Nonperturbative theory of atom-surface interaction: Corrections at short separations

M Bordag, G L Klimchitskaya and V M Mostepanenko

1Institute for Theoretical Physics, Leipzig University, Postfach 100920, D-04009, Leipzig, Germany
2Central Astronomical Observatory at Pulkovo of the Russian Academy of Sciences, Saint Petersburg, 196140, Russia
3Institute of Physics, Nanotechnology and Telecommunications, Peter the Great Saint Petersburg Polytechnic University, Saint Petersburg, 195251, Russia
4Kazan Federal University, Kazan, 420008, Russia

E-mail: vmostepa@gmail.com

Abstract. The nonperturbative expressions for the free energy and force of interaction between a ground-state atom and a real-material surface at any temperature are presented. The transition to the Matsubara representation is performed, whereupon the comparison is made with the commonly used perturbative results based on the standard Lifshitz theory. It is shown that the Lifshitz formulas for the free energy and force of an atom-surface interaction follow from the nonperturbative ones in the lowest order of the small parameter. Numerical computations of the free energy and force for the atoms of He* and Na interacting with a surface of an Au plate have been performed using the frequency-dependent dielectric permittivity of Au and highly accurate dynamic atomic polarizabilities in the framework of both the nonperturbative and perturbative theories. According to our results, the maximum deviations between the two theories are reached at the shortest atom-surface separations of about 1 nm. Simple analytic expressions for the atom-surface free energy are derived in the classical limit and for an ideal-metal plane. In the lowest order of the small parameter, they are found in agreement with the perturbative ones following from the standard Lifshitz theory. Possible applications of the obtained results in the theory of van der Waals adsorption are discussed.

PACS numbers: 68.49.Bc, 68.43.Mn, 12.20.Ds

Keywords: atom-surface interaction, Lifshitz formula, nonperturbative theory.

Submitted to: J. Phys.: Condens. Matter
1. Introduction

It is well known that an electrically neutral but polarizable atom is attracted to a closely spaced material surface by the force which increases rapidly with decreasing atom-surface separation. The long-range forces of this kind were predicted by van der Waals in the end of the nineteenth century \[1\]. After the development of quantum field theory it was understood that the atom-surface force is of entirely quantum nature and originates from the zero-point and thermal fluctuations of the electromagnetic field modified by a material boundary. According to nonrelativistic London’s theory \[2\], the interaction potential between a polarizable atom and an ideal-metal plane at zero temperature is inverse proportional to the third power of their separation \[3\].

The account of relativistic effects leads, however, to important changes in the character of atom-surface interaction. As was shown in the seminal work by Casimir and Polder \[4\], at sufficiently large separations at zero temperature the interaction potential between an atom and an ideal-metal plane becomes inverse proportional to the fourth power of separation. This result was obtained using the second-order perturbation theory in the dipole-dipole interaction within the framework of quantum electrodynamics. The nonperturbative generalization of the zero-temperature Casimir-Polder force between an atom and an ideal-metal plane has been derived only a few years ago \[5\].

One more phenomenon caused by the zero-point fluctuations of the electromagnetic field is the attractive force between two plane parallel, uncharged ideal-metal surfaces in vacuum. The exact (nonperturbative) expression for this force at zero temperature was obtained by Casimir \[6\] in the framework of quantum electrodynamics. The Lifshitz theory \[7\] presented a far-reaching generalization of the Casimir result for the case of two plane parallel material surfaces (semispaces) kept at any temperature $T$ in thermal equilibrium with the environment. In so doing the materials of the walls were described by the frequency-dependent dielectric permittivities. The Lifshitz formulas for the fluctuation-induced force contain the limiting case of the nonrelativistic van der Waals force and, for the ideal-metal planes, reproduce the Casimir result \[6\] as well as its generalization to nonzero temperature.

By rarefying the material of one of the semispaces, it is customary to obtain the Lifshitz formulas for the free energy and force between a polarizable atom and a surface of the plate made of some real material at temperature $T$ \[7, 8, 9, 10\]. The Lifshitz formulas describing an atom-surface interaction are not as exact as the original Lifshitz formulas derived for the case of two parallel surfaces. In fact the former are obtained from the latter in the lowest perturbation order of the small parameter equal to the dynamic atomic polarizability multiplied by the number of atoms per unit volume in the rarefied plate. If the second wall is made of an ideal metal at zero temperature, the Lifshitz formulas for an atom-surface interaction return us back to the perturbative Casimir and Polder result \[4\].

It should be particularly emphasized that the Lifshitz formulas describing the
Nonperturbative theory of atom-surface interaction: Corrections at short separations

Atom-surface interaction have found a lot of recent applications in various areas. They have been used to investigate the dependences of atom-surface forces on the material properties of a surface and on the characteristics of an atom [11, 12, 13, 14, 15, 16, 17, 18, 19]. The obtained information was used for interpretation of experiments on quantum reflection [20, 21, 22], Bose-Einstein condensation [23, 24, 25, 26], investigation of the resonance interaction of two atoms near an ideal-metal wall [27], and of the role played by fluctuations at the interface between a metallic boundary and the vacuum [28]. The extent of agreement between the measured atom-surface forces and the Lifshitz theory has been also used in fundamental physics to place stronger limits on the Yukawa-type corrections to Newton’s law of gravitation [29] and on the parameters of axion-like particles [30]. Currently the Lifshitz formulas are employed to describe the interaction of different atoms with graphene and graphene-coated substrates [31, 32, 33, 34, 35, 36]. All the above makes important the derivation of the nonperturbative Lifshitz-type formula describing the free energy of an atom interacting with a surface of the plate made of real material at any nonzero temperature. In the framework of the Lifshitz theory this formula would be as exact as the famous Lifshitz expression describing the Casimir interaction between two parallel material plates.

