Temperature-dependent Casimir-Polder forces on polarizable molecules

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Abstract

We demonstrate that the thermal Casimir-Polder forces on molecules near a conducting surface whose transition wavelengths are comparable to the molecule-surface separation are dependent on the ambient temperature and molecular polarization and they can even be changed from attractive to repulsive via varying the temperature across a threshold value for anisotropically polarizable molecules. Remarkably, this attractive-to-repulsive transition may be realized at room temperature. Let us note that the predicted repulsion is essentially a nonequilibrium effect since the force we calculated on a ground-state (or an excited-stated) molecule actually contains the contribution of the absorption (or emission) of thermal photons.

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Casimir \[1\] and Casimir-Polder forces \[2\], are examples of striking phenomena that provide convincing evidence for the reality of quantum fluctuations of vacuum. One usually uses “Casimir” \[1\] to describe the force between two bulk material bodies such as conducting or dielectric plates, and “Casimir-Polder” (CP) \[2\] to refer to that between a polarizable object and a material surface. However, the underlying physical mechanisms are largely the same and there also exist similar behaviors of the forces. In addition to their fascination in fundamental research, Casimir and CP forces are becoming increasingly important in technological applications \[3–5\].

Recently, the CP forces at finite temperature have attracted a great deal of attention on both theoretical and experimental fronts \[6–22\] (for a recent review, see for example, Refs. \[23–25\]). The force felt by an atom near a planar surface at a finite temperature \(T\) was first considered by Lifshitz \[6\] and is sometimes called the Lifshitz force. At a distance \(z\) which is larger than the thermal photon wavelength \(\hbar c/k_B T\), the attractive Lifshitz force decays as \(1/z^4\) and is proportional to the temperature. In a previous paper \[18\], adopting an approach based upon the formalism proposed by Dalibard, Dupont-Roc and Cohen-Tannoudji \[26, 27\], which allows a distinct microscopic treatment to atoms in the ground and excited states in contrast to the macroscopic approach where atoms are treated as a limiting case of a dielectric, we have calculated the thermal CP force on a neutral polarizable two-level atom in interaction with quantized electromagnetic fields in a thermal bath of temperature \(T\) in the presence of an infinite conducting plane, and analyzed its behavior in three different regimes of the distance in both the low-temperature and the high-temperature limits for both the ground-state and excited-state atoms (see also Ref. \[12\] for a similar treatment). Let us note that the same thermal CP force, was reinvestigated in Ref. \[20\] from the perspective of molecules in the framework of macroscopic QED \[28\]. It is shown there that the CP force is independent of the temperature for a typical molecule placed near a plane metal surface whose transition wavelength is much larger than the typical experimental molecule-surface separation in the nanometer to micrometer range. This is in contrast to the temperature-dependent CP force for atoms \[6, 18\]. As a result, the CP forces on molecules with long-wavelength transitions can not be altered via the ambient temperature.

In this paper, we demonstrate that the thermal CP forces on anisotropically polarizable molecules whose transition wavelengths are comparable to the molecule-surface separation
are however temperature-dependent and can even be changed from attractive to repulsive as the temperature varies across a threshold value, and therefore can be dramatically altered via the ambient temperature. Let us note here that the attractive-to-repulsive transitions as a function of temperature have also been found in the so-called thermodynamic (critical) Casimir effect [29, 30].

We model, for simplicity, a polarizable molecule as a two-level system which has stationary states \(|-\rangle\) and \(|+\rangle\), with energies \(-\frac{1}{2}\hbar\omega_0\) and \(\frac{1}{2}\hbar\omega_0\), and a level spacing \(\hbar\omega_0\) and assume that it is placed at a distance \(z\) from an infinite conducting plane wall. With a definition of the molecule’s static scalar polarizability

\[
\alpha_0 = \sum_j \alpha_j = \sum_j \frac{2|\langle b|\mu_j(0)|d\rangle|^2}{3\omega_0\hbar},
\]

where \(\alpha_j\) represents polarizability in \(j\) direction, \(\mu_j\) is the spatial component of the molecule’s dipole moment and molecule is in its initial state \(|b\rangle\), we have shown that the molecule-wall potentials, which are the position-dependent corrections to the energy-shifts of the molecule, are given by [18],

\[
U^{CP}_- = \frac{3\hbar\omega_0\alpha_j}{128\pi\xi_0} \left[ \frac{2}{e^{\beta\omega_0/c} - 1} f_j(\omega_0, z) - g_j(\omega_0, z, \beta) \right],
\]

for the ground state, and

\[
U^{CP}_+ = \frac{3\hbar\omega_0\alpha_j}{128\pi\xi_0} \left[ \left( 2 + \frac{2}{e^{\beta\omega_0/c} - 1} \right) f_j(\omega_0, z) - g_j(\omega_0, z, \beta) \right],
\]

