G'' is an odd function of omega (see [8])

$$\frac{1}{(1 - e^{-\frac{\hbar\omega}{k_BT}})(\omega + \omega_{na})} =$$
$$\left(\coth\frac{\hbar\omega}{2k_BT} - \frac{1}{e^{\frac{\hbar\omega}{k_BT}} - 1}\right)\left(\frac{\omega_{na}}{\omega_{na}^2 - \omega^2} - \frac{\omega}{\omega_{na}^2 - \omega^2}\right).$$

Multiplying by G'' and keeping only the even parts of the product, one has:

$$\int_{-\infty}^{+\infty} d\omega\frac{1}{(1 - e^{-\frac{\hbar\omega}{k_BT}})(\omega + \omega_{na})}G''_{\alpha\alpha}(\omega) =$$
$$\int_{-\infty}^{+\infty} d\omega[A(\omega) + B(\omega) + C(\omega)]G''_{\alpha\alpha}(\omega) \quad (\text{B.8})$$

with:

$$A(\omega) = \coth\frac{\hbar\omega}{2k_BT}\left(\frac{\omega_{na}}{\omega_{na}^2 - \omega^2} - \frac{\omega}{\omega_{na}^2 - \omega^2}\right)$$

when multiplied by G'', the first term of A only contributes to the integral (B.8)

$$B(\omega) = -\frac{1}{e^{\frac{\hbar\omega}{k_BT}} - 1}\frac{\omega_{na}}{\omega_{na}^2 - \omega^2}$$
$$= -\frac{1}{2}\left(-1 + \coth\frac{\hbar\omega}{2k_BT}\right)\frac{\omega_{na}}{\omega_{na}^2 - \omega^2},$$

when multiplied by G'', only the second term of B contributes to the integral

$$C(\omega) = \frac{1}{e^{\frac{\hbar\omega}{k_BT}} - 1}\frac{\omega}{\omega_{na}^2 - \omega^2}$$
$$= \frac{1}{2}\left(-1 + \coth\frac{\hbar\omega}{2k_BT}\right)\frac{\omega}{\omega_{na}^2 - \omega^2}.$$

Here only the first term will contribute to the integral (B.8), which becomes an integral over positive frequencies

$$\int_{-\infty}^{+\infty} d\omega[A(\omega) + B(\omega) + C(\omega)]G''_{\alpha\alpha}(\omega) =$$
$$\int_0^\infty d\omega G''(\omega)\coth\left(\frac{\hbar\omega}{2k_BT}\right)\frac{\omega_{na}}{\omega_{na}^2 - \omega^2}$$
$$- \int_0^\infty d\omega G''(\omega)\frac{\omega}{\omega_{na}^2 - \omega^2}.$$

This gives in fine:

$$\int_{-\infty}^{+\infty} d\omega\frac{G''_{\alpha\alpha}(\omega)}{(1 - e^{-\frac{\hbar\omega}{k_BT}})(\omega + \omega_{na})} =$$
$$\int_0^\infty d\omega G''(\omega)\frac{2}{e^{\frac{\hbar\omega}{k_BT}} - 1}\frac{\omega_{na}}{\omega_{na}^2 - \omega^2}$$
$$+ \int_0^\infty d\omega G''(\omega)\frac{1}{\omega_{na} + \omega}. \quad (\text{B.9})$$

The term on the left-hand side of equation (B.9) corresponds to our formula (2.7 or B.5) giving $\delta F_a(T)$. On the right-hand side, the second term represents the shift $\delta E_a(0) = \delta F_a(0)$ for $T = 0_+$ and the first one is Barton's formula (B.7) giving $\delta F_a^B(T)$.

So, we have the identity $\delta F_a^B(T) = \delta F_a(T) - \delta E_a(0)$.

Note that Barton gives his theoretical result under the form of an integral over real frequencies. On the opposite, the integration of (2.7) in the analytical plane allows us to discriminate the resonant terms in absorption or in emission, and, at the same time, the discrete sum over Matsubara poles (2.11). We have taken a single surface-polariton model for the medium to illustrate the non-retarded case for a single plane interface, but equation (2.11) has been obtained in the general retarded case for any form of surface and any real medium.

As an illustration, let us consider the main resonance of sapphire [9] which corresponds to a surface-polariton at 12.21 μm and model it with transverse and longitudinal modes under the form:

$$\varepsilon(\omega) = \eta \frac{\omega_L^2 - \omega^2 - i\omega\Gamma}{\omega_T^2 - \omega^2 - i\omega\Gamma}.$$

When we take as unit the frequency of the surface-polariton ω_s, we obtain:

$$\varepsilon(x) = \eta \frac{x_L^2 - x^2 - ix\delta}{x_T^2 - x^2 - ix\delta},$$

with: $x = \omega/\omega_s, \delta = \Gamma/\omega_s$.

We have in this way the numerical value we use to do some simulations (Figs. 1, 3 and 4):

$$\varepsilon(x) = 2.71 \frac{1.09^2 - x^2 - ix(1.5 \times 10^{-2})}{0.70^2 - x^2 - ix(1.5 \times 10^{-2})}.$$

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