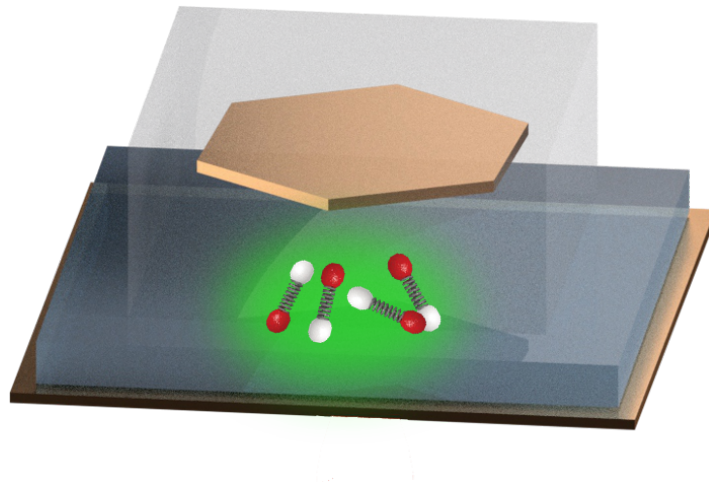




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Manipulating self-assembly of microcavities through lateral Casimir forces

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Nano and Biophysics
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A MASTER'S THESIS IN NANOSCIENCE

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Cover: Illustration of optical microcavity formed between a gold mirror and a nanoflake in an aqueous solution with CTAB

Abstract

Gold nanoflakes in a liquid solution have been found to form stable optical microcavities through self-assembly in room temperature. By applying the nanoflake solution on a gold mirror, the nanoflakes order themselves at a stable distance of $\sim 100 - 200$ nm from the mirror. The size of the cavity allows for a fundamental optical resonance modes in the visible spectral regime. By depositing a thin film of SiO_2 on the gold mirror it is possible to increase the cavity size and enable the optical modes to reach the infrared regime. The visible and infrared regime are highly interesting in technological applications such as controlling chemical reaction rates and nanomachines. The configuration of the system makes it possible to actively tune the resonance modes of the cavities using laser light to exert a pressure upon the nanoflake, which is interesting for applications in light-matter coupling. The main forces acting in this system are attractive Casimir forces and repulsive electrostatic forces. The forces are described by the Lifshitz formalism and diffusive double layer, respectively within the frames of the DLVO theory. An introduction of nanoholes in the SiO_2 thin film (called spacer) generate areas on the mirror that have a lower energy potential, which in turn attracts the nanoflakes. The nanoholes exerts a mean of control over where the microcavities form on the mirror.

To deduce the impact nanoholes have on the formation of the microcavities, a nanofabrication process was developed to create a gold mirror with a spacer containing nanoholes. A combination methods such as thermal evaporation, reactive sputtering, electron beam lithography and reactive ion sputtering was used to create 80 nm deep nanoholes with vertical walls in the spacer. An optical setup was constructed containing an inverted microscope, a fibre coupled spectrometer and a continuous wave laser. The setup allowed for real-time observation of the nanoflakes, reflectivity measurements of the microcavities and the laser is utilized as optical tweezers to gain real-time control of the nanoflakes. The nanoflakes was found to form microcavities inside the nanoholes rather than outside, which corresponds with results from calculations made with the Lifshitz formalism. The quality of the nanofabrication process turned out to have a significant impact on the reflectivity measurements and on how the nanoflakes react to the nanoholes.

Keywords: self-assembly, Casimir force, nanofabrication, reflectivity, optical cavity, Lifshitz theory, laser tweezers, nanoflake

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1

Introduction

This master thesis encompasses a system where optical microcavities effortlessly self-assemble due to counteracting forces between nanoflakes and a gold mirror in a solution. Moreover, the system enables the study of the Casimir force and how it may be utilized to control self-assembly. To begin with, a brief introduction to all important concepts of the project are presented in section 1.1. Next, the purpose and aim for this thesis are proclaimed in section 1.2, followed by the thesis outline in section 1.3.

1.1 Background

Self-assembly of nanoparticles is a phenomenon which encompass the spontaneous arrangement of particles to structured formations, from an initially disorganised state. The nature of self-assembly is driven by the system organising itself to minimize the energy and form a static equilibrium. To gain control over the process of self-assembly, zealous attention must be payed to the synthesis of the nanoparticles, for the shape, size and surface properties play an important role in how and if self-assembly occur [1]. The idea of self-assembly has been studied since the middle of the last century, for example in the very famous talk “There’s Plenty of Room at the Bottom” held by Richard Feynman in 1959, where he describes the idea of arranging small system in a controlled manner[2]. Self-assembly of nanoparticles and molecules is still a field, where scientist hope to gain more control over, in order to find future applications at the interface of nanotechnology and life sciences. The mere nature of this process holds information about the physical and chemical properties that can push today’s research forward in a variety of fields like nano-optics, material science, and nanotechnology [3, 4, 5]. Usually, self-ordering leads to emergence of useful properties and functions, for instance, appearance of new optical resonances.