The recently developed formalism [37] allows a unified nonperturbative description of the fluctuation-induced forces between two atoms, an atom and a material surface (plate), and between two material plates with taken into account dissipation properties at any nonzero temperature. This formalism is based on the heat bath approach and earlier works devoted to a quantum oscillator interacting with a blackbody radiation field [38] and to nonperturbative derivation of the van der Waals [39] and Casimir-Polder [40] interaction between two oscillating dipoles. For the case of two material plates paper [37] reproduces the familiar Lifshitz formula, whereas for an atom interacting with a material surface suggests its nonperturbative generalization.

In this paper, we compare the nonperturbative formulas for the free energy and force of a ground-state atom, interacting with a surface of thick real-material plate (semispace) at temperature $T$, and the commonly used perturbative Lifshitz formulas obtained by means of the rarefying procedure. In so doing, the atom is characterized by the dynamic atomic polarizability and the plate material by the frequency-dependent dielectric permittivity. We show that the commonly known Lifshitz formulas for the free energy and force of an atom-surface interaction are reproduced from the exact ones as the first expansion orders in powers of the dynamic atomic polarizability divided by the third power of separation. We perform numerical computations of the free energy and force for atoms of metastable helium He$^*$ and Na interacting with an Au plate by using the exact formulas and the standard perturbative Lifshitz formulas. It is shown that at the shortest separation distance, where the Lifshitz theory is still applicable, the relative deviations between the obtained free energies exceed 1.1% for He$^*$ and 0.6% for Na. The respective deviations in the force are 2.3% and 1.25% for the atoms of He$^*$ and Na, respectively. At separations exceeding 4 nm the exact and perturbative theories lead to almost coinciding results. We also obtain simple analytic expressions for the
nonperturbative atom-surface free energies and forces in the classical limit and for an ideal-metal plane and demonstrate that in these cases the deviations between the exact and perturbative results are negligibly small.

The paper is organized as follows. In section 2, we briefly summarize the main results of the nonperturbative theory of atom-surface interaction and make a transition to the Matsubara representation. In section 3, we reobtain the standard Lifshitz formulas for an atom-surface interaction in the first perturbation order and perform numerical computations of the free energy and force between metastable He and Na atoms and an Au plate using both the exact and perturbative formulas. Section 4 contains simple analytic results in the classical limit and for an ideal-metal surface. In section 5 the reader will find our conclusions and a discussion.

2. Nonperturbative formulas for the free energy and force of atom-surface interaction

We consider the polarizable atom in the ground state described by the dynamic atomic polarizability \( \alpha(\omega) \) separated by a distance \( a \) from the surface of a thick plate (semispace) kept at temperature \( T \) in thermal equilibrium with the environment. The material of the plate is characterized by the frequency-dependent dielectric permittivity \( \epsilon(\omega) \). In the nonperturbative theory, developed recently [37], both the external atom and the atoms of the plate are considered as point dipoles interacting through the electromagnetic field. The dynamics of the atoms is described by the oscillator equations with some mass, the intrinsic frequency and the damping parameter to account for dissipation. The oscillators are subjected to the external forces equal to the sums of the electric and Langevin forces. The latter may be introduced by coupling the heat baths to the oscillators and integrating out the bath variables [41]. To describe the wall, an infinite collection of the dipoles, which are distributed homogeneously in the half space, is taken with subsequent increase of their density to form a continuous distribution.

Finally, one arrives to the following expression for the free energy of an atom-surface interaction [37]

\[
F(a, T) = \frac{1}{\pi} \int_{0}^{\infty} d\omega \left[ \frac{\hbar \omega}{2} + k_B T \ln \left( 1 - e^{-\frac{\hbar \omega}{k_B T}} \right) \right] \frac{\partial \Delta(\omega)}{\partial \omega},
\]

(1)

where \( k_B \) is the Boltzmann constant and the so-called phase is defined as

\[
\Delta(\omega) = -\frac{1}{2i} \ln \left( \frac{L(\omega)}{L(-\omega)} \right).
\]

(2)

The quantity \( L(\omega) \) in (2) can be expressed via the difference \( \Delta G \) of photon Green’s functions in the presence of a material half-space and of the free space

\[
L(\omega) = 1 - 4\pi \alpha(\omega) \frac{\omega^2}{c^2} \Delta G(\omega).
\]

(3)

The latter difference is given by [37]

\[
\Delta G(\omega) = \frac{1}{4\pi \omega^2} \int_{0}^{\infty} \frac{k_\perp dk_\perp}{q} e^{-2aq}
\]

(4)
Nonperturbative theory of atom-surface interaction: Corrections at short separations

$\times \left[ (2k^2 - \omega^2)r_{TM}(\omega, k) + \omega^2 r_{TE}(\omega, k) \right],$

where $k$ is the magnitude of the wave vector projection on the surface of the plate, $q = k^2 - \omega^2/c^2$, and the reflection coefficients for the two independent polarizations of the electromagnetic field on this surface, transverse magnetic (TM) and transverse electric (TE), take the usual form

$$r_{TM}(\omega, k) = \frac{\varepsilon(\omega)q - k}{\varepsilon(\omega)q + k},$$

$$r_{TE}(\omega, k) = \frac{q - k}{q + k}, \quad k^2 \equiv k^2 - \varepsilon(\omega)\frac{\omega^2}{c^2}.$$

It is convenient now to pass in (1) to the Matsubara representation. For this purpose we present (2) for the phase as

$$\Delta(\omega) = -\frac{1}{2i} \ln L(\omega) + \frac{1}{2i} \ln L(-\omega).$$

(6)

We take into account that in the first term on the right-hand side of (6) all singularities are in the lower half of the plane of complex frequency, whereas the singularities of the second term are in the upper half-plane. When substituting (6) in (1), we turn the integration path in the first term of the free energy towards the positive imaginary axis, $\omega = i\xi$, and in the second term — to the negative imaginary axis.

The expression in the square brackets in (1) can be written in the form

$$\frac{\hbar \omega}{2} + k_B T \ln(1 - e^{-\hbar \omega/(k_B T)}) = k_B T \ln \left( \frac{2 \sinh \frac{\hbar \omega}{2k_B T}}{2} \right).$$

(7)

The analytic continuation of the logarithm on the right-hand side of (7) is performed according to

$$\ln \left( 2 \sinh \frac{i\hbar \xi}{2k_B T} \right) = \ln \left| 2 \sin \frac{i\hbar \xi}{2k_B T} \right| + i\pi \sum_{l=0}^{\infty} \theta(\xi - \xi_l),$$

$$\ln \left( 2 \sinh \frac{i\hbar \xi}{2k_B T} \right) = \ln \left| 2 \sin \frac{i\hbar \xi}{2k_B T} \right| - i\pi \sum_{l=-\infty}^{0} \theta(-\xi + \xi_l)$$

for $\xi > 0$ and $\xi < 0$, respectively. Here $\xi_l = 2\pi k_B T l/\hbar$, $l = 0, \pm 1, \pm 2, \ldots$ are the Matsubara frequencies, $\theta(x)$ is the Heaviside step function, and the prime on the summation sign denotes that the contribution from the zeroth term should be taken with the factor 1/2. The relation (8) follows from the fact that the logarithm has cuts starting at $\xi = \xi_l$.

Substituting (6) and (7) in (1) and turning the integration paths as described above with account of (8), we find

$$F(a, T) = -k_B T \int_0^{\infty} d\xi \sum_{l=0}^{\infty} \theta(\xi - \xi_l) \frac{\partial}{\partial \xi} L(i\xi).$$

(9)

After integrating by parts in (9), we come to the final formula for the free energy of atom-surface interaction

$$F(a, T) = k_B T \sum_{l=0}^{\infty} \ln L(i\xi_l).$$

(10)
Nonperturbative theory of atom-surface interaction: Corrections at short separations

For the function \( L(i\xi_l) \) from (3) and (4) one obtains

\[
L(i\xi_l) = 1 - \alpha(i\xi_l) \int_0^\infty \frac{k_{l}dk_{\perp}}{q_{l}} e^{-2aq_l} \times \left[ \left( 2k_{l}^2 + \frac{\xi_l^2}{c^2} \right) r_{TM}(i\xi_l, k_{\perp}) - \frac{\xi_l^2}{c^2} r_{TE}(i\xi_l, k_{\perp}) \right],
\]

where \( q_{l} = k_{l}^2 + \xi_l^2/c^2 \) and \( r_{TM} \) and \( r_{TE} \) are again given by (5) with the substitution \( \omega = i\xi_l \).

Calculating the negative derivative of the free energy (10) and (11) with respect to separation, one obtains the nonperturbative expression for the atom-surface force

\[
F(a, T) = -2k_B T \sum_{l=0}^{\infty} \frac{\alpha(i\omega_c \zeta_l)}{L(i\xi_l)} \int_0^\infty k_{l}dk_{\perp} e^{-2aq_l} \times \left[ \left( 2k_{l}^2 + \frac{\xi_l^2}{c^2} \right) r_{TM}(i\xi_l, k_{\perp}) - \frac{\xi_l^2}{c^2} r_{TE}(i\xi_l, k_{\perp}) \right].
\]

In the next section we compare the exact (nonperturbative) results (10)–(12) with the commonly used perturbative free energies and forces given by the Lifshitz formulas for an atom-surface interaction.

3. Computations of the atom-surface interaction by means of the nonperturbative and perturbative theories

It is convenient to rewrite the obtained nonperturbative expressions for the free energy (10) and force (12) of atom-surface interaction in terms of the dimensionless variables

\[
y = 2aq_l, \quad \zeta_l = \frac{\xi_l}{\omega_c}, \quad \omega_c = \frac{2a\xi_l}{c}.
\]

Then the exact free energy (10) takes the form

\[
\mathcal{F}(a, T) = k_B T \sum_{l=0}^{\infty} \ln \left\{ 1 - \frac{\alpha(i\omega_c \zeta_l)}{8a^3} \int_0^\infty dy e^{-y} \times \left[ (2y^2 - \zeta_l^2)r_{TM}(i\zeta_l, y) - \zeta_l^2 r_{TE}(i\zeta_l, y) \right] \right\}.
\]

In a similar way, the exact atom-surface force (12) with account of (11) is given by

\[
F(a, T) = -\frac{k_B T}{a} \sum_{l=0}^{\infty} \frac{\alpha(i\omega_c \zeta_l)}{8a^3} \int_0^\infty dy e^{-y} \times \left[ (2y^2 - \zeta_l^2)r_{TM}(i\zeta_l, y) - \zeta_l^2 r_{TE}(i\zeta_l, y) \right] \\
\times \left[ 1 - \frac{\alpha(i\omega_c \zeta_l)}{8a^3} \int_0^\infty dy e^{-y} \left[ (2y^2 - \zeta_l^2)r_{TM}(i\zeta_l, y) - \zeta_l^2 r_{TE}(i\zeta_l, y) \right] \right].
\]

Expanding (14) and (15) up to the first power of a small parameter \( \alpha/a^3 \), one obtains the standard, perturbative, expressions \( [8, 9, 10, 11] \) for the free energy and force of an atom-surface interaction

\[
\mathcal{F}_{\text{per}}(a, T) = -\frac{k_B T}{8a^3} \sum_{l=0}^{\infty} \alpha(i\omega_c \zeta_l) \int_0^\infty dy e^{-y}
\]
Nonperturbative theory of atom-surface interaction: Corrections at short separations

\[ F_{\text{per}}(a, T) = -\frac{k_B T}{8a^4} \sum_{l=0}^{\infty} \left\{ \alpha(i\omega_c \xi_l) \int_{-\infty}^{\infty} dy y e^{-y} \right\} \]

\times \left[ (2y^2 - \zeta_l^2) r_{\text{TM}}(i\xi_l, y) - \zeta_l^2 r_{\text{TE}}(i\xi_l, y) \right], \quad (16)

The reflection coefficients entering (14)–(16) are obtained from (5) by the substitution \( \omega = i\xi_l \) and the change of variables (13):

\[ r_{\text{TM}}(i\xi_l, y) = \frac{\varepsilon_l y - \sqrt{y^2 + \zeta_l^2(\varepsilon_l - 1)}}{\varepsilon_l y + \sqrt{y^2 + \zeta_l^2(\varepsilon_l - 1)}} \]

\[ r_{\text{TE}}(i\xi_l, y) = \frac{y - \sqrt{y^2 + \zeta_l^2(\varepsilon_l - 1)}}{y + \sqrt{y^2 + \zeta_l^2(\varepsilon_l - 1)}} \], \quad (17)

where \( \varepsilon_l \equiv \varepsilon(i\omega_c \xi_l) \). Note that (16) and (17) are well known as the Lifshitz formulas for an atom-surface interaction [7, 8, 9, 10].

We calculate the free energies \( F, F_{\text{per}} \) and forces \( F, F_{\text{per}} \) of an atom-surface interaction for the atoms of metastable helium, He*, and natrium, Na, spaced in close proximity to the Au plate. Taking into account that the atomic polarizability \( \alpha \) along the imaginary frequency axis takes the maximum values of order of \( 10^{-29} \text{m}^3 \), one concludes that the dimensionless parameter \( \alpha/a^3 \), entering (14) and (15), remains small down to \( a = 1 \text{nm} \) separation. Since the description of a plate material by means of the dielectric permittivity is applicable only at the distances much larger than the atomic sizes, within the Lifshitz theory one cannot consider atom-surface separations smaller than 8–10 Å. This means that the maximum deviations between the atom-surface interactions computed exactly and perturbatively are expected at separations of order of 1 nm.

Precise computations of the atom-surface free energy and force at separations of a few nanometers require the knowledge of dynamic atomic polarizabilities accurate up to the frequencies of order of \( 10^{17} - 10^{18} \text{rad/s} \) (the single-oscillator model cannot be used at so short separation distances [10, 11, 13]). The nonrelativistic highly accurate dynamic atomic polarizability of He*\((2^3S)\) was obtained in [42] (see also [43]) with the relative error of about \( 10^{-6} \). It is shown by the line labeled He* in figure 1 as a function of frequency. Note that in the relativistic framework the polarizability of He* includes also the tensor part. The static atomic polarizability of He* is equal to \( \alpha_{\text{He}}(0) = 467.727 \times 10^{-31} \text{m}^3 \). The highly accurate dynamic atomic polarizability of Na in the ground state can be found in [44]. It is shown as a function of frequency by the line labeled Na in figure 1 (for Na the static atomic polarizability is equal to \( \alpha_{\text{Na}}(0) = 241.067 \times 10^{-31} \text{m}^3 \)).

The dielectric permittivity of Au wall along the imaginary frequency axis enters (14)–(16) through the reflection coefficients (17). It is found from the optical data for the complex index of refraction of Au [45] using the Kramers-Kronig relation. Since the optical data are available only within some restricted frequency region, at low frequencies down to zero frequency they have to be extrapolated with the help of some theoretical model. There is widely discussed problem [10, 46] that an extrapolation by
means of the Drude model, which takes into account the dissipation of free electrons, results in drastic contradictions between theoretical predictions of the Lifshitz theory and all precise experiments on measuring the Casimir force for two metallic test bodies [47, 48, 49, 50, 51, 52, 53, 54]. If the extrapolation is made by means of the lossless plasma model, the experimental data are found to be in a very good agreement with theory [47, 48, 49, 50, 51, 52, 53, 54, 55]. Different theoretical predictions arise due to different values taken by the transverse electric reflection coefficient at zero frequency when two dissimilar extrapolations of the optical data are employed. Similar problem arises with the transverse magnetic reflection coefficient in the case of dielectric surfaces when the free charge carriers are either taken into account or omitted at nonzero temperature [56, 57, 58]. It should be stressed, however, that for an atom-surface configuration under consideration here the Drude-plasma dilemma does not influence the computational results. The reason is that in (14) and (15), as well as in (16), the transverse electric coefficient $r_{TE}(0, y)$ does not contribute to the result, as it is multiplied by the factor $\zeta^2_0 = 0$. To be specific, in computations below we extrapolate the optical data for Au to zero frequency by means of the experimentally consistent plasma model [10, 46].

The magnitude of the (negative) free energy of an atom-surface interaction was computed using the new expression (14) and the standard, perturbative, expression (16). The computational results multiplied by the third power of separation between an atom and a wall are shown in figure 2 as functions of separation by the bottom and top lines for the standard and exact theories, respectively. Figure 2(a) refers to the atom of metastable He$^*$ and figure 2(b) — to the atom of Na. Computations are performed at room temperature $T = 300\,\text{K}$. As is seen in figure 2(a), the largest difference between the exact and perturbative free energies for an atom of He$^*$ is reached at the shortest separation considered, $a = 0.8\,\text{nm}$, where it is equal to approximately 0.146 eV. For the atom of Na at $a = 0.8\,\text{nm}$ from an Au plate the difference between the exact and perturbative predictions is equal to 0.053 eV. At $a > 4\,\text{nm}$ the exact and perturbative theories lead to almost coinciding free energies and forces.

In figure 3 the computational results for the magnitude of atom-surface force at $T = 300\,\text{K}$ multiplied by the fourth power of separation are plotted as the bottom and top lines for the standard and exact theories, respectively. Computations are performed by (15) and (16). The case of an atom of He$^*$ is shown in figure 3(a) and of an atom of Na — in figure 3(b). The largest differences between theoretical predictions of the exact and perturbative theories are again reached at the shortest separation considered $a = 0.8\,\text{nm}$. For the atoms of He$^*$ and Na the largest force differences are equal to 0.178 pN and 0.081 pN, respectively. Taking into account that at the moment the experimental sensitivity to small forces is of the order of a fraction of 1 fN [54, 59], the above differences between the exact and perturbative theories should be considered as quite measurable.

It is interesting also to consider the relative deviations between the free energies
and forces of an atom-surface interaction computed exactly and perturbatively
\[ \delta F(a, T) = \frac{F(a, T) - F^{\text{per}}(a, T)}{F^{\text{per}}(a, T)}, \]
\[ \delta F(a, T) = \frac{F(a, T) - F^{\text{per}}(a, T)}{F^{\text{per}}(a, T)}. \] (18)

In figure 4 the relative deviations between the atom-surface free energies (lines labeled 1) and forces (lines labeled 2) are shown at \( T = 300 \text{ K} \) as functions of separation for (a) the atom of He* and (b) the atom of Na. As is seen in figure 4(a), for the atom of He* the maximum relative deviations in the free energy and force exceed 1.1% and 2.3%, respectively. For the atom of Na the maximum relative deviations are 0.6% for the free energy and 1.25% for the force. At the atom-surface separations exceeding 4 nm both the exact and perturbative theories lead to almost coinciding predictions for free energies and forces. Note that the decrease of temperature down to \( T = 100 \text{ K} \) makes only a minor impact on these results.

4. Analytic results in classical limit and for ideal-metal surface

It has been known that in the classical limit (i.e., at large separations or high temperatures) the main contribution to the Lifshits formulas for the free energy and force of an atom-surface interaction is given by the zero-frequency term. The contribution of all terms with \( l \geq 1 \) remains exponentially small in this case. It is easily seen that the same holds for the nonperturbative atom-surface free energy (14) and force (15). As an example, let us consider the contribution of the first Matsubara frequency to the free energy (14), i.e.,
\[ F_1(a, T) = k_B T \ln \left\{ 1 - \frac{\alpha(i\omega_c\zeta_1)}{8a^3} \int_{\zeta_1}^{\infty} dy e^{-y} \times \left[ (2y^2 - \zeta_1^2)r_{TM}(i\zeta_1, y) - \zeta_1^2 r_{TE}(i\zeta_1, y) \right] \right\}, \] (19)

From (19) one easily obtains
\[ |F_1(a, T)| \approx k_B T \frac{\alpha(i\omega_c\zeta_1)}{8a^3} \int_{\zeta_1}^{\infty} dy e^{-y} \times \left[ 2y^2 r_{TM}(i\zeta_1, y) - \zeta_1^2 \left[ r_{TM}(i\zeta_1, y) + r_{TE}(i\zeta_1, y) \right] \right]. \] (20)

Taking into account that the dynamic atomic polarizability decreases with increasing frequency and that \( |r_{TE}| < r_{TM} \leq 1 \), we find from (20)
\[ |F_1(a, T)| < k_B T \frac{\alpha(0)}{4a^3} r_{TM}(0) \int_{\zeta_1}^{\infty} y^2 e^{-y} dy \] (21)
\[ = k_B T \frac{\alpha(0)}{4a^3} r_{TM}(0)(\zeta_1^2 + 2\zeta_1 + 2)e^{-\zeta_1}, \]
where, in accordance with (13), \( \zeta_1 = 4\pi a k_B T/(\hbar c) \), i.e., \( F_1 \) is really exponentially small. Note that due to (5)
\[ r_{TM}(0) = \frac{\varepsilon(0) - 1}{\varepsilon(0) + 1} \quad \text{and} \quad r_{TM}(0) = 1 \] (22)
Nonperturbative theory of atom-surface interaction: Corrections at short separations

for dielectric and metallic surfaces, respectively.

By taking the zero-frequency term, \( l = 0 \), in \( 14 \), one arrives at the nonperturbative free energy of an atom-surface interaction in the classical limit

\[
\mathcal{F}_0(a, T) = \frac{k_B T}{2} \ln \left[ 1 - \frac{\alpha(0)}{4a^3} \int_0^\infty y^2 e^{-y} dy \right] = \frac{k_B T}{2} \ln \left[ 1 - \frac{\alpha(0)}{2a^3} \right].
\]

(23)

In the first perturbation order in the small parameter \( \alpha(0)/a^3 \) this result is the familiar classical limit of an atom-surface interaction following from the Lifshitz formula \( 16 \)

\[
\mathcal{F}_{0 \perp}^0(a, T) = -\frac{k_B T}{4a^3} \alpha(0).
\]

(24)

In a similar way, for the nonperturbative atom-surface force from \( 15 \) we obtain the classical limit

\[
F_0(a, T) = \frac{k_B T \alpha(0)}{8a^4} \ln \left[ 1 - \frac{\alpha(0)}{4a^3} \int_0^\infty y^2 e^{-y} dy \right] = -\frac{3k_B T}{4a^4} \alpha(0) \frac{1}{1 - \frac{\alpha(0)}{4a^3}},
\]

(25)

In the first perturbation order this leads to

\[
F_{0 \perp}^0(a, T) = -\frac{3k_B T}{4a^4} \alpha(0),
\]

(26)
i.e., to the same result as follows \([10]\) from the standard Lifshitz formula \( 16 \).

Now we consider the exact free energy of an atom interacting with an ideal-metal plane. In this case

\[
r_{TM}(i\zeta, y) = -r_{TE}(i\zeta, y) = 1
\]

(27)

and from \( 14 \) one obtains

\[
\mathcal{F}(a, T) = k_B T \sum_{l=0}^\infty \ln \left[ 1 - \frac{\alpha(i\omega_c \zeta)}{4a^3} \int_0^\infty y^2 e^{-y} dy \right]
\]

\[
= k_B T \sum_{l=0}^\infty \ln \left[ 1 - \frac{\alpha(i\omega_c \zeta)}{4a^3} \left( \zeta^2 + 2\zeta + 2 \right) e^{-\zeta} \right].
\]

(28)

Expanding the logarithm in a power series we present the results in the following convenient form:

\[
\mathcal{F}(a, T) = -k_B T \sum_{n=1}^\infty \frac{1}{n} \left( \frac{\alpha(0)}{4a^3} \right)^n \sum_{l=0}^\infty \left( \frac{\alpha(i\omega_c \zeta)}{\alpha(0)} \right)^n \left( \zeta^2 + 2\zeta + 2 \right)^n e^{-n\zeta}. \tag{29}
\]

The transition to zero temperature is performed by the standard replacement

\[
k_B T \sum_{l=0}^\infty \ln \rightarrow \frac{\hbar c}{4\pi a} \int_0^\infty \zeta.
\]

(30)

This transforms the atom-surface free energy \( 29 \) into the energy

\[
E(a) = -\frac{\hbar c}{4\pi a} \sum_{n=1}^\infty \frac{1}{n} \left( \frac{\alpha(0)}{4a^3} \right)^n \times \int_0^\infty \zeta \left( \frac{\alpha(i\omega_c \zeta)}{\alpha(0)} \right)^n \left( \zeta^2 + 2\zeta + 2 \right)^n e^{-n\zeta}. \tag{31}
\]
Nonperturbative theory of atom-surface interaction: Corrections at short separations

At sufficiently large atom-surface separations considered by Casimir and Polder [4] one can put $\alpha(i\omega_c\zeta) = \alpha(0)$. Separating the term with $n = 1$ in (31), we find

$$E(a) = -\frac{\hbar c\alpha(0)}{16\pi a^4} \int_0^\infty d\zeta (\zeta^2 + 2\zeta + 2)e^{-\zeta}$$

$$- \frac{\hbar c}{4\pi a} \sum_{n=2}^\infty \frac{1}{n} \left( \frac{\alpha(0)}{4a^3} \right)^n \int_0^\infty d\zeta (\zeta^2 + 2\zeta + 2)^n e^{-n\zeta}.$$ 

After an integration and changing the index of summation, one finally obtains

$$E(a) = -\frac{3\hbar c\alpha(0)}{8\pi a^4} - \frac{\hbar c\alpha(0)}{16\pi a^4} \sum_{k=1}^\infty \frac{1}{k+1} \left( \frac{\alpha(0)}{4a^3} \right)^k$$

$$\times \int_0^\infty d\zeta (\zeta^2 + 2\zeta + 2)^{k+1} e^{-(k+1)\zeta}.$$ 

Note that one power of $\alpha(0)/(4a^3)$ is placed in front of the summation sign. The first term on the right-hand side of (33) is the famous result by Casimir and Polder [4], whereas the infinite sum in powers of the parameter $\alpha(0)/(4a^3)$ presents small nonperturbative correction to this result.

5. Conclusions and discussion

In the foregoing, we have considered the nonperturbative theory describing the interaction of a ground-state atom with a real-material surface at any temperature in thermal equilibrium with the environment. After presenting several main equations of this theory, we have made a transition to the Matsubara representation which allowed detailed comparison between the exact free energies and forces of atom-surface interaction and that ones calculated perturbatively using the standard Lifshitz formulas. The latter have been obtained from the nonperturbative results as the first perturbation order in the small parameter equal to the dynamic atomic polarizability divided by the third power of an atom-surface separation.

Computations of the atom-surface free energies and forces have been performed by using both the exact and perturbative theories for the atoms of He* and Na interacting with an Au wall at room temperature. In so doing the highly accurate dynamic atomic polarizabilities and the tabulated optical data for the complex index of refraction of Au have been used. It was shown that the maximum deviations between the predictions of both theories are reached at the minimum separation considered ($a = 0.8$ nm). For an atom of He*, the maximum relative deviations between the two theories in the computed free energy and force are equal to approximately 1.1% and 2.3%, respectively. For an atom of Na, the maximum deviations reach 0.6% for the free energy and 1.25% for the force. It was concluded that the predicted deviations from the results of perturbative theory are experimentally observable.

Finally, we have derived simple analytic expressions for the classical free energy and force of an atom-surface interaction in the framework of nonperturbative theory. In the lowest order of the small parameter mentioned above, the obtained expressions
The nonperturbative theory of atom-surface interaction: Corrections at short separations coincide with the well known results following from the standard Lifshitz formulas. The free energy of an atom interacting with an ideal-metal wall has also been found using the nonperturbative theory. In the lowest order of the same small parameter it coincides with the commonly known Casimir and Polder perturbative result.

The exact expressions for an atom-surface interaction considered in this paper are interesting not only from the fundamental point of view, but may find applications for the interpretation of experiments on quantum reflection and in the theory of the van der Waals adsorption. The latter may need the more precise interaction potentials at the shortest atom-surface separation than that ones obtained perturbatively using the standard approach.

Acknowledgments

The work of V.M.M. was partially supported by the Russian Government Program of Competitive Growth of Kazan Federal University.

References

[1] Parsegian V A 2005 Van der Waals forces: A Handbook for Biologists, Chemists, Engineers, and Physicists (Cambridge: Cambridge University Press)
[2] London F 1930 Z. Phys. 63 245
[3] Lennard-Jones J E 1932 Trans. Faraday Soc. 28 333
[4] Casimir H B G and Polder D 1948 Phys. Rev. 73 360
[5] Passante R, Rizzuto L, Spagnolo S, Tanaka S and Petrosky T Y 2012 Phys. Rev. A 85 062109
[6] Casimir H B G 1948 Proc. K. Ned. Akad. Wet. 51 793
[7] Lifshitz E M 1955 Zh. Eksp. Teor. Fiz. 29 94 (1956 Sov. Phys. JETP 2 73)
[8] Dzyaloshinskii I E, Lifshitz E M and Pitaevskii L P 1961 Adv. Phys. 10, 165 (1961 Usp. Fiz. Nauk 73 381)
[9] Lifshitz E M and Pitaevskii L P 1984 Statistical Physics, Pt II (Oxford: Pergamon Press)
[10] Bordag M, Klimchitskaya G L, Mohideen U and Mostepanenko V M 2015 Advances in the Casimir Effect (Oxford: Oxford University Press)
[11] Babb J F, Klimchitskaya G L and Mostepanenko V M 2004 Phys. Rev. A 70 042901
[12] Antezza M, Pitaevskii L P and Stringari S 2004 Phys. Rev. A 70 053619
[13] Caride A O, Klimchitskaya G L, Mostepanenko V M and Zanette S I 2005 Phys. Rev. A 71 042901
[14] Buhmann S Y, Knöll L, Welsch D-G and Dung H T 2004 Phys. Rev. A 70 052117
[15] Buhmann S Y and Welsch D-G 2007 Progr. Quant. Electronics 31 51
[16] Bezerra V B, Klimchitskaya G L, Mostepanenko V M and Romero C 2008 Phys. Rev. A 78 042901
[17] Safavi H, Welsch D-G, Buhmann S Y and Scheel S 2008 Phys. Rev. A 78 062901
[18] Buhmann S Y, Safavi H, Dung H T and Welsch D-G 2007 Opt. Spectrosc. 103 374
[19] Bimonte G, Klimchitskaya G L and Mostepanenko V M 2009 Phys. Rev. A 79 042906
[20] Shimizu F 2001 Phys. Rev. Lett. 86 987
[21] Friedrich H, Jacoby G and Meister C G 2002 Phys. Rev. A 65 032902
[22] Druzhinina V and DeKieviet M 2003 Phys. Rev. Lett. 91 193202
[23] Harber D M, McGuirk J M, Obrrecht J M and Cornell E A 2003 J. Low. Temp. Phys. 133 229
[24] Leanhardt A E, Shin Y, Chikkatur A P, Kiepinski D, Ketterle W and Pritchard D E 2003 Phys. Rev. Lett. 90 100404
[25] Lin Y-j, Teper I, Chin C and Vuletić V 2004 Phys. Rev. Lett. 92 050404
Nonperturbative theory of atom-surface interaction: Corrections at short separations

[26] Obrecht J M, Wild R J, Antezza M, Pitaevskii L P, Stringari S and Cornell E A 2007 *Phys. Rev. Lett.* **98** 063201

[27] Lattuca M, Marino J, Noto A, Passante R, Rizzuto L, Spagnolo S and Zhou W 2017 *J. Phys.: Conf. Series* **880** 012042

[28] Bartolo N, Butera S, Lattuca M, Passante R, Rizzuto L and Spagnolo S 2015 *J. Phys.: Condens. Matter* **27** 214015

[29] Bezerra V B, Klimchitskaya G L, Mostepanenko V M and Romero C 2010 *Phys. Rev. D* **81** 055003

[30] Bezerra V B, Klimchitskaya G L, Mostepanenko V M and Romero C 2014 *Phys. Rev. D* **89** 035010

[31] Chaichian M, Klimchitskaya G L, Mostepanenko V M and Tureanu A 2012 *Phys. Rev. A* **86** 012515

[32] Klimchitskaya G L and Mostepanenko V M 2014 *Phys. Rev. A* **89** 012516

[33] Klimchitskaya G L and Mostepanenko V M 2014 *Phys. Rev. A* **89** 062508

[34] Ribeiro S and Scheel S 2013 *Phys. Rev. A* **88** 042519

[35] Ribeiro S and Scheel S 2014 *Phys. Rev. A* **89** 039904(E)

[36] Nichols N S, Del Maesto A, Wexler C and Kotov V N 2016 *Phys. Rev. B* **93** 205412

[37] Bordag M 2017 *Phys. Rev. A* **96** 062504

[38] Ford G W, Lewis J T and O’Connell R F 1985 *Phys. Rev. Lett.* **55** 2273

[39] Berman P R, Ford G W and Milonni P W 2014 *Phys. Rev. A* **89** 022127

[40] Ciccarello F, Karpov E and Passante R 2005 *Phys. Rev. A* **72** 052106

[41] Bordag M 2017 *Theor. Math. Phys.* accepted for publication (arXiv:1707.06214v1)

[42] Yan Z-C and Babb J F 1998 *Phys. Rev. A* **58** 1247

[43] Pérat M, Caffarel M and Pouchan C 1993 *Phys. Rev. A* **48** 161

[44] Derevianko A, Johnson W R, Safronova M S and Babb J F 1999 *Phys. Rev. Lett.* **82** 3589

[45] Palik E D (ed) 1985 *Handbook of Optical Constants of Solids*, vol 1 (New York: Academic)

[46] Klimchitskaya G L, Mohideen U and Mostepanenko V M 2009 *Rev. Mod. Phys.* **81** 1827

[47] Decca R S, Fischbach E, Klimchitskaya G L, Krause D E, López D and Mostepanenko V M 2003 *Phys. Rev D* **68** 116003

[48] Decca R S, López D, Fischbach E, Klimchitskaya G L, Krause D E and Mostepanenko V M 2005 *Ann. Phys. NY* **318** 37

[49] Decca R S, López D, Fischbach E, Klimchitskaya G L, Krause D E and Mostepanenko V M 2007 *Phys. Rev D* **75** 077101

[50] Decca R S, López D, Fischbach E, Klimchitskaya G L, Krause D E and Mostepanenko V M 2014 *Phys. Rev. D* **75** 077101

[51] Chang C-C, Banishev A A, Castillo-Garza R, Klimchitskaya G L, Mostepanenko V M and Mohideen U 2012 *Phys. Rev. B* **85** 165443

[52] Banishev A A, Klimchitskaya G L, Mostepanenko V M and Mohideen U 2013 *Phys. Rev. Lett.* **110** 137401

[53] Banishev A A, Klimchitskaya G L, Mostepanenko V M and Mohideen U 2013 *Phys. Rev. B* **88** 155410

[54] Bimonte G, López D and Decca R S 2016 *Phys. Rev. B* **93** 184434

[55] Mostepanenko V M 2015 *J. Phys.: Condens. Matter* **27** 214013

[56] Klimchitskaya G L, Mohideen U and Mostepanenko V M 2012 *J. Phys.: Condens. Matter* **24** 424202

[57] Klimchitskaya G L and Korikov C C 2015 *J. Phys.: Condens. Matter* **27** 214007

[58] Klimchitskaya G L and Mostepanenko V M 2017 *J. Phys.: Condens. Matter* **29** 275701

[59] Chen Y-J, Tham W K, Krause D E, López D, Fischbach E and Decca R S 2016 *Phys. Rev. Lett.* **116** 221102
Figure 1. The highly accurate dynamic atomic polarizabilities for the atoms of He\(^*\) and Na are shown as functions of imaginary frequency in the double logarithmic scale.
Figure 2. The computational results for the magnitude of the free energy of atom-surface interaction at $T = 300$ K multiplied by the third power of separation are shown as functions of separation by the bottom and top lines computed using the perturbative and exact theories, respectively, for (a) the atom of He$^*$ and (b) the atom of Na.
Figure 3. The computational results for the magnitude of the force of atom-surface interaction at \( T = 300 \, \text{K} \) multiplied by the fourth power of separation are shown as functions of separation by the bottom and top lines computed using the perturbative and exact theories, respectively, for (a) the atom of He\(^*\) and (b) the atom of Na.
Figure 4. The computational results for the relative deviations between the exact and perturbative free energies (lines labeled 1) and forces (lines labeled 2) of atom-surface interaction at $T = 300\,\text{K}$ are shown as functions of separation for (a) the atom of He$^*$ and (b) the atom of Na.