Medium effects on the van der Waals force

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We consider the van der Waals interaction between two ground-state atoms embedded in adjacent semi-infinite magnetodielectric media, with emphasis on medium effects on it. We demonstrate that, in this case, at small atom-atom distances the van der Waals interaction is screened by the surrounding medium in the same way as in an effective (single) medium. At larger atomic distances, however, its dependence on the material parameters of the system and the positions of the atoms is more complex. We also calculate the Casimir-Polder potential of an atom A arising from a uniform distribution of atoms B in the medium across the interface. Comparison of this potential with the corresponding result deduced from the Casimir force on a thin composite slab in front of a composite semi-infinite medium, both obeying the Clausius-Mossotti relation, suggests a hint on how to improve a well-known formula for the van der Waals potential with respect to the local-field effects.

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Owing to the gradually increasing role of the van der Waals (and Casimir) forces with decreasing dimensions of the system on the one side and rapid progress in miniaturization of modern technologies on the other side, the van der Waals (atom-atom) interaction in complex systems is an issue of great importance, both fundamentally and practically. The van der Waals interaction in a confined space was usually considered assuming the atoms in an empty region bounded by perfectly reflecting (conducting) walls, e.g., in a planar cavity or in front of a plate. Its properties near realistic boundaries have been addressed only very recently. However, although it is known for quite some time that the van der Waals interaction, considerations of the combined medium and boundary effects in realistic systems on it are very rare. Actually, so far only Marcovitch and Diamant have addressed the van der Waals interaction in a system of this kind (namely, a three-layer dielectric system) and demonstrated its strong modification with the material parameters of the system. One of the reasons for this is certainly the necessity of consideration of the local-field effects on the atom-atom force in material systems; an issue which so far has not been explicitly addressed. In this work, we extend our previous consideration of the van der Waals force in a magnetodielectric medium to the case when the atoms are embedded in different semi-infinite media, with emphasis on medium effects on this force. Besides being of obvious interest, e.g., in surface physics and related sciences, these considerations also provide a hint on the local-field corrections in the theory of the van der Waals interaction.

I. VAN DER WAALS INTERACTION ACROSS AN INTERFACE

Consider two electrically polarizable atoms A and B embedded in an inhomogeneous magnetodielectric system described by the permittivity \( \varepsilon(\mathbf{r}, \omega) \) and permeability \( \mu(\mathbf{r}, \omega) \). The van der Waals interaction energy between the atoms is then given by

\[
U_{AB}(\mathbf{r}_A, \mathbf{r}_B) = -\frac{\hbar}{2 \pi c^2} \int_0^\infty d\xi \xi^4 \alpha_A(i\xi) \alpha_B(i\xi) \times \text{Tr} \left[ \mathbf{G}(\mathbf{r}_A, \mathbf{r}_B; i\xi) \cdot \mathbf{G}(\mathbf{r}_B, \mathbf{r}_A; i\xi) \right],
\]

where \( \alpha_A(B)(\omega) \) are the atomic vacuum polarizabilities and \( \mathbf{G}(\mathbf{r}, \mathbf{r}'; \omega) \) is the classical Green function for the system satisfying

\[
\left[ \nabla \times \frac{1}{\mu(\mathbf{r}, \omega)} \nabla \times -\varepsilon(\mathbf{r}, \omega) \frac{\omega^2}{c^2} \mathbf{I} \right] \mathbf{G}(\mathbf{r}, \mathbf{r}'; \omega) = 4\pi \mathbf{I} \delta(\mathbf{r} - \mathbf{r}'),
\]

with the outgoing wave condition at infinity. This form for \( U_{AB}(\mathbf{r}_A, \mathbf{r}_B) \) was firstly obtained by Mahanty and Ninham for two atoms in the free space and, relying on heuristic arguments, it was generally believed that, with the appropriate Green function, Eq. I describes the van der Waals potential in inhomogeneous systems as well. Very recently, this conjecture has been proved in various ways to be indeed correct, provided that the local-field effects can be neglected.

Assuming that the atoms A and B are embedded, respectively, in medium 1 occupying the half-space \( z < 0 \) and medium 2 occupying the half-space \( z > 0 \), as depicted in Fig. 1 we have

\[
\mathbf{G}(\mathbf{r}_A, \mathbf{r}_B; i\xi) = \int \frac{d^2 k}{(2\pi)^2} e^{i \mathbf{k} \cdot (\mathbf{r}_A - \mathbf{r}_B)} \mathbf{G}(\mathbf{k}, i\xi; z_A, z_B),
\]
FIG. 1: Two atoms interacting across an interface shown schematically. Media are described by (complex) refraction indexes \(n_i(\omega) = \sqrt{\varepsilon_i(\omega)\mu_i(\omega)}\).

\[
\hat{G}(\mathbf{k}, i\xi; z_A, z_B) = 2\pi \frac{\mu_1}{\kappa_1} \left[ t_{12}^p i\kappa_1 \mathbf{k} + k\mathbf{z} \right] e^{i\kappa_1 z_A - i\kappa_2 z_B} + i\kappa_2 \mathbf{k} \times \hat{\mathbf{z}} \right] e^{i\kappa_1 z_A - i\kappa_2 z_B}. \tag{3}
\]

Here \(i\kappa_i\), with

\[
\kappa_i = \sqrt{-k_i^2(i\xi) + k^2} = \sqrt{n_i^2(i\xi) \xi^2 + k^2} \tag{4}
\]

is the perpendicular wave vector at the imaginary frequency in the \(i\)th medium, whereas \(r_{12}^2(i\xi, k)\) and

\[
r_{12}^p(i\xi, k) = \gamma_{12}^p(1 + r_{12}^p) = \frac{\gamma_{12}^p}{\gamma_{12}^p \kappa_1 + \gamma_{12}^p \kappa_2} \tag{5}
\]

with \(\gamma_{12}^p = \varepsilon_1/\varepsilon_2\) and \(\gamma_{12}^p = \mu_1/\mu_2\), are the Fresnel coefficients for the 1–2 interface.

Equations (10)–(12) provide a straightforward way for calculating the van der Waals interaction energy between two atoms in different media. Evidently, in this case, \(U_{AB}\) is anisotropic and depends not only on the distance between the atoms, but also on their mutual orientation with respect to the interface between the media. Clearly, the simplest situation for consideration is when the atoms lie on a line perpendicular to the interface, i.e., when \(r_{A||} = r_{B||} = 0\) and, to examine the medium effects on the van der Waals interaction in the present system, we briefly consider the small- and large-distance behavior of \(U_{AB}\) in this particular case.

Letting \(r_{A||} = r_{B||} = 0\) in Eq. (12) and performing the angular integration \([\mathbf{k} = k(\cos \varphi \mathbf{x} + \sin \varphi \mathbf{y}]\), the Green function takes the diagonal form

\[
\hat{G}(r_A, r_B; i\xi) = G_{||}(z_A, z_B; i\xi)(\mathbf{x} \mathbf{x} + \mathbf{y} \mathbf{y}) + G_{\perp}(z_A, z_B; i\xi)\hat{\mathbf{z}} \hat{\mathbf{z}}, \tag{6a}
\]

\[
G_{||}(z_A, z_B; i\xi) = \frac{\mu_1}{2} \int_0^\infty \frac{dkk \left( t_{12}^p \right)}{k_{12}} e^{i\kappa_{12} z_A - i\kappa_{12} z_B}, \tag{6b}
\]

\[
G_{\perp}(z_A, z_B; i\xi) = \mu_1 \int_0^\infty \frac{dkk^3 \left( t_{12}^p \right)}{k_{12}} e^{i\kappa_{12} z_A - i\kappa_{12} z_B}. \tag{6c}
\]

Using

\[
\hat{G}(r_B, r_A; i\xi) = \hat{G}^T(r_A, r_B; i\xi), \tag{7}
\]

we find that, in this case, the van der Waals potential is given by

\[
U_{AB}(r_A, r_B) = -\frac{\hbar}{2\pi e^4} \int_0^\infty d\xi \xi^4 \alpha_A(i\xi)\alpha_B(i\xi) \tag{8}
\]

\[
\times \left[ 2G_{||}(z_A, z_B; i\xi) + G_{\perp}^2(z_A, z_B; i\xi) \right].
\]

Evidently, the integrals in Eqs. (6b) and (6c) cannot be calculated analytically in the general case. For \(n_1 = n_2 = n\), we obtain

\[
G_{||}(z_A, z_B; i\xi) = \frac{\mu}{z \left[ 1 + \frac{c}{n_2 \xi} + \left( \frac{c}{n_2 \xi} \right)^2 \right] e^{-\frac{\pi \xi}{c}}} \tag{9a}
\]

\[
G_{\perp}(z_A, z_B; i\xi) = -\frac{2\mu}{z n_2 \xi} \left( 1 + \frac{c}{n_2 \xi} \right) e^{-\frac{\pi \xi}{2c}}, \tag{9b}
\]

which, of course, in conjunction with Eq. (6), gives the extension of the well-known result for the free-space van der Waals potential 11 to magnetodielectric media (see also Refs. 3, 11).

The integral in Eq. (8) effectively extends up to a frequency \(\omega_{\text{max}}\) corresponding to the largest characteristic frequency of the system 14. Therefore, owing to the presence of the exponential factors in Eqs. (6b) and (6c), the main contribution to \(G_{||}(z_A, z_B; i\xi)\) and \(G_{\perp}(z_A, z_B; i\xi)\) at small atomic distances, \(z_2 - z_A \ll c/\omega_{\text{max}}\), comes from the large-\(k\) waves. Letting \(\kappa_i \rightarrow k\) in the integrands, we obtain their nonretarded values

\[
G_{||}(z_A, z_B; i\xi) \simeq \frac{\hbar^2}{2} \frac{1}{\xi^2 \varepsilon_1 + \frac{2}{Z}}, \tag{10}
\]

\[
G_{\perp}(z_A, z_B; i\xi) \simeq -\frac{\hbar^2}{2} \frac{2}{\xi^2 \varepsilon_1 + \frac{2}{Z}}, \tag{11}
\]

where \(Z = z_B - z_A\). With this inserted in Eq. (8), we find that at small distances between the atoms

\[
U_{AB}(r_A, r_B) = -\frac{3\hbar}{\pi Z} \int_0^\infty \frac{d\xi \alpha_A(i\xi)\alpha_B(i\xi)}{\xi^2(c^2)} \tag{12}
\]

where \(\varepsilon = (\varepsilon_1 + \varepsilon_2)/2\), i.e., the same result as if the atoms were embedded in a single medium 3, 7, 10 with the dielectric function \(\varepsilon(\omega)\).
At larger atom-atom distances, retardation of the electromagnetic field starts to play a role and, owing to the different speed of light in the two media, $U_{AB}$ is not a function of $Z$ any more but rather a function of separate atomic coordinates $z_A$ and $z_B$. To see this more clearly, we proceed in the standard way and make the substitution $\kappa_1 = n_1 \xi p/c$ in Eqs. (13a) and (13b). We obtain

$$G_{\parallel(L)}(z_A, z_B; i\xi) = \frac{\mu_1 n_1 \xi}{c} \int_1^\infty dp g_{\parallel(L)}(p, i\xi) \times e^{-\frac{\pi}{\kappa_1}(sz_B - p z_A)}, \quad (13a)$$

$$g_{\parallel}(p, i\xi) = \frac{\mu_2 p}{\mu_2 p + \mu_1 s} + p^2 \frac{\varepsilon_1 s}{\varepsilon_2 p + \varepsilon_1 s}, \quad (13b)$$

$$g_{\perp}(p, i\xi) = 2(1 - p^2) \frac{\varepsilon_1 p}{\varepsilon_2 p + \varepsilon_1 s}, \quad (13c)$$

where $s(p, i\xi) = \sqrt{p^2 - 1 + n_2^2/n_1^2}$. Inserting this into Eq. (8) and changing the order of integrations, we have

$$U_{AB}(r_A, r_B) = \frac{\hbar}{2\pi e^6} \int_1^\infty dp \int_1^\infty dp' \int_0^\infty d\xi \xi^6 \alpha_{A\alpha B} \times \mu_1^2 n_1^2 \{2g_{\parallel}(p, i\xi)g_{\parallel}(p', i\xi) + g_{\perp}(p, i\xi)g_{\perp}(p', i\xi)\} \times e^{-\frac{\pi}{\kappa_1}(sz_B - (p + p') z_A)}. \quad (14)$$

Now, for $z_A \omega_{\min}/c \gg 1$ and/or $z_B \omega_{\min}/c \gg 1$, where $\omega_{\min}$ is the minimal characteristic frequency of the atoms and the surrounding media, the main contribution to the integral over $\xi$ comes from the $\xi \approx 0$ region. Approximating the frequency-dependent quantities with their static values, the integration becomes elementary and for the van der Waals potential at large distances between the atoms we obtain

$$U_{AB}(r_A, r_B) = \frac{360 \hbar c}{\pi \varepsilon_1^3(0)n_1(0)} \int_1^\infty dp \int_1^\infty dp' \times \frac{2g_{\parallel}(p, 0)g_{\parallel}(p', 0) + g_{\perp}(p, 0)g_{\perp}(p', 0)}{[(s_0 + s_0') z_B - (p + p') z_A]^7}, \quad (15)$$

where $s_0 = \sqrt{p^2 - 1 + n_2^2(0)/n_1^2(0)}$. As one may easily verify, for a single medium ($n_2 = n_1$) this result reduces to $\Box$ $\Box$

$$U_{AB}^{(1)}(r_A, r_B) = \frac{23 \hbar c \alpha_A(0)\alpha_B(0)}{4\pi \varepsilon_1^3(0)n_1(0) Z^7}. \quad (16)$$

Evidently, as before, there is a combined medium effect on $U_{AB}$ at large atom-atom distances. This time, however, the strength of the screening of the van der Waals interaction by each medium is determined by the position of the atom embedded in it. We illustrate this in Fig. 2 where we have plotted the ratio $U_{AB}/U_{AB}^{(1)}$ in a nonmagnetic system as a function of $z_B$ for a fixed (large) distance $Z$ between the atoms and for different values of $\varepsilon_2(0)/\varepsilon_1(0)$. At $z_B = 0$, except for its modification because of the field transmission at the interface (described by the nominator in Eq. (15)), the potential is screened entirely by medium 1. With increasing $z_B$, the screening of $U_{AB}$ by medium 1 is gradually replaced by that of medium 2. Accordingly, since $U_{AB}^{(2)}/U_{AB}^{(1)} = \varepsilon_2^5(0)/\varepsilon_1^5(0)$, the relative potential $U_{AB}/U_{AB}^{(1)}$ increases for $\varepsilon_2(0) < \varepsilon_1(0)$ and decreases for $\varepsilon_2(0) > \varepsilon_1(0)$.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig2.pdf}
\caption{Relative van der Waals potential $U_{AB}/U_{AB}^{(1)}$ as a function of $z_B/Z$ for a large atom-atom distance $Z = z_B - z_A$. Media are assumed nonmagnetic ($\mu_1 = \mu_2 = 1$). The upper and the lower curve correspond to $\varepsilon_2(0) = 0.5\varepsilon_1(0)$ and $\varepsilon_2(0) = 2\varepsilon_1(0)$, respectively.}
\end{figure}

\section{Local-Field Corrections}

As already mentioned, Eq. (11) does not account for the local-field effects appearing in optically dense media. A hint on how to improve this result with respect to the local-field effects can be found by considering the Casimir-Polder potential as implied by Eqs. (11) and (13) in the case of a (uniform) distribution of B atoms across the medium 2 (see Fig. 3) and by comparing it with the corresponding result deduced from the Casimir force on a thin slab in front of a composite medium obeying the Clausius-Mossotti equation (15).

Assuming the atomic number density $N_B$ small enough, the Casimir-Polder potential $U_A^{(B)}$ of the atom A arising from its interaction with atoms B is obtained by pairwise summation of the van der Waals potentials $U_{AB}$, i.e.,

$$U_A^{(B)}(r_A) = \int_{z_B \geq 0} d^3r_B U_{AB}(r_A, r_B). \quad (17)$$

Equations (11) and (13) straightforwardly lead to (see the
The (complex) refraction index of the slab is
\[ n = \left( \frac{\epsilon_B}{n_1^2} \right) \] in a medium near a mirror (as depicted in Fig. 3). For a thin slab, so that \( \kappa_s d_s \ll 1 \) in the relevant frequency range, we have
\[ r^q (i \xi, k) = r^q_1 \frac{1 - e^{-2 \kappa_s d_s}}{1 - r^q_1 e^{-2 \kappa_s d_s}} \approx 2 r^q_1 \kappa_s d_s. \] (20)

Assuming that the surrounding medium is a collection of polarizable particles (atoms or molecules), the dielectric function of the slab is given by the Clausius-Mossoti equation [13] (the frequency dependence of \( \varepsilon \)'s and \( \alpha \)'s is understood)
\[ \varepsilon_s - 1 = \frac{4 \pi}{3} (N_1 \alpha_1 + N_A \alpha_A) = \varepsilon_1 - 1 + \frac{4 \pi}{3} N_A \alpha_A, \] (21)
where in the last line we have again used the Clausius-Mossotti equation, this time for medium 1 alone. Accordingly, the dielectric function of the slab can be written as
\[ \varepsilon_s = \varepsilon_1 + 4 \pi N_A \tilde{\alpha}_A, \] (22)
where \( \tilde{\alpha}_A \) is the effective polarizability of an A atom given by
\[ \tilde{\alpha}_A = \frac{\alpha_A (\varepsilon_1 + \frac{2}{3})}{1 - \frac{4 \pi}{3} N_A \alpha_A}, \] (23)
with the last line being valid when \( N_A \alpha_A \ll 1 \).

With Eq. (22), we have for small \( N_A \tilde{\alpha}_A \)
\[ \kappa_s \approx \kappa_1 \left( 1 + 2 \pi N_A \tilde{\alpha}_A \mu_1 \frac{\xi^2}{\kappa_1^2 c^2} \right), \] (24)
so that the medium-slab reflection coefficients are to the first order in \( N_A \tilde{\alpha}_A \) given by
\[ r^q_s = \frac{\varepsilon_s \kappa_1 - \varepsilon_1 \kappa_s}{\varepsilon_s \kappa_1 + \varepsilon_1 \kappa_s} \approx \frac{2 \pi N_A \tilde{\alpha}_A}{\varepsilon_1} \left( 1 - \frac{\nu_1^2 c^2}{2 \kappa_1^2 c^2} \right), \] (25a)
\[ r^q_1 = \frac{\kappa_1 - \kappa_s}{\kappa_1 + \kappa_s} \approx - \pi N_A \tilde{\alpha}_A \mu_1 \frac{\xi^2}{\kappa_1^2 c^2}. \] (25b)

Combining Eqs. (24) and (25) with Eq. (20) and inserting these \( r^q \)'s into Eq. (19), we find
\[ f_s (d) = N_A d_s f_A (d), \] (26)
where, with \( d \equiv d_A \),
\[ f_A (d_A) = \frac{\hbar}{2 \pi c^2} \int_{0}^{\infty} d \xi \xi^2 \mu_1 \tilde{\alpha}_A \int_{0}^{\infty} d k k e^{-2 \kappa_A d_A} \times \left( \frac{2 \kappa_1^2 c^2}{n_1^2 c^2} - 1 \right) \left[ R^p - R^q \right] \] (27)
is the Casimir-Polder force on an atom. We note that this equation extends (in different directions) previous results for the atom-mirror force in various circumstances by accounting for the magnetic properties of the media (see also Refs. 21, 22, 23) and including the local-field corrections within the Lorentz model for the local field.

Equation (27) enables one to calculate the force on the atom due to the uniform distribution of atoms in a magnetodielectric medium. Assuming that the mirror is a mixture of type 2 (electrically) polarizable particles and type B atoms, its dielectric function and the perpendicular wave vector inside it are given by Eqs. (22)-(24), with \( \{s, 1, A\} \rightarrow \{m, 2, B\} \). Accordingly, for the reflection coefficients of the mirror we find to the first order in \( N_B \alpha_B \)

\[
R^p = \frac{\varepsilon_m \kappa_1 - \varepsilon_1 \kappa_m}{\varepsilon_m \kappa_1 + \varepsilon_1 \kappa_m} = r_{12}^p + 2 \frac{\pi N_B \alpha_B \mu_2 \xi^2}{\kappa_2^2 c^2} \left( \frac{2 \kappa_2 c^2}{\kappa_2^2 c^2} - 1 \right),
\]

\( (28a) \)

where the single-interface Fresnel coefficients \( r_{12}^s \) and \( t_{12}^s \) are given by Eq. (17). Inserting this into Eq. (27), we find for the Casimir-Polder force near such a composite mirror

\[
f_A(d_A) = f_A^{(2)}(d_A) + f_A^{(B)}(d_A),
\]

(29)

where \( f_A^{(2)}(d_A) \) is the Casimir-Polder force of the atom in the vicinity of medium 2 alone [given by Eq. (27), with \( R^p \rightarrow r_{12}^p \) and \( f_A^{(B)}(d_A) \) is the force on the atom due to the uniform distribution of B atoms across medium 2. As seen, this latter force coincides precisely with the Casimir-Polder force obtained from Eq. (18) (note that \( z_A = -d_A \))

\[
f_B^{(A)}(z_A) = -\nabla_A U^{(A)}_B(r_A),
\]

(30)

provided that we let

\[
\alpha_{A(B)}(i\xi) \rightarrow \hat{\alpha}_{A(B)}(i\xi) \simeq \alpha_{A(B)}(i\xi) \left[ \frac{\varepsilon_{1(2)}(i\xi) + 2}{3} \right]^2.
\]

(31)

This suggests that, with the above replacement, Eq. (11) can also be used to describe the atom-atom interaction in optically dense media where the local-field effects cannot be neglected.

III. SUMMARY

In this work we have presented basic equations for consideration of the van der Waals interaction between two ground-state atoms embedded in adjacent semi-infinite magnetodielectric media and obtained a few results concerning the medium effects on this interaction. By considering a simple configuration, we have demonstrated that the atom-atom interaction in this system is at small distances screened by the surrounding media in the same way as in an effective (single) medium. At larger atomic distances, however, its dependence on the material parameters of the system and the positions of the atoms is more complex. We have also calculated the Casimir-Polder potential of an atom A arising from a collection of atoms B uniformly distributed in the medium across the interface. Comparison of this potential with the corresponding result deduced from the Casimir force on a thin composite slab in front of a composite semi-infinite medium, both obeying the Clausius-Mossotti relation, suggests that Eq. (11) can be adopted to describe the van der Waals potential in optically dense media as well, provided that the atomic polarizabilities are replaced by the effective ones.

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APPENDIX

Combining Eqs. (11) and (17), we have

\[
U_A^{(B)}(r_A) = -\frac{N_B \hbar}{2\pi c^2} \int_0^\infty d\xi d^{4}\xi_0 \alpha_{A0B} \left[ e^{i\xi r_A} + e^{-i\xi r_A} \right] \cdot \tilde{G}(r_A, \xi_0) \cdot \tilde{G}(r_B, \xi_0).
\]

(A.1)

Noting that \( \tilde{G}(r_A, \xi_0) = \int d^3k \frac{e^{i\mathbf{k} \cdot \mathbf{r}_A}}{(2\pi)^3} \tilde{G}^+(\mathbf{k}) \tilde{G}^-(\mathbf{k}) \)

(A.2)

and using Eq. (3), we find that the space integral in Eq. (A.1) is equal
\[
\int \frac{d^2k}{(2\pi)^2} \int_0^\infty dz_0 \text{Tr} \left[ \mathcal{G}(k, i\xi; z_A, z_B) \cdot \mathcal{G}^T(-k, i\xi; z_A, z_B) \right] = \int d^2k \left( \frac{\mu_1}{\kappa_1} \right)^2 \left[ (t_{12}^\ast)^2 \kappa_2^2 + k_1^2 + k_2^2 + k_1^2 + k_2^2 \right] \frac{e^{2\kappa_1 z_A}}{2\kappa_2}.
\]

\text{(A.3)}

Noting that \((\mu_1/\kappa_1)^2 = (\mu_2/\kappa_2)^2\), and using Eq. (4), we arrive at Eq. (18).