A Green’s function approach to modeling molecular diffraction in the limit of ultra-thin gratings

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In recent years, matter-wave diffraction at nanomechanical structures has been used by several research groups to explore the quantum nature of atoms and molecules, to prove the existence of weakly bound molecules or to explore atom-surface interactions with high sensitivity. The particles’ Casimir-Polder interaction with the diffraction grating leads to significant changes in the amplitude distribution of the diffraction pattern. This becomes particularly intriguing in the thin-grating limit, i.e. when the size of a complex molecule becomes comparable with the grating thickness and its rotation period comparable to the transit time through the mask. Here we analyze the predictive power of a Green’s function scattering model and the constraints imposed by the finite control over real-world experimental factors on the nanoscale.

1 Introduction

Matter-wave diffraction at a double slit or grating is a paradigmatic example of fundamental quantum physics [1], which has been demonstrated with electrons [2], neutrons [3], atoms [4, 5], and small [6, 7] and complex molecules [8, 9]. Babinet’s theorem predicts also quantum fringes in diffraction at opaque obstacles, and Poisson’s spot was observed with atoms [10] and diatomic molecules [11] - with an application also in Fresnel zone plates [12]. In all these experiments attractive interactions between the grating and the matter-wave play an important role. They determine the relative population of the diffraction orders, influence the overall transmission through the grating and lead to substantial phase shifts. Hence, a detailed understanding of the interactions is of major importance for the design of any new experiment.

Atomic diffraction at nanomechanical masks has often been analyzed using the near-field potential \( V_{CP} = -C_3/r^3 \) as the short-range approximation of the Casimir-Polder interaction [13] — often referred to as van der Waals potential — with a constant \( C_3 \) which depends on the particle’s polarizability and the dielectric boundary. However, for large composite systems the complexity of this interaction increases considerably: Molecules may vibrate in many modes, rotate at high frequencies, and change their states even while they are flying across the grating. Furthermore, some theoretical approximations that served well in earlier work with atoms [7, 14, 15] have to be reconsidered in the limit of ultra-thin gratings. It is then no longer justified to distinguish between the inside of a diffraction slit and a position at the slit entrance. In addition, the attraction to the wall may become time-modulated when an anisotropic molecule exposes different axes of its polarizability tensor to the grating wall over time. A full description then has to include the initial random orientation of all molecules as well as their rotation in transit through the grating. Since a single \( C_3 \)
factor may then be insufficient to describe the interaction we here present a theoretical model which builds on the full Casimir–Polder potential. We explore the predictive power of the integrated phase that is accumulated by the molecular de Broglie wave during its approach towards, transit through, and exit from the grating. In hindsight this will justify the use of a coarse simplification, i.e. the parametrization of many subtle diffraction effects in an effective slit width – as has often been done in various earlier experiments with atoms and molecules.

2 Experiment

In Fig. 1a we show a typical molecular diffraction experiment, which has been described in more detail in Ref. [9]. It is contained in a vacuum chamber at \( p < 10^{-7} \) mbar to make sure that the molecules propagate freely from the source to the detector after they were evaporated from the entrance window by a focused laser beam. The molecular beam is laterally defined by the size of the source slit \( S(x_i) \) of 1-2 \( \mu \)m as well as by one piezo-driven vertical slit \( S(x_2) \). It reaches a divergence of about 10 \( \mu \)rad for a width of 20 \( \mu \)m at the detector screen. This prevents the diffraction orders from overlapping. A horizontal slit \( S(y) \) is used to constrain the free-flight parabola between source and detector to select a given velocity class at a certain height of the detector. The diffraction pattern is monitored by collecting all transmitted molecules on a quartz plate at distance \( L_2 = 564 \) mm behind the grating. The laser-induced fluorescence is collected by a microscope objective and registered by an electron multiplying CCD camera. Even though the interaction with the laser in the source is limited to about 1 ms the molecules are substantially heated and reach a speed of 100 – 350 m/s. The test particle phthalocyanine (PcH\textsubscript{2}) has a mass of \( m = 514 \) atomic mass units, covering de Broglie wavelengths between \( \lambda_{dB} = h/mv \approx 8 \times 10^{-12} \) – 2.2 \( \times 10^{-12} \) m in this experiment. If we assume thermalization of the internal and external degrees of freedom in the source we can assign a macrocanonical internal temperature of around 1200 K to PcH\textsubscript{2}. Even though this is low enough to avoid decoherence caused by the emission of thermal radiation [16] it influences the interaction of the molecules with the diffracting element also through the molecular rotation. In total we compare the performance of four different silicon nitride (SiN\textsubscript{4}) nanogratings G1–G4 to each other, which vary in their thickness by up to a factor of eight. Their geometry parameters are compiled in Fig. 1. Sending the molecules with a mean molecular velocity of 215 m/s through either one of these gratings we have obtained diffraction patterns as shown in Fig. 2. In all cases we observe almost maximal fringe contrast, i.e. between the diffraction peaks the fluorescence signal falls to its background level – with only a minimal contrast reduction for the thickest of all gratings. In the following we will discuss different approaches to analyze these observed molecular diffraction patterns.

3 Casimir–Polder potential in the thick grating limit

If we treat the molecules as structureless point particles, defined only by their mass and momentum, the formal equivalence between the stationary Schrödinger equation and the Helmholtz equation allows us to use the Kirchhoff–Fresnel integral to compute the propagation of the de Broglie waves from the source to the detector. The situation is simplified if the detector is situated in the far-field at \( L_2 > (N \cdot d)^2/\lambda_{dB} \) depending on the number of coherently illuminated slits \( N \) and the periodicity \( d \). The diffraction pattern can then be described by the Fourier transform of the complex grating transmission function. From a transverse coherence of 1.5 \( \mu \)m at the grating (\( N \sim 15 \)) it follows that the detector is placed in the transition regime between far– and near field. Hence, the quadratic terms of the wave function have to be considered for our experiment.

In earlier experiments on atom diffraction at ‘thick’ gratings [17, 18] it has been useful to approximate the wall inside of each grating slit as a semi-infinite plane, such that the particle’s interaction with one side of the slit can be described by \( V_{CP} \) with the Casimir-Polder coefficient

\[
C_3 = \frac{\hbar}{16\pi^2\varepsilon_0} \int_{0}^{\infty} \alpha(\omega) r(\omega) d\omega.
\]

(1)

\( C_3 \) is determined by the particle polarizability \( \alpha(\omega) \), the vacuum permittivity \( \varepsilon_0 \) and the dielectric function \( \varepsilon(\omega) \) of the grating material, where \( r(\omega) = (\varepsilon(\omega) - 1)/\varepsilon(\omega) + 1 \) is its surface reflection coefficient. All material constants depend on the frequency \( \omega \) of the virtual photons that mediate the Casimir–Polder force. The phase shift that is imprinted onto the molecular matter-wave in the diffraction process results from the attraction to both walls of each slit, integrated over the grating thickness \( b \). The interference pattern at the detector position \( x_d \) in the distance \( L_2 \) behind the grating is then computed via the one-dimensional Kirchhoff–Fresnel integral over the grating aperture \( A \), i.e. a comb of \( N \) slits of width \( s \),

```plaintext
\[
C_3 = \frac{\hbar}{16\pi^2\varepsilon_0} \int_{0}^{\infty} \alpha(\omega) r(\omega) d\omega.
\]
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Figure 1  a) A focused laser beam evaporates molecules from a spot of about 10 μm diameter. The required transverse coherence of the molecular de Broglie waves at the diffraction grating is prepared by means of an additional 1 micron slit 87 cm further downstream, i.e. 70 cm before the grating (\(L_1\)). Beam collimation to 10 μrad ensures that the diffraction fringes are separated at the detector screen; b) The oblate molecular dye phthalocyanine (PcH\(_2\), C\(_{32}\)H\(_{18}\)N\(_8\)) is numerically represented by an ellipsoid with a polarizability anisotropy of 5:1; c) Illustration of the relevant grating parameters: periodicity \(d\), slit width \(s\), thickness \(b\) and wedge angle \(\beta\); d) Electron micrograph of the grating G3; e) Due to the Casimir–Polder interaction between the molecule and the grating bars the higher diffraction orders of the molecular density pattern on the detectionscreen are more strongly populated than expected for structureless point particles; the table lists the parameters of the four silicon nitride gratings G1-G4. Their period and opening fraction were determined by scanning transmission electron microscopy, the thickness and wedge angle \(\beta\) using electron energy loss spectroscopy.

separated by the period \(d\). Pictorially, this integral sums over all elementary wavelets of wave vector \(|k| = 2\pi/\lambda_{DB}\) emanating from the grating aperture with an interaction-dependent phase:

\[
\psi(x_d) \propto \int_{-\infty}^{\infty} f(v_z) \int_{-D/2}^{D/2} I(x_d - x_0 \cdot L_2 / L_1, v_z) \, dx_0 \, dv_z
\]

(4)

All arguments above assume the validity of the Eikonal approximation, i.e. straight trajectories through the slits. This is justified by the fact that a molecule can only reach the detector further downstream if its interaction with the grating wall deflects it by less than 340 μrad. We introduce the cut-off distance as the closest possible separa-
1.0
0.5
0.0
1.0
0.5
0.0

Figure 2 Molecular diffraction pattern recorded in the band of (215 ± 15) m/s (solid line) and fitted using the Kirchhoff–Fresnel approximation and an approximate Casimir–Polder potential as in Eq.(4) (red circles). In this fit the $C_3$ coefficient was the only fit parameter. The Casimir–Polder coefficients extracted from the fit are a) $C_3 = 170$ meV·nm$^3$ for grating G1, b) $C_3 = 40$ meV·nm$^3$ for grating G2, c) $C_3 = 80$ meV·nm$^3$ for grating G3, and d) $C_3 = 50$ meV·nm$^3$ for grating G4. Within the experimental uncertainties the experiment is always very well reproduced, but with $C_3$ varying by 400% in this simplified model.

### Table 1

| Grating     | G1     | G2     | G3     | G4     |
|-------------|--------|--------|--------|--------|
| Non-retarded cut-off/nm | 2 × 3.4 | 2 × 7.2 | 2 × 3.3 | 2 × 4.7 |
| Slit width reduction/nm   | 36     | 38     | 28     | 28     |
| Fitted $C_3$/meV·nm$^3$    | 170    | 40     | 80     | 50     |
| Phase factor $\eta$        | 7.2    | 2.0    | 8.2    | 5.0    |

which may even vary somewhat across the grating, the listed values may have larger error bars. The correction factor $\eta$ accounts for this uncertainty.

From a fit of Eq. (4) to the molecular diffraction patterns we find the $C_3$-coefficients listed in Fig. 2. The overall reproduction of the shape and amplitude distribution is excellent for all gratings, with only small deviations for the thickest grating G2. However, the fitted $C_3$ coefficients vary by a factor up to four, even though they describe the same molecules and the same material. This indicates that the physics is not fully captured by this simplified approach.

### 4 Effective slit approximation

Since the exact determination of $C_3(\omega)$ is non-trivial, it has often proved useful in atom interferometry to encode an ‘effective potential’ in the transmission function. This assumes that a virtual reduction of a grating slit can mimic the transverse spreading of the molecular wave function that would otherwise be obtained at a larger slit in the presence of the attractive Casimir–Polder interaction [7, 19]. An ‘effective slit’ description is capable of predicting the population of higher diffraction orders since the far-field interference pattern can be described as the convolution of single slit and grating diffraction, i.e. a product of their Fourier transforms.

The method of ‘effective slits’ has proven particularly useful when the key goal is to compare atomic or molecular polarizabilities in diffraction at one and the same grating [15]. We implement it here by replacing the trans-
Molecular diffraction pattern recorded in the band of (215 ± 15) m/s for grating a) G1, b) G2, c) G3, and d) G4. The population of higher diffraction orders increases from G1 to G4. The fit is solely based on a reduction of the geometrical slit width to an effective one. The effective slit width in the ‘thick-grating’ approximation is $s_{\text{eff}} = 48, 20, 22, 16$ nm for G1-G4 rather than $s = 84, 58, 49, 44$ nm.

$V_{\text{CP}}(\mathbf{r}_A) = -\frac{\hbar \mu_0}{2\pi} \int_{0}^{\infty} d\xi \xi^2 \text{Tr} \left[ \mathbf{\alpha}(i\xi) \cdot \mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, i\xi) \right], \quad (5)$
with the reduced Planck constant $\hbar$, the vacuum permeability $\mu_0$, the molecular polarisability tensor $\alpha(i\xi)$ and the scattering Green tensor $G(r_A, r_A, i\xi)$. This relation accounts for the interaction of the fluctuating field at the (imaginary) frequency $\xi$ with the molecule, thereby creating a dipole moment whose strength is governed by the polarisability, and whose interaction with its own image is encoded in the classical propagator function $G(r_A, r_A, i\xi)$. The Green function is the fundamental solution of the vector Helmholtz equation [20]

$$\nabla \times \nabla \times G(r, r', \omega) - \frac{\epsilon(r, \omega) \omega^2}{c^2} G(r, r', \omega) = \delta(r-r'), \quad (6)$$

where the material properties and the grating geometry are encoded in the position- and frequency-dependent dielectric function $\epsilon(r, \omega) = 1 + \chi(r, \omega)$. With the boundary condition $G(r, r', \omega) \rightarrow 0$ for $|r-r'| \rightarrow \infty$, which is equivalent to the Sommerfeld radiation condition, the Green function is the unique solution to Eq. (6). In the scattering representation, the Green function is decomposed into a bulk component $G^{(0)}(r, r', \omega)$ that governs the propagation within a homogeneous materials, and a scattering contribution $G^{(s)}(r, r', \omega)$ that is necessary to fulfill the Maxwell boundary conditions at the interface(s) between free space and the grating.

Analytical solutions are only known for simple geometries with high symmetry. Constructing a Green function therefore requires usually considerable numerical effort. However, it is often sufficient to treat the scattering perturbatively using a Born series expansion, i.e. a multiple scattering expansion. For that the dielectric body is divided into small disjoint volume elements $dV$, which are still large enough to be treated as a homogeneous medium. We can then write [20]

$$G^{(s)}(r_A, r_A, \omega) = \frac{\omega^2}{c^2} \int_V d^3s G^{(0)}(r_A, s', \omega) \chi(s', \omega) G^{(0)}(s', r_A, \omega)$$

$$+ \frac{\omega^2}{c^2} \int_V d^3s' \int_V d^3s'' G^{(0)}(r_A, s', \omega) \chi(s', \omega) G^{(0)}(s'', r_A, \omega) \chi(s'', \omega) G^{(0)}(s'', r_A, \omega) + \cdots \quad \text{(7)}$$

The approximate scattering Green function $G^{(s)}$ is constructed from a reference Green function $G^{(0)}$, which we choose to be the free space propagator since this is analytically known [20]. The first term in Eq. (7) describes the propagation of a photon from the molecule at $r_A$ to the volume element at $s'$ and back to the molecule as shown in Fig. 4. The second term in the series, $G^{(0)}(s', s'', \omega)$, includes scattering between two volume elements at $s'$ and $s''$ within the dielectric. Since the n-th order scattering amplitude in insulating materials

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**Figure 5** Components of the polarisability tensor $\alpha(i\xi)$ at imaginary frequencies in atomic units (hartree energy $E_H = 27.2$ eV). The diagonal components $\alpha_{xx}$ and $\alpha_{yy}$ are represented by the blue solid line and vary by only a factor of four over the entire spectral range, from constant fields (0 cm$^{-1}$) to photons at 80 nm $(1.25 \times 10^5$ cm$^{-1}$). The out of plane component $\alpha_{zz}$ is represented by the red dashed line. These diagonal elements dominate entirely the off-diagonals elements, indicated as a gray shade at the bottom of the figure. The coordinates $x'$, $y'$, $z'$ refer to the principal axes of CH$_2$, as shown in Figure 1. The numerically calculated and experimentally measured values [24] of the polarisability agree in the static limit ($\xi \rightarrow 0$, $\omega \rightarrow 0$).

**Figure 6** Calculated squared dipole matrix elements for transitions from the ground state to the first vibrationally excited state. Transitions in the molecular plane are plotted in blue, out-of-plane components in grey.
falls rapidly with $\chi^{\prime\prime}(\omega)$ we can truncate the expansion after the first term. The correction due to higher-order terms around the grating bars is estimated in analogy to the case of a molecule in front of an infinite plate. It yields in the non-retarded limit the correction factor

$$\gamma = \frac{3}{\gamma} \int_0^\infty \frac{d\xi\alpha(i\xi)}{\xi^2 \Omega_1^2 + \gamma^2} \approx 1.1799$$

as the ratio between the exact Casimir–Polder potential for an infinite plate [21] and the potential in first-order of the Born series

$$V^{(1)}_{CP}(z) = \frac{3\hbar\mu_0 c^2}{64\pi^2 z^2} \int_0^\infty d\xi\alpha(i\xi) \frac{\varepsilon(i\xi) - 1}{\varepsilon(i\xi) + 2}.$$  

The scattering Green function contains all information about the electromagnetic response and the geometry of the grating. In case of the grating material SiN$_x$, its magnetic response can be neglected and only the electric part of the Casimir–Polder potential (5) contributes. For the dielectric susceptibility we used the model [18, 22]

$$\text{Im} \varepsilon(\omega) = \Theta(\omega - \Omega_T) \int d\omega \text{Im} \varepsilon(\omega) \left( \frac{\varepsilon(\omega) - \Omega_T^2}{(\omega^2 - \Omega_T^2) + \gamma^2 \omega^2} \right)^2$$

with the parameters $\Omega_T = 3.48 \cdot 10^{15}$ rad/s, $\Omega = 1.09 \cdot 10^{16}$ rad/s, $f = 1.13 \cdot 10^{17}$ rad/s, and $\gamma = 1.6 \cdot 10^{16}$ rad/s. In order to convert the imaginary part of the permittivity at real frequencies to the permittivity at imaginary frequencies, we use the Kramers-Kronig relation [22]

$$\chi(i\xi) = \varepsilon(i\xi) - 1 = \frac{2}{\pi} \int_0^\infty d\omega \frac{\text{Im} \varepsilon(\omega)}{\omega^2 + \xi^2}.$$  

Evaluating Eq. (5) requires in principle the complete knowledge of the polarisability at all imaginary frequencies. For atoms it is often sufficient to know the polarisability around a few strong electronic transitions which can be measured or computed with high accuracy [15]. For large molecules, on the other hand, the strongest transitions are often situated in the ultraviolet and therefore in an experimentally inaccessible range. They need to be derived from quantum chemical calculations which we have performed for Pch$_2$ using the software package TURBOMOLE [23]. The results are depicted in Fig. 5.

We also need to include thermal excitations and transitions in the molecules, as shown in Fig. 6. Even though we can neglect the thermal population of the electronic states the vibrational modes will be populated according to a Bose–Einstein distribution $n(\omega)$ which we use in the derivation of the Casimir–Polder potential. The poles of the Bose–Einstein distribution in the upper complex plane allows us to replace the integral over the imaginary frequencies in Eq. (5) by an infinite sum over the discrete Matsubara frequencies $\xi_j = 2\pi k_B T / h \cdot j$ [25]

$$V^{\text{res}}_{CP}(r) = \sum_n p_n \mu_0 T \sum_{j=0}^\infty \varepsilon^{\omega}_{n,j} \text{Tr} \left[ \alpha_n(i\xi_j) \cdot G^{(S)}(r, r, i\xi_j) \right],$$

where the primed sum denotes the relation

$$\sum_{j=0}^\infty \varepsilon_i \omega_i = \frac{1}{2} \varepsilon_i \omega_i + \sum_{j=1}^\infty \varepsilon_i \omega_i.$$

Here $k_B$ is the Boltzmann constant. The potential (12) is an average over all possible – and therefore ‘non-resonant’ – intramolecular states $|n\rangle$ weighted by their population probability $p_n$. Since we neglect thermal population of the electronic states the polarisability is constant $\alpha_n = \alpha$ and the average over all excitations trivial.

On the other hand, because the molecule is not in thermal equilibrium with its environment, the Casimir–Polder potential may acquire a resonant part which causes attractive and repulsive forces for transitions into higher states and lower states, respectively [25]. They need to be derived from quantum chemical calculations which we have performed for Pch$_2$ using the software package TURBOMOLE [23]. The results are depicted in Fig. 5.

We also need to include thermal excitations and transitions in the molecules, as shown in Fig. 6. Even though
that measures \( \sim 1.5 \) nm across. We employ a polynomial correction function to the Casimir–Polder potential for point dipoles \( V_{CP}^{dip}(z) \) which now treats the molecules as an ellipsoidally shaped electron density distribution

\[
V_{CP}(z) = V_{CP}^{dip}(z) \sum c_i(e) \left( \frac{a_i}{z} \right)^{2i},
\]

(16)

The length of the principal axis \( a \) and the eccentricity \( e \) are defined by the distance beyond which the electron density has fallen below \( \rho_{\text{e}} < 10^{-3} e \cdot a_0^{-3} \), where \( a_0 \) denotes the Bohr radius. Both density shape parameters have been computed using the software package GULSFAN (LC-BLYP/cc-pVTZ) [26]. They represent the geometry of the molecule and can be used to compute the polarizability ellipsoid [24]. The coefficients \( c_i \) are analytically known. For phthalocyanine we find \( a = 17 a_0 = 0.9 \) nm and \( e = 4 \) which yields

\[
V_{CP}(z) = V_{CP}^{dip}(z) \left( 0.9 + 4.9 \left( \frac{a}{z} \right)^2 \right).
\]

(17)

The isotropic distribution of initial orientations and the rotational states that are sampled in transit through the grating are taken into account in a coherent sum over the molecular density patterns for different rotational interactions. Based on the known rotational constants of phthalocyanine [27] we compute a mean rotational quantum number of \( J \approx 600 \) at \( T = 1200 \) K. This corresponds to a rotational period of around 10 ps, which must be compared to the 50 ps transit time of a molecule flying at 200 m/s through a 10 nm thick grating. While for most molecules in the ensemble the parameters are such that we can treat the molecule-wall interaction as effectively isotropic, the situation will change for the slowly rotating part of the ensemble, for gratings with large wedge angles and atomically thin gratings [28].

For ultra-thin gratings and fast molecules, the orientation and rotation of the molecules are no longer negligible, which means that the different rotational states enter the interference pattern incoherently. The interference pattern thus becomes orientation-dependent, \( \langle I(x_d) \rangle \rightarrow \langle I(x_d) , \Omega \rangle \) where \( \Omega \) denotes the solid angle. In analogy to Eq. (4) one would therefore have to average incoherently over all interferograms for the different orientational states as

\[
\langle I(x_d) \rangle = \int d\Omega \langle I(x_d), \Omega \rangle.
\]

(18)

Here, the integration measure \( d\Omega \) is assumed to include the proper normalisation factor and a possible (e.g. temperature-dependent) weight function. For the relativistically thick gratings used in the present experiments, however, we used the simpler approach of an averaged phase.

### 6 Scattering analysis of the diffraction patterns

Following the results of Section 5 we compute the potential for all distances and integrate the resulting de Broglie phase shift along straight trajectories – i.e. within the Eikonal approximation. Since the potential falls with at least the third power of the distance to the grating, we can limit the integral to a region \( \Delta z = \pm 30 \mu \text{m} \) before and after the slit. The integrated phase then simplifies the transmission function of Eq. (3) which then reads

\[
t(x, v_z) = \exp \{-i \Phi_{CP}(x, v_z)\},
\]

with

\[
\Phi_{CP}(x, v_z) = \frac{1}{\hbar v_z} \int_{-\Delta z}^{\Delta z} dz V_{CP}(x, z).
\]

(20)

This is used in Eq. (4) to compute the diffraction patterns. When we compare our ab initio calculation with the experimental data we still see discrepancies in the representation of the higher diffraction orders. However, a near-perfect fit to the experiment can be retrieved if we introduce a multiplicative phase factor \( \eta \) which adjusts the strength of the potential for each grating. The transmission function then reads

\[
t(x, v_z) = \exp \{-i \eta \cdot \Phi_{CP}(x, v_z)\},
\]

(21)

The result is shown in Fig. 7. The values of \( \eta \) we extract for the single gratings varies between 2.0 and 8.2, e.g. by 410 %.

### 7 Discussion

All three models of Sections 3–6 indicate that each grating has its own individual character and requires its own correction to either the Casimir–Polder potential or the effective slit width. They all exert stronger forces than expected based on the potential between a neutral dielectric and polarizable particles alone. We therefore need to discuss the possible sources for these deviations and their relevance for a number of emerging experiments, also in modern atom interferometry.

On the one hand, an uncertainty in the theoretical description is due to the unknown stoichiometry of
the silicon nitride membranes. However, no reasonable variation in the nitrogen concentration (‘x’ in SiNₓ) can explain η > 5, as observed above. On the other hand, an experimental accuracy in the original fabrication and measurement of the slit width may enter. Even though the grating period can be written with a precision higher than 1 nm using interferometric tables in focused ion beam writing (as done for gratings G1, G3, G4) or even with an accuracy of 0.01 nm using photolithography [29, 30] (as was the case for grating G2), the local etching process will introduce variations on the scale of several nanometers.

The lateral etching accuracy of focused ion beam writing is of the order of Δx = 5 nm and earlier atom diffraction experiments showed that changing the slit width by 1 nm could change the atomic C₃ coefficient by 25% [31]. In order to estimate the influence of this effect we have fitted the diffraction pattern of G2 using the full Casimir–Polder treatment for a series of different slit widths, separated by 1 nm in the interval 57 – 48 nm. The resulting phase factor η = 2.0(3) at s = 57 nm decreases linearly with the slit width to η = 1 for s = 50 nm. This slit width reproduces the experimental results best with the analytically computed potential, but contradicts the width that was determined in electron microscopy as shown in Fig. 1d. Geometry effects alone therefore are insufficient to explain the observed variations between the gratings.

In the comprehensive theoretical treatment in Section 5, the temperature influences both the resonant and the non-resonant part of the Casimir–Polder potential. For the non-resonant part it is argued that the polarizability is determined by the electronic state of the molecule. Here, it is safe to neglect contributions from electronically excited states as the internal temperature is not high enough to populate them and potential excitations would definitely have decayed by the time the molecules reach the grating, i.e. after milliseconds. The resonant contributions to the Casimir–Polder based on the molecular eigenstates are roughly three orders of magnitude smaller than the non-resonant ones. This is due to the small vibrational transition dipole moments dₘₙ. However, these vibrations may cause a time-varying dipole moment in the molecule, which could couple to the grating. Molecular modeling suggests that even at high temperatures, phthalocyanine will at most develop dipole moment fluctuations below 1 Debye. Since we don’t see any indications of decoherence this dipole moment does not shift the pattern but at most contributes to the effective molecular polarizability. We may therefore ignore this effect as an explanation for the variations in C₃ for the different gratings. The effect of rotations onto the molecular diffraction patterns has recently been studied in detail by Fiedler and Scheel [32] who find that the rotational motion has a pronounced influence on the relative population and a small effect on the position of different diffraction orders.

An important clue to the interpretation of our results is given by the observation that the fabrication of silicon nitride membranes is always accompanied by processes which lead to the deposition or implantation of charges. Focused ion beams have been reported to cause surface charge densities up to 10¹³ e/cm² in SiNₓ [33], whereas reactive ion etching after photolithography (used for
G2) is expected to generate lower charge densities. This reasoning is consistent with our Casimir-Polder fits since the value of $\eta = 2.0$ for G2 is much lower than the respective values for all FIB milled gratings, $\eta \in [5.0 - 8.2]$. The detailed charge variation is difficult to image with established technologies, such as Kelvin probe microscopy, since the local forces exerted by that method are sufficient to deform the very fragile gratings. Also electron microscopic methods are not ideally suited as they may add even further charges to the surface. Molecule diffraction is interestingly a non-destructive and sensitive probe of charges on freely suspended nanostrings. An efficient means to calibrate this method for a quantitative analysis, is still to be developed. Conceptually it will be interesting to revisit this problem with atoms in the future, where the internal particle dynamics is of lesser relevance. Additionally to the charging of the grating, gallium ions may be implanted into the silicon nitride membrane, changing the composition of the membrane material locally. This doping, which depend on the materials’ thickness and the FIB parameters, should be pronounced most for grating G4. However, the higher values of $\eta$ for G1 and G3 make it unrealistic that the gallium ions play a leading role.

8 Conclusions

We have presented a quantitative comparison of molecular interferograms that emerge in the diffraction at ultra-thin nanomechanical gratings. Three complementary approaches were used to describe the patterns: first, a simplified Casimir-Polder approach that includes the grating geometry. It is based on the assumption that one can approximate each grating as an infinite semi-space. Second, an approximation that reduces the entire problem to one single slit width, and finally a detailed scattering Green’s function approach that includes many details of the molecular shape, excitation and dynamics as well as the details of the grating. We find that they all have their merits and drawbacks.

The scattering approach is conceptually most comprehensive and most demanding as it includes a large variety of fundamental and experiment specific details. It allows us to draw conclusions about the presence of charges in the grating, even though a quantitative comparison would still profit from a well-defined calibration standard.

The diffraction pattern can, however, also be rather well described by the much simpler approximation of non-retarded Casimir-Polder interactions in front of an extended grating. At low diffraction orders, the model of effectively narrowed slits still describes the reality surprisingly well. We attribute the high qualitative agreement between very different theoretical approaches and levels of sophistication in the description of the molecular diffraction patterns to the fact that molecules close to the vicinity of the material walls will be effectively removed from the detected beam. This justifies an effective slit description.

A quantitative fit to the data always requires the assumption of additional local forces between the molecules and the grating walls that surpass the Casimir-Polder expectation by several hundred percent. We argue that it is unlikely that these forces and their variation between the gratings can be explained by any molecular property or the grating geometry alone. Our observation rather naturally indicates the presence of charges that have most likely been deposited in the manufacturing process, may have been accumulated during electron microscopy, or might have been added in vacuum by residual contaminations. Any way, they are difficult to control or eliminate selectively on the nanometer level.

Matter-wave diffraction may therefore be developed into a sensitive tool for detecting surface charges on the nanoscale if further work is invested into a better characterization and calibration of these distributions, possibly also using optical imaging of dispersed NV centers in nanodiamonds which are very sensitive and very localized field probes [34].

Our experiments rise a flag of warning for experiments that aim at quantitative measurements of Casimir-Polder forces or studies that envisage to explore deviations from Newton’s law of gravity on the micron scale. Whenever they operate with dielectric materials they will have to devise means to verify the level of surface charges.

For matter-wave interferometry it is an interesting challenge to further explore the role of these charges on the diffraction of polar molecules, as almost every biomolecule exhibits a permanent dipole moment. Hence, they are expected to interact even more strongly and more dispersively with nanomechanical masks.

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