Self-assembly may occur in various kind of environments, one in particular is within systems of small particles in liquid also referred to as colloid science. Here, the study of long range interaction of small particles and surfaces are in focus. Typical subjects that are studied in these systems are van der Waals forces and diffusive double layers [6]. The DLVO theory (named after Derjaguin, Landau, Verwey and Overbeek) explain colloidal stability by quantitatively describing the forces acting in the system. It incorporate repulsive electrostatic forces through a double layer potential and attractive forces usually described by a van der Waals potential [7, 8]. However, there are system where the van der Waals description of the potential do not subscribe. For systems where the interaction of colloids are at longer range, the attractive potential may be described by the Casimir potential. The Casimir force, first calculated by the physicist from whom it has its name, has a quantum nature and is present even

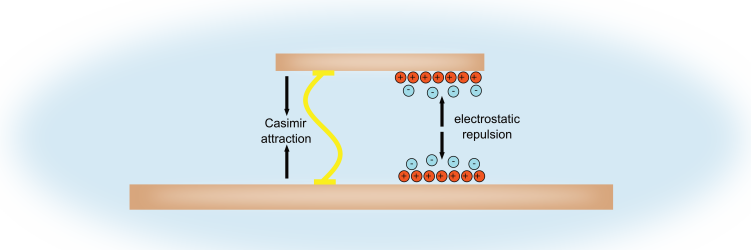


Figure 1: Schematic illustration of Casimir and electrostatic forces, between a flake and a surface, counteracting each other in line with the DLVO theory.

at zero temperature. Casimir derived the force by looking at the change in the electromagnetic zero point energy for two perfectly conducting plates[9]. Figure 1 show an illustration of the electrostatic and Casimir force between a small particle and a surface. To incorporate the Casimir potential in a colloidal system the Lifshitz formalism can be used. In contrast to the Casimir derivation of the force, intermediate mediums between the plates are included [10]. To calculate the force using Lifshitz formalism the only property of the materials needed is the permittivity for imaginary frequencies, giving it the range to describe systems with countless of different material combinations.

1.2 Purpose and aim

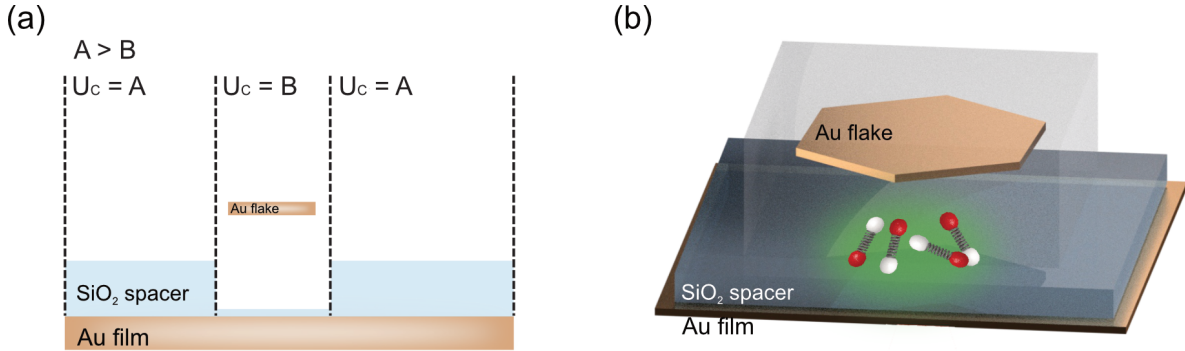


Figure 2: (a) The nanoflake in the solution experience different Casimir potential U_C whether it is above a nanohole or above the spacer. U_C is lower in the nanohole than on the spacer due to the different material properties of water and SiO_2 . (b) Illustration of the system of interest with a nanoflake in a solution containing CTAB over a gold mirror with a spacer. The green colour represent the Fabry-Pérot resonance mode in the visible regime.

A team of researchers at Chalmers has introduced an approach to micro-scale self-assembly based on the joined action of the attractive Casimir and the repulsive electrostatic forces arising between charged metallic nanoflakes in a solution [11]. Such system forms an optical Fabry-Pérot microcavity through self-assembly, with the fundamental mode in the visible range (separation distance $\sim 100\text{-}200\text{ nm}$), whose equilibrium configuration is tunable and formation reversible. This master thