Impact of effective polarisability models on the predicted release dynamics of CH$_4$ and CO$_2$ from premelted ice

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We present a theory for Casimir–Polder forces acting on greenhouse gas molecules dissolved in a thin water film. Such a nanosized film has recently been predicted to arise on the surface of melting ice as stabilized by repulsive Lifshitz forces. We show that different models for the effective polarizability of greenhouse gas molecules in water lead to different predictions for how Casimir–Polder forces influence the extraction of CH$_4$ and CO$_2$ molecules from the melting ice surface. In the most intricate model of a finite-sized molecule inside a cavity, dispersion potentials push the methane molecules towards the ice surface whereas the carbon dioxide typically will be attracted towards the closest interface (ice or air). Previous models for effective polarizability had suggested that CO$_2$ would also be pushed towards the ice surface. Release of greenhouse gas molecules from the surface of melting ice can potentially influence climate greenhouse effects.

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I. INTRODUCTION

Theoretical and experimental interest has been directed towards an understanding of fluctuation induced dispersion forces (Casimir, Casimir–Polder and van der Waals forces) in the last decades [1–4]. In the process of ice melting at the triple point a nanosized film of water has been predicted. It is stabilized by repulsive Casimir forces [5–7]. One important question is how Casimir–Polder forces influence release of greenhouse gas molecules trapped from surface of porous ice. Some experiments indicate enhanced concentrations of methane in drinking water associated with shale-gas extraction [8, 9]. In a similar way, release of methane from melting ice in the arctic due to increased temperatures may enhance climate greenhouse effects and pose threats to wildlife [10, 11]. We explore in this article how molecules dissolved in the equilibrium ice-water-air system experience Casimir–Polder forces. We focus our attention on methane and carbon dioxide molecules in the water phase. The Casimir–Polder force influences the extraction of greenhouse gas molecules, starting from being near the ice surface, then going into the bulk of the water nanosheet on the ice surface, and finally towards the water-air interface. New models for the effective polarizability of greenhouse gas molecules in water, which
account for the finite size of the particles and the vacuum bubble arising from Pauli repulsion will be used [12].

Notably, the most advanced model predicts (in contrast to simpler models) Casimir–Polder forces to push carbon dioxide molecules towards the closest interface. In simpler models previously used the carbon dioxide is pushed towards the ice surface. In contrast, methane is in all considered models pushed towards the ice surface. This means that carbon dioxide and methane will behave fundamentally different inside a premelting water layer. We will calculate the Casimir–Polder potential acting on the molecules inside the three-layer system and show that both will behave differently at the water-air interface by a change from attractive to repulsive force.

II. THEORY

We have recently demonstrated that finite size effects acting on atoms and molecules can be neglected at distances larger than close contact [13]. We therefore neglect finite size effects and use the local-field corrected van der Waals force acting on polarizable particles (e.g. CH₄ and CO₂ molecules) in a three layer system (ice-water-air, see Fig. 1). The thickness \( L = 32 \) Å of the water nanosheet at the triple point with ice-water-air at equilibrium is given by Lifshitz forces acting on the system [5].

The Casimir–Polder potential for a particle embedded between two infinite half spaces separated by the distance \( L \) can be written as [4]

\[
U(z) = \frac{\mu_0 k_B T}{4 \pi} \sum_{n=0}^{\infty} \xi_n^2 \alpha^* (\xi_n) \int_0^\infty dk ||k|| \kappa_1^2 \frac{k_{n}||}{k_1^2} \\
\times \left\{ \frac{r^{-}_s}{D_s} - \left( 1 + \frac{2 k_{||}^2 c^2}{\varepsilon_1 (i \xi_n) \xi_n^2} \right) \frac{r^{-}_p}{D_p} e^{-2 \kappa_1^2 z} \right. \\
+ \left. \frac{r^{+}_s}{D_s} - \left( 1 + \frac{2 k_{||}^2 c^2}{\varepsilon_n (i \xi_n) \xi_n^2} \right) \frac{r^{+}_p}{D_p} e^{-2 \kappa_1^2 (L-z)} \right\},
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and the prime indicates that the \( n = 0 \) term should be divided by 2. The corresponding Fresnel reflection coefficients for s- and p-polarized light read

\[
r_{s}^\pm = \kappa_1^\pm - \kappa_{2\pm}^\pm, \quad r_{p}^\pm = \frac{\varepsilon_2 \pm \kappa_1^\pm - \varepsilon_1 \kappa_{2\pm}^\pm}{\varepsilon_2 \pm \kappa_1^\pm + \varepsilon_1 \kappa_{2\pm}^\pm},
\]

with the imaginary part of the perpendicular component of the wave vector

\[
\kappa_{j}^\pm = \sqrt{\varepsilon_j (i \xi) \frac{c^2}{\varepsilon_2} + k_{||}^2},
\]

and the multiple reflection coefficients

\[
D_{s,p} = 1 - r_{s,p}^+ r_{s,p}^- e^{-2 \kappa_1^2 L}.
\]

In the non-retarded limit \( (k_{||} \gg \sqrt{\varepsilon_j \omega / c}) \) the perpendicular component of the wave vectors simplify to

\[
\kappa_{j}^\pm = \kappa_{1}^\pm \approx k_{||},
\]

leading to vanishing reflection coefficients for s-polarized waves, \( r_{s}^+ = 0 \). For p-polarized waves they simplify to the Fresnel reflection coefficients

\[
r_{p}^\pm = \frac{\varepsilon_2 \pm \varepsilon_1}{\varepsilon_2 \pm \varepsilon_1}.
\]

Thus, the integral along the \( k_{||} \)-axis can be performed and the Casimir–Polder potential in the nonretarded limit, Eq. (1), results in

\[
U(z) = -C_3^- (z) - C_3^+ (z) \frac{(L - z)^3}{z^3},
\]

with the distance-dependent \( C_3^\pm (z) \) coefficients.
The generalized hypergeometric function \( _4 F_3 \) denotes a measure for the impact of multiple reflections on the Casimir–Polder potential. Figure 2 illustrates the behavior of this function and marks the relevant parameter regime for the scenario considered here. It can be seen that the force is additive with respect to both interfaces for this situation. This is caused by the weak reflectivity of the water-ice interface, the dielectric functions of water and ice being similar.

By neglecting multiple reflections in the given geometry we can conclude that retardation effects can be neglected as well. Retardation plays an important role at larger distances. A well reflecting cavity, as is formed by the middle layer bound by two interfaces, virtually increases the path length of the propagating waves. Thus, retardation will be important for cavities with high reflection coefficients. As this is not the case in the considered scenario, these effects will not be important. However, we will compare the approximated potentials with the exact one.

Furthermore \( \alpha^*(i\xi_n) \) is the effective molecular polarizability in water at the Matsubara frequencies \( \xi_n = 2\pi k_B T n / \hbar \). For the free-space polarizabilities the adjusted parameters \( \alpha_j \) and ionization potentials \( \omega_j \) given in Ref. [12] were fitted to agree with the free space polarizability obtained from ab initio calculations[19]

\[
\alpha(i\xi_n) = \sum_j \frac{\alpha_j}{1 + (\xi_n/\omega_j)^2}.
\]

These and the hard sphere radii \( a \) for methane and carbon dioxide were derived as in several papers by Parsons and Ninham [18,19]. The cavity radii \( a_C \) were derived by solving the electrostatic Maxwell equations for particles embedded in a continuous medium. The different radii were taken from Ref. [12]. The combination of pressure and temperature at which liquid water, solid ice, and water vapor can coexist in a stable equilibrium occurs at \( T = 273.16 \mathrm{K} \) and a partial vapor pressure of 611.73 Pa. The dielectric functions of ice (\( \varepsilon_{2-} \), water (\( \varepsilon_1 \)), and vapor (air) (\( \varepsilon_{2+} = 1 \)) were taken from the work of Elbaum and Schick [4].

Three different models are used for the effective polarizabilities \( \alpha^*(i\xi_n) \) of the molecule in water: (i) Onsager’s real-cavity model for local-field corrections assumes that the molecule is situated in a small spherical vacuum bubble embedded in the water medium [20]. One finds that [14,21]

\[
\alpha_{\text{Ons}}^* = \alpha \left( \frac{3\varepsilon_1}{2\varepsilon_1 + 1} \right)^2.
\]

(ii) The hard sphere model posits that the molecule can be described as a homogeneous dielectric sphere of radius \( a \). Its effective permittivity \( \tilde{\varepsilon} \) can be deduced from the free-space polarizability, Eq. [10] via the Clausius–Mossotti relation [12,22]

\[
\alpha = 4\pi\varepsilon_0 a^3 \frac{\tilde{\varepsilon} - 1}{\tilde{\varepsilon} + 2}.
\]

The excess polarizability of the homogeneous-sphere molecule in water is then [23]

\[
\alpha_{\text{HS}}^* = 4\pi\varepsilon_0 \varepsilon_1 a^3 \frac{\tilde{\varepsilon} - \varepsilon_1}{\tilde{\varepsilon} + 2\varepsilon_1}.
\]

(iii) A generalization of both models is a homogeneous-sphere molecule embedded in a vacuum bubble of radius \( a_C \) including finite-size effects of the particles (subscribe \( f s \)). The resulting polarizability in water reads

\[
\alpha_{f s}^* = \alpha_{C}^* + \alpha \left( \frac{3\varepsilon_1}{2\varepsilon_1 + 1} \right)^2 \frac{1}{1 + 2\alpha_{C}^* \alpha/(8\pi^2\varepsilon_0^2\varepsilon_1 a_C^6)}.
\]

\[
C_3^- = \frac{k_B T}{8\pi\varepsilon_0} \sum_{n=0}^{\infty} \frac{\alpha^*(i\xi_n)}{\varepsilon_1(i\xi_n)} r_p^4 F_3 \left( 1, \frac{z}{L}; \frac{z}{L}, \frac{z}{L}, 1 + \frac{z}{L}; 1 + \frac{z}{L}, 1 + \frac{z}{L}; r_p^4 r_p^4 \right),
\]

\[
C_3^+ = \frac{k_B T}{8\pi\varepsilon_0} \sum_{n=0}^{\infty} \frac{\alpha^*(i\xi_n)}{\varepsilon_1(i\xi_n)} r_p^4 F_3 \left( 1, \frac{L-z}{L}, \frac{L-z}{L}, \frac{L-z}{L}, 2L-z, 2L-z, 2L-z; r_p^4 r_p^4 \right).
\]
with

$$\alpha^*_C = 4\pi\varepsilon_0\varepsilon_1 a_C^3 \frac{1 - \varepsilon_1}{1 + 2\varepsilon_1} \tag{15}$$

denoting the excess polarizability of the bubble.

All three models are based on physical assumptions with different depth of approximations. Onsager’s real cavity assumes a point-like particle in a vacuum bubble and takes the transmission through the interface into account. This is valid for atoms in a large cavity. The hard-sphere model assumes a finite-size particle without a vacuum layer between the particle and the environmental medium and can be applied to larger particles such as clusters when the cavity radius is comparable to the particle’s radius. The finite-size model is a composition of both models. It separates into two terms, the first one denotes the pure polarizability of an empty vacuum bubble and the second one is equivalent to Onsager’s real cavity model and describes the transmission through the interface and the multiple scattering inside between the particle and the cavity. The finite-size model reduces to both other models by applying the corresponding limits.

Applying the three models to methane and carbon dioxide embedded in water, one finds the effective polarizabilities depicted in Figs. 3 and 4 respectively. In both cases one finds an increase in the magnitude of the polarizability for the hard-sphere and Onsager’s real cavity model compared to the free-space polarizabilities. One also observes that the finite-size model affects both cases very differently. For carbon dioxide, this model results in a large frequency region with negative polarizability, which is caused by the crossing of the dielectric functions of water and CO₂. In contrast, this model applied to methane shows a much smaller frequency region with negative values.

| Model           | $C_3^−$ in $\mu$eV(nm)$^3$ | $C_3^+$ in $\mu$eV(nm)$^3$ |
|-----------------|----------------------------|----------------------------|
| Free particle   | 12.36                      | -444.34                    |
| Onsager’s cavity| 10.86                      | -553.96                    |
| Hard-sphere     | 5.92                       | -406.42                    |
| Finite-size     | 3.20                       | -45.87                     |
| Free particle   | 20.47                      | -524.24                    |
| Onsager’s cavity| 19.22                      | -651.27                    |
| Hard-sphere     | 13.91                      | -483.68                    |
| Finite-size     | 9.44                       | 31.26                      |

Table I. Table of $C_3$ coefficients for the water-ice interface ($C_3^−$) and for the water-air interface ($C_3^+$) for methane and carbon dioxide.

### III. RESULTS

The results for the $C_3$-coefficients of the water-air (right) and water-ice interface (left) are given in Table I. As predicted, the correction due to multiple reflections inside the cavity yields a relative error of less than 0.5 percent which is caused by the low reflection coefficient at the water-ice interface. Due to this fact, the resulting forces are independent of the thickness of the water layer. We restricted attention to the premelted water layer on top of an ice sheet; however the resulting Casimir–Polder potential is additive in the considered scenario with re-
that CO₂ taking into account the finite size of a particle, predicts results are shown in more detail in Figs. 5 and 6. The vicinity surrounding the CO₂ molecule residing in the water region is predicted to be attracted towards the ice surface and pushed away from the optically thinner region by Casimir–Polder forces. Specifically, the gas molecule as described in Ref. [12]. This leads to the surprising conclusion that some molecules, like carbon dioxide, may potentially be pushed towards an optically thinner region than by Casimir–Polder forces. Specifically, the gas molecule in water is attracted towards air. This suggests that some greenhouse molecules may be able to escape from melting ice more easily and enter the surrounding air. The calculations may be further refined by using a continuous cavity profile as informed by microscopic simulations of the environmental medium.

IV. CONCLUSIONS

While the free space polarizabilities of methane and carbon dioxide can be seen to behave in very similar ways, the effective polarizabilities in water are very distinct. In order to study this effect a new model has been explored that accounts for the finite size of the gas molecule in a cavity. The dimensions of the cavity are determined from the positions of the surrounding water molecules around the gas molecule as described in Ref. [12]. This leads to the surprising conclusion that some molecules, like carbon dioxide, may potentially be pushed towards an optically thinner region by Casimir–Polder forces. Specifically, the gas molecule in water is attracted towards air. This suggests that some greenhouse molecules may be able to escape from melting ice more easily and enter the surrounding air. The calculations may be further refined by using a continuous cavity profile as informed by microscopic simulations of the environmental medium.

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