Strong van der Waals Adhesion of a Polymer Film on Rough Substrates

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ABSTRACT: We propose that chemically inert polymeric films can enhance van der Waals (vdW) forces in the same way as nanofabrication of biomimetic adhesive materials. For the vdW adhesion of an ethylene-chlorotrifluoroethylene (ECTFE) film on rough metal and dielectric substrates, we present a model that combines microscopic quantum-chemistry simulations of the polymer response functions and the equilibrium monomer–substrate distance with a macroscopic quantum-electrodynamics calculation of the Casimir force between the polymer film and the substrate. We predict adhesive forces up to 2.22 kN/mm², where the effect is reduced by substrate roughness and for dielectric surfaces.

The discovery that van der Waals (vdW) forces are responsible for the remarkable sticking properties of gecko feet on dry surfaces has inspired the nanofabrication of biomimetic adhesive materials. For the vdW adhesion of an ethylene-chlorotrifluoroethylene (ECTFE) film on rough metal and dielectric substrates, we present a model that combines microscopic quantum-chemistry simulations of the polymer response functions and the equilibrium monomer–substrate distance with a macroscopic quantum-electrodynamics calculation of the Casimir force between the polymer film and the substrate. We predict adhesive forces up to 2.22 kN/mm², where the effect is reduced by substrate roughness and for dielectric surfaces.

We propose to exploit the flexibility of a polymer film to ensure close contact and hence high adhesive force on a solid substrate. In particular, ECTFE is a partially fluorinated polymer whose semicrystalline films have been experimentally demonstrated to exhibit a resistance against permeation of water and also high chemical resistance. Wettability measurements of ECTFE in polar liquids have revealed a considerable influence of vdW forces on the ECTFE–liquid interaction. Our proposed setup of such a polymer film sticking to a solid surface operates in a very different regime than the traditional Casimir setups. The polymer is expected to come into close contact with the substrate so that effects of retardation are negligible. The adhesion force per unit area between two smooth surfaces separated by a distance is hence given by the nonretarded limit of the Lifshitz formula:

\[
C_3 = \frac{\hbar}{8\pi^2} \int_0^\infty d\omega \text{Li}_3 \left[ \frac{\epsilon_1(\omega) - 1}{\epsilon_1(\omega) + 1} \frac{\epsilon_2(\omega) - 1}{\epsilon_2(\omega) + 1} \right]
\]

(1)

Here, \(\text{Li}_3(x) = \sum_{n=1}^{\infty} x^n / n^3\) is the polylogarithm and \(\epsilon_1(\omega)\) and \(\epsilon_2(\omega)\) are the dielectric permittivities at angular frequency \(\omega\) of the polymer film and substrate, respectively. The Lifshitz formula is originally expressed as an integral over real frequencies with the permittivities being a strongly oscillating functions. For mathematical convenience, we have used a Wick rotation to equivalently express the \(C_3\) coefficient as an integral over purely imaginary frequencies \(i\omega\) with \(\omega > 0\). The integrand is then
much easier to evaluate numerically, as it is a monotonously decreasing function. To illustrate the use of such imaginary-frequency integrals, we first quote the formula for the closely related van der Waals potential between two ground-state atoms

\[ U(r_{AB}) = -\frac{1}{24\pi^2 \varepsilon_0^2 r_{AB}^6} \sum_{kl} |d_{kl}^A|^2 |d_{kl}^B|^2 \equiv -\frac{C_6}{r_{AB}^6} \]

Here, \( r_{AB} \) is the distance between the atoms, and the sum represents virtual transitions of atoms A and B from their ground states to excited states \( l, k \) with transition energies \( E_{0l}^A \) and \( E_{0k}^B \) respectively. The respective dipole-matrix elements are denoted as \( d_{kl}^A \) and \( d_{kl}^B \). The potential \( U(r_{AB}) \) can be expressed as an integral over frequency

\[ U(r_{AB}) = -\frac{3\hbar}{16\pi^2 \varepsilon_0^2 r_{AB}^6} \int_0^{\infty} d\omega \alpha(\omega) \alpha(\omega) \]

where

\[ \alpha(\omega) = \frac{2}{3} \frac{E_{0l}^A |d_{kl}^A|^2}{(E_{0l}^A)^2 + \hbar^2 \omega^2} \]

describes the polarizability of atom A at imaginary frequencies (similarly for atom B).

In eq 1 we have neglected the effect of thermal fluctuations of the electromagnetic field and that of spatial dispersion. The assumption of a spatially local response implies the use of dielectric functions \( \varepsilon_0(\omega) \) and \( \varepsilon_1(\omega) \), which depend on the wave vector \( k \) only via its absolute value \( |k| = \omega/c \). A spatially nonlocal response and thermal effects combined have been shown to modify the Casimir force by a factor of 2 at distances larger than the thermal wavelength. At room temperature, the thermal wavelength assumes a value of about 48 \( \mu m \) and is, hence, much smaller than the distances considered here. The effect of nonlocal responses has also been studied at smaller distances where it was found that, depending on the model used, the force may be increased or decreased on a percent level. Finally, we note that, for moderate roughness, one may expect the polymers to adapt to the surface profile of the substrate, so that the corrugated surfaces of the interacting objects intertwine (see Figure 1).

While the optical properties of common solid substrates are well studied and tabulated, those of polymer species require microscopic simulations. Periodic simulations of long polymer chains packed in a box have been performed, for example, ref 20. However, in order to reproduce vibrational frequencies, polarizabilities, and polymerization mechanisms, careful investigations of monomeric or dimeric units are often applied instead, where the molecular properties are evaluated by quantum chemical methods or via combined quantum and molecular mechanical approaches. In the following, we will estimate the total adhesive force of ECTFE films on different substrates by combining macroscopic Lifshitz theory with microscopic simulations of the polymer response function. We begin by determining the polarizability of the polymer and the equilibrium distance of its monomers from different substrate media. Combining this information, we will determine the maximum total adhesive force for perfectly smooth substrates and finally study the effect of surface roughness on this force.

Let us start by determining the dielectric response of ECTFE. Microscopically, it is encoded in the dynamical polarizability \( \alpha(\omega) \) at imaginary frequencies. We are interested in the average dielectric properties of a large ensemble of ECTFE chains of various lengths and resort to a simple model: we study the polarizability of simple ECTFE monomers and represent the ensemble as a set of such monomeric units with random orientations. We calculate the monomer polarizabilities by means of combining quantum chemical methods as described in Supporting Information, A. To check the validity of the assumption that the polarizability of the polymers can be decomposed into those of single monomers, we compare monomer and dimer polarizabilities. After averaging over orientations, the isotropic polarizability of the dimer is almost equal to twice that of the monomer (Figure 2), justifying our model.

**Figure 1.** Setup: One-dimensional periodic sawtooth corrugations. The roughness is characterized by the mean distance between peaks, \( 2L \), and their average height, \( h \), related via the angle \( \theta = \arctan \left( \frac{h}{L} \right) \).

**Figure 2.** ECTFE monomers: Upper panel: Dynamical polarizabilities \( \alpha(\omega) \) of ECTFE monomer and dimer units at imaginary frequencies. After averaging over orientations, the isotropic polarizability of the dimer is almost equal to twice that of the monomer. This justifies the assumption that the polarizability of the polymers can be decomposed into those of single monomers. Lower right panel: Three-dimensional structures corresponding to the two conformers of the ECTFE monomer and the dimer.
We use additive single- or two-resonance Drude-Lorentz models instead. The obtained fit parameters can be found in Table III of section C of the Supporting Information. For the ECTFE film, we use the Clausius-Mosotti formula that relates its permittivity \( \varepsilon \) to the simulated polarizability: 
\[
\alpha_{\text{eff}} = \frac{3(\varepsilon - 1)}{4\varepsilon + 2},
\]
where \( \eta \) is the number density of particles. In Figure 3, we display the dimensionless polarizability \( 3(\varepsilon - 1)/(\varepsilon + 2) \) for all materials under study.

The figure reveals that the polarizabilities of the dielectrics ECTFE and silicon dioxide show a similar response in terms of the imaginary-axis polarizabilities. On the other hand, the metals gold and steel and the metalloid silicon all display a high static polarizability, with the polarizability of gold dropping fastest with increasing frequency. As the dispersive adhesion force depends on the integrated polarizabilities, one may hence expect this force to be significantly smaller for gold than for steel and silicon.

Using the optical data, we can now evaluate the dispersion force coefficients (eq 1) for ECTFE films on each of the four substrate materials. Using the equilibrium separations \( a \) between ECTFE monomers and the various substrates, we can hence determine the respective adhesive dispersion force
\[
\tilde{f} = f(a).
\]
The results are shown in Table 1, where for comparison, we have also given the approximate values obtained from a pairwise-additive approach. The findings are illustrated in Figure 3 which displays the dispersion force as a function of separation with the respective equilibrium separations indicated. One notes that silicon dioxide, which has the weakest force coefficient, has the smallest equilibrium distance, thus, enhancing the total force. As a result, the series silicon dioxide—gold—steel of increasing adhesive dispersion forces retains its order, but the relative differences between the substrates are less pronounced than they are for the force coefficients. The difference between forces for silicon dioxide and steel is a factor of 1.5. In addition, we note that the large equilibrium separation of gold has had the effect of reducing its total adhesion force, which is now more similar to that of silicon rather than that of steel. To summarize, the force coefficient and equilibrium separation are both equally relevant in determining the strength of the total adhesion force.

Realistic substrates exhibit roughness. We here address the question how this influences the adhesive force. As a model system, we study the one-dimensional periodic sawtooth corrugations as depicted in Figure 1. The roughness is characterized by the mean distance between peaks, \( 2L \), and their average height, \( h \), related via the angle \( \theta = \arctan \left( \frac{h}{L} \right) \). We assume the polymer film to be sufficiently elastic such that its shape adapts to the substrate surface. The effect of roughness will be cast into a correction factor \( \lambda \) which relates the average force per unit area of a rough surface to that of a perfectly smooth one via
\[
\lambda(a,L,\theta) = \lambda(a,L,\theta) f(a,L,\pi/2).
\] The roughness exhibited by real materials can be accounted for via the proximity force approximation (PFA). Here, irregular geometries are approximated by piecewise parallel ones, each subject to the Lifshitz force per unit area for infinitely extended plates. One way to treat the peaks of our model is to approximate their profile by small plane-parallel steps. The effective Casimir force is then obtained from eq 1 and it carries a correction factor
\[
\lambda(\theta) = \sin^3 \theta \leq 1
\]

In this simple treatment, \( \lambda \) only depends on \( \theta \) and becomes arbitrarily small for very rough surfaces. This may be
understood from a reduced contact due to enhanced distance in the z-direction as the ECTFE film gets pushed away from the substrate for steep corrugations. An alternative way of employing the PFA is to decompose the model peaks into their tilted parallel sections. The length of such sections equals

\[ A = \frac{L}{\sin \theta} - \frac{a}{\tan \theta} \]

Combined with the tilting factor, \( \sin \theta \), this leads to

\[ \lambda(\theta, L, a) = 1 - \frac{a}{L} \cos \theta \leq 1 \]  

(7)

For strong roughness, the effective force does not necessarily vanish but rather depends on the ratio of equilibrium distance \( a \) to mean separation of peaks \( 2L \). In this model, the roughness-reduction of the force is due to a reduction of contact area. The angle-dependence of \( \lambda \) for both models is illustrated in Figure 4.

As an alternative method, we study the effect of roughness via the Hamaker approximation, \(^{34}\) which reproduces the two-body contribution to the geometry-dependence (see Supporting Information, D). The corresponding result, also displayed in Figure 4, agrees with the tilted-surface PFA for small values of \( a/L \). For large values of \( a/L \), it lies in between the predictions from the stepwise-profile PFA and the tilted-surface PFA. We note that \( \lambda \leq 1 \) in all cases, meaning that roughness always reduces the adhesion force.

Finally, we want to address the assumption of complete contact between the ECTFE film and the substrate, which was made throughout this work. As depicted in Figure 5, complete contact means that the ECTFE film is perfectly pulled into the substrate’s asperities by the adhesive force and hence is in perfect contact with the substrate. The middle panel instead depicts partial contact while the right panel depicts the extreme of a perfectly inelastic film, which does not give in to the substrate’s asperities at all and therefore has only pointlike contact with the latter.

Figure 3. Adhesive force: Left: Dimensionless polarizabilities of all materials studied. From top to bottom: steel (blue), gold (orange), silicon (green), silicon dioxide (red), and ECTFE (black). The polarizabilities of the dielectrics ECTFE and silicon dioxide show a similar response. On the other hand, the metals gold and steel and the metalloid silicon all display a high static polarizability. Right: Total adhesive forces \( f \) per unit area as a function of the ECTFE–substrate separation. Solid and dashed lines correspond to exact theory and pairwise approximation, respectively. Diamonds indicate the respective equilibrium separations for the various substrates. Colors: steel (blue), gold (orange), silicon (green), silicon dioxide (red).

Figure 4. Surface roughness: Roughness correction \( \lambda \) which relates the average dispersion force per unit area of a rough surface to that of a perfectly smooth one via \( f(a,L,\theta) = \lambda(a,L,\theta)f(a,L,\pi/2) \). Shown in the figure are three different approximations: first, the Hamaker approximation (solid lines), with the parameter \( a/L = 0.01 \) (green, uppermost solid line), 0.1 (red, middle solid line), and 1 (blue, lowest solid line); second, we show the tilted-surface proximity force approximation (dashed lines) with the same choices of \( a/L \); and third, we include the stepwise proximity force approximation (dot-dashed line).

Figure 5. Complete, partial, and no contact. The left panel depicts the ideal of a perfectly elastic polymer film, which is completely pulled into the substrate’s asperities by the adhesive force and hence is in perfect contact with the substrate. The middle panel instead depicts partial contact while the right panel depicts the extreme of a perfectly inelastic film, which does not give in to the substrate’s asperities at all and therefore has only pointlike contact with the latter.
perfectly inelastic film would instead not adjust at all to the substrate’s roughness and hence have only point-like contact with it. This effect evidently affects the strength of the van der Waals adhesion between the ECTFE film and the substrate. Our predictions for such forces as presented in Table 1 only hold for the case of complete contact. This is motivated by the process of applying the ECTFE film to the substrate, during which the film is actually heated, causing it to adopt the shape of the roughness of the substrate as its zero-stress configuration. Nevertheless, one may consider the situation in which no heating is performed. Whether the ECTFE then adjusts to the shape of the substrate depends on the elastic modulus $\sigma$ of ECTFE on the one hand and the adhesive force per area $f$ between ECTFE and the respective substrate on the other hand. The elastic modulus is defined as the ratio between the applied stress $f$ and the resulting strain $\delta l/l$ of the material to which the stress is applied,

$$\sigma = \frac{f}{\delta l/l}$$  \hspace{1cm} (8)

Here, $\delta l$ refers to a change in length. Now, at any point at a lateral distance $x$ from a roughness peak of the interface, there is the competition between elastic energy lost,

$$E_{el} = \sigma \left( \frac{x}{\tan \theta} \right)^2$$  \hspace{1cm} (9)

and adhesion energy gained,

$$E_{adh} = 3C_3 \sin \theta \left( \frac{1}{a^2} - \frac{1}{(x \cos \theta + a)^2} \right)$$  \hspace{1cm} (10)

when bending into the substrate’s asperities. Depending on which of the two dominates, ECTFE at a lateral distance $x$ from a peak does or does not stick to the substrate. For the simplified geometry considered here, this leads to a correction or filling factor $\kappa = \tilde{x}^2/L^2$, with $\tilde{x}$ being the distance $x$ from a peak at which loss and gain balance. Such filling factors are given in Figure 6 for the elasticity modulus $\sigma = 1655$ MPa of ECTFE$^{56}$ and micron roughness $L = 10^{-6}$ m, were used. The filling factors depend on the respective $C_3$ coefficient, the equilibrium distance $a$, roughness angle $\theta$, and absolute roughness scale $L$.

![Figure 6](imageurl)  

**Figure 6.** Filling factor and critical angle: Filling factors for steel (blue), gold (orange), and silicon/silicon dioxide (green/red). The elasticity modulus $\sigma = 1655$ MPa of ECTFE$^{56}$ and micron roughness, $L = 10^{-6}$ m, were used. The filling factors depend on the respective $C_3$ coefficient, the equilibrium distance $a$, roughness angle $\theta$, and absolute roughness scale $L$.

and micron-scale roughness, $L = 10^{-6}$ m. Such filling factors depend on the respective $C_3$ coefficient, the equilibrium distance $a$, roughness angle $\theta$, and absolute roughness scale $L$. This figure illustrates that from $\theta = 10^\circ$ onward, perfect contact may be presupposed for all substrates considered here.

To conclude, we have shown that chemically inert polymer films such as ECTFE can be used to achieve high van der Waals adhesion forces on dielectric or metallic substrates. We have predicted these forces by combining quantum-chemistry simulations of the polymers microscopic properties with a macroscopic quantum electrodynamics calculation of the Lifshitz force between polymer film and substrate. A simple model of one-dimensional corrugations implies that substrate roughness will diminish the adhesion force. This model operates in a new regime of distances being comparable to or even smaller than the length scales characterizing the corrugations. The predicted forces are based on the assumption that the polymer film is sufficiently flexible to follow the substrate surface profile and achieve contact distances equal to those found for monomers. They thus have to be regarded as an upper bound to the forces found on practical implementations. To get a more precise estimate of the latter, further simulations of the microscopic structure of the polymer film will be necessary.

### REFERENCES