for the excited state. Here we have defined

\[
f_x(\omega_0, z) = f_y(\omega, 0, z) = \frac{4z^2\omega_0^2 - c^2}{z^3c^2} \cos(2z\omega_0/c) - \frac{2\omega_0}{z^2c} \sin(2z\omega_0/c),
\]

\[
f_z(\omega_0, z) = -\frac{2}{z^3} \cos(2z\omega_0/c) - \frac{4\omega_0}{z^2c} \sin(2z\omega_0/c),
\]

\[
g_x(\omega_0, z, \beta) = g_y(\omega_0, z, \beta) = \frac{64c}{\pi} \sum_{k=-\infty}^{\infty} \int_0^\infty du \frac{1}{(uc + k\beta)^2 + 4\omega_0^2} e^{-\omega_0u},
\]

\[
g_z(\omega_0, z, \beta) = -\frac{64c}{\pi} \sum_{k=-\infty}^{\infty} \int_0^\infty du \frac{1}{((uc + k\beta)^2 + 4z^2)^2} e^{-\omega_0u},
\]

where \(\beta = \hbar c/(k_B T)\) is the wavelength of thermal photons and summation over repeated indexes is implied. The above result shows clearly the dependence of the CP potential on
polarization of molecules while isotropy is usually assumed in other works [12, 20]. The force on the molecule can be calculated from the potential

$$F_{CP} = -\frac{\partial}{\partial z} U_{CP}. \quad (8)$$

For a given distance $z$, we can, in the notation of Ref. [20], define a spectroscopic temperature associated with the molecule transition frequency $T_{\omega_0} = \hbar \omega_0 / k_B$, and a geometric temperature with the distance $T_z = \hbar c / z k_B$. For a typical long-wavelength molecule whose transition wavelength is much larger than the typical molecule-wall distance, $z \ll c / \omega_0$, $T_{\omega_0} \ll T_z$. We now analyze how the CP potential behaves as the temperature varies in three different regimes of temperature, i.e., the low temperature, where the temperature $T$ is much lower than the spectroscopic temperature ($T \ll T_{\omega_0} \ll T_z$), the intermediate temperature, where the temperature $T$ is much higher than the spectroscopic temperature but much lower than the geometric temperature ($T_{\omega_0} \ll T \ll T_z$), and the high temperature, where the temperature $T$ is much higher than the geometric temperature ($T_{\omega_0} \ll T_z \ll T$).

Let us start with a typical molecule with long-wavelength transitions such that $z \ll c / \omega_0$. Now the oscillating functions, Eqs. (4) and (5), can be written as

$$f_x(\omega_0, z) = f_y(\omega_0, z) \approx -\frac{1}{z^3} + \frac{2\omega_0^2}{z c^2} - \frac{6\omega_0^4 z}{c^4}, \quad (9)$$

$$f_z(\omega_0, z) \approx -\frac{2}{z^3} - \frac{4\omega_0^2}{z c^2} + \frac{4\omega_0^4 z}{c^4}. \quad (10)$$

In the low temperature regime, i.e., when $T \ll T_{\omega_0} \ll T_z$, we have $z \ll c / \omega_0 \ll \beta$. So the exponential function, $\frac{2}{e^{\beta\omega_0 / c} - 1}$, approaches zero. And functions $g_i(\omega_0, z, \beta)$ can be approximated as

$$g_x(\omega_0, z, \beta) = g_y(\omega_0, z, \beta) = \frac{1}{2} g_z(\omega_0, z, \beta) \approx -\frac{1}{z^3}. \quad (11)$$

Plugging Eqs. (9)-(11) into Eqs. (2) and (3) and taking derivative of the potentials with respect to the distance $z$, we obtain the forces acting on the molecules in both ground and excited states,

$$F_{-}^{CP} \approx F_{+}^{CP} \approx -\frac{\hbar}{4\pi \varepsilon_0} \frac{9\omega_0}{32z^4} (\alpha_\parallel + 2\alpha_z), \quad (12)$$

where $\alpha_\parallel = \alpha_x + \alpha_y$ denotes the molecular polarizability in the transverse direction. This is just the usual temperature-independent van der Waals force.
If the temperature is higher than the spectroscopic temperature, \( T \gg T_0 \), we have \( \beta \ll c/\omega_0 \). In this case the exponential function, \( \frac{2}{e^{\beta \omega_0 c/\omega} - 1} \) can be approximated by \( \frac{2c}{\beta \omega_0 c/\omega - 1} \), and we find

\[
g_x(\omega_0, z, \beta) = g_y(\omega_0, z, \beta) = \frac{1}{2} g_z(\omega_0, z, \beta) \approx -\frac{2c}{\beta \omega_0 c^3}.
\] (13)

Consequently, in the spectroscopic high-temperature limit \( T \gg T_0 \), the forces become

\[
F_{CP}^- \approx -\frac{\hbar}{4\pi e_0} \left[ \frac{9\omega_0}{32z^4} (\alpha_\parallel + 2\alpha_z) + \frac{3\omega_0^2}{8c\beta z^2} (\alpha_\parallel - 2\alpha_z) + \frac{9\omega_0^4}{8c^3\beta} \left( \alpha_\parallel - \frac{2}{3} \alpha_z \right) \right],
\] (14)

\[
F_{CP}^+ \approx -\frac{\hbar}{4\pi e_0} \left[ \frac{9\omega_0}{32z^4} (\alpha_\parallel + 2\alpha_z) - \frac{3\omega_0^2}{8c\beta z^2} (\alpha_\parallel - 2\alpha_z) - \frac{9\omega_0^4}{8c^3\beta} \left( \alpha_\parallel - \frac{2}{3} \alpha_z \right) \right].
\] (15)

Let us now further analyze these forces in two subcases, i.e., \( T_0 \ll T \ll T_z \) and \( T_0 \ll T \ll T_z \ll T \). In the intermediate temperature regime, where the temperature \( T \) is much higher than the spectroscopic temperature but much lower than the geometric one \( (T_0 \ll T \ll T_z) \), we have \( z \ll \beta \ll c/\omega_0 \). So, the first term in both Eqs. (14) and (15) is much larger than the other terms. As a result, the forces are still independent of the temperature in the leading term. However, if the temperature moves to the high temperature regime, i.e., when \( T_0 \ll T \ll T_z \), or equivalently \( \beta \ll z \ll c/\omega_0 \), then the second term in Eqs. (14) and (15) will be dominant when \( \beta < \frac{|\alpha_\parallel - 2\alpha_z|}{3c} \cdot \frac{4\omega_0^2z^2}{|e_k|} \), or equivalently \( T > \frac{|\alpha_\parallel + 2\alpha_z|}{3c} \cdot \frac{4\omega_0^2z^2}{|e_k|} \), for molecules which are not isotropically polarized. In other words, above a threshold temperature, \( T_{\text{threshold}} \sim \frac{|\alpha_\parallel + 2\alpha_z|}{3c} \cdot \frac{4\omega_0^2z^2}{|e_k|} \), the force becomes temperature-dependent. If molecules are isotropically polarized, the second term in both Eqs. (14) and (15) vanishes. In this case, the threshold temperature appears at \( T_{\text{threshold}} \sim \frac{3c^4\omega_0^4}{4k_B\omega_0z^2} \) above which the third term dominates so that the CP force varies with temperature. Noteworthily, for a molecule in its ground state which is anisotropically polarized such that \( \alpha_\parallel - 2\alpha_z < 0 \), the CP force changes sign at the threshold temperature and turns to repulsive from attractive once the point is crossed, whereas for a molecule in its excited state, the force change sign at the threshold temperature when \( \alpha_\parallel - 2\alpha_z > 0 \). However, for isotropically polarizable molecules, the force is always attractive for the ground state, but it can change sign and become repulsive for excited states. So the properties of the CP force depend crucially on the polarization of molecules.

Let us now estimate the threshold temperature for a typical long-wavelength molecule. Taking LiH whose vibrational transition frequency is \( \omega_0 = 4.21 \times 10^{13} \text{ Hz} \) [31] as an example, we find that at a distance of \( z = 1 \mu\text{m} \) \( (z\omega_0/c = 0.14) \), the threshold temperature for a ground
state anisotropic molecule with only longitudinal polarization is $T_{\text{threshold}} \sim 1.2 \times 10^4$ K, and that for an excited state molecule which is isotropically polarizable is $T_{\text{threshold}} \sim 6.4 \times 10^5$ K. These threshold temperatures are not currently accessible in experiments. As a result, the temperature-dependent terms in Eqs. (14) and (15) which come from the oscillating functions $f_j(\omega_0, z)$ can be ignored in practical experimental sense. So, for typical long-wavelength molecules, the thermal CP forces are essentially temperature-independent [20], at least within the experimentally accessible temperature regimes. However, this may change dramatically when the molecule-wall distance is comparable to the transition wavelength of the molecule, as we will demonstrate next by numerical analysis.

Taking LiH as an example again, we have plotted, in Fig. 1, the CP force as a function of temperature $T$ for a LiH molecule in its ground state at a distance $z \sim c/\omega_0 \simeq 7 \mu$m and $z = 6 \mu$m respectively. The plots show clearly the temperature dependence of the force. One can see, from Fig. 1(a), that for a ground state LiH molecule which is polarizable only in the $z$-direction, the CP force becomes positive when the temperature is above a threshold value. For the molecule-wall distance $z = 7 \mu$m, numerical computation reveals that the threshold temperature occurs at about only 270 K. But for the molecules which are polarizable only in the direction parallel to the conducting plane wall or polarizable isotropically, the temperature dependent CP forces are always attractive as shown in Figs. 1(b) and 1(c).

This means that a repulsive CP force may be observed at room temperature for a longitudinally polarizable molecule in its ground state and a manipulation of the CP forces via the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{The temperature-dependent CP force between a ground state LiH molecule and a conducting plane wall, when the molecule is polarizable (a) in the $z$-direction, (b) in the direction parallel to the conducting plane wall, (c) isotropically. Here the distance is respectively $z \sim c/\omega_0 \simeq 7 \mu$m (solid line) and $z = 6 \mu$m (dashed line). The force is in the unit of $\hbar c \omega_0^2 \alpha_0/(128 \pi \varepsilon_0)$.}
\end{figure}
ambient temperature can be demonstrated in laboratory. If we decrease the molecule-wall distance, for instance, if we place the LiH molecule at a distance \( z = 6 \mu m \), the CP force as a function of temperature becomes what is plotted with dashed lines in Fig. 1. Now the threshold temperature appears at 340 K. So, for a given molecule, the threshold temperature increases with the decrease of the distance and it goes up too high to reach in experiment for \( z \ll c/\omega_0 \).

In the above discussions, we have examined the CP force for a molecule in its ground and excited states. Now we turn our attention to the thermal average of the force for a molecule in equilibrium with thermal photons, which can be written as

\[
F_{CP} = \frac{1}{1 + e^{-\omega_0 \beta/c}} F_{CP}^- + \left(1 - \frac{1}{1 + e^{-\omega_0 \beta/c}}\right) F_{CP}^+.
\] (16)

First, we consider molecules whose transition wavelengths are larger than the molecule-wall distance, \( z \ll c/\omega_0 \). In the low temperature regimes, \( T \ll T_{\omega_0} \left(\omega_0 \beta/c \gg 1\right) \), the average force is essentially given by the force of a ground state molecule, i.e., Eq. (12), which is independent of temperature. In the intermediate and high temperature regimes, the temperature is much higher than the spectroscopic temperature, i.e., \( T_{\omega_0} \ll T \left(\omega_0 \beta/c \ll 1\right) \). So, the contributions of the ground state and the excited one are almost equally weighted in the thermal average and therefore the temperature-dependent parts (refer to Eqs. (14) and (15)) cancel, leading to a temperature-independent final result the same as Eq. (12). Thus, the average force is temperature-independent over the entire range. This is in coincidence with the result in Ref. [20]. However, what we want to further show here is that this temperature independence of the average force is not universal. As a matter of fact, when the molecule-wall distance is comparable to the transition wavelength of the molecule, i.e., \( z \sim c/\omega_0 \), the average force becomes temperature-dependent in some regime, as is demonstrated in Fig. 2 where the average force of a isotropically polarizable LiH molecule at distance \( z \sim c/\omega_0 \approx 7 \mu m \) is plotted. The figure shows that when the temperature \( T < 30 \text{ K} \), the average force is equal to that for a ground state molecule. This comes as no surprise, since the energy of thermal photons in this case is much smaller than the transition energy \( \hbar \omega_0 \) so that transitions from the ground state to excited states are virtually impossible. However, as the temperature goes higher, the average force decreases obviously with the increase of temperature until temperature reaches the high temperature regime \( T_z \sim T_{\omega_0} \ll T \) where the average force becomes temperature-independent again. This temperature-independence
FIG. 2: The behavior of the average CP force for an isotropically polarizable LiH molecule as a function of temperature $T$ for a distance $z \sim c/\omega_0 (\approx 7 \mu m)$. Here the force is in the unit of $\hbar \omega_0^2 \alpha_j / (128 \pi \varepsilon_0)$. When the temperature $T < 30$ K, the average force is essentially equal to that of a ground state molecule (dotted line). In the high temperature regime $T \sim T_0 \ll T$, the force approximates to a temperature-independent value (dashed line).
transition wavelengths which are long as compared to the molecule-wall distance is dependent on the temperature, but this temperature dependence can not be exploited to alter the CP force via ambient temperature since the threshold temperature beyond which the CP forces become temperature-dependent is not currently accessible in experiments. However, if the molecule-wall separation is comparable to the transition wavelength, then CP forces on molecules display interesting temperature dependence at room temperature which allows us to dramatically manipulate them via the ambient temperature, and the force can even be changed from attractive to repulsive in experiments at room temperature.

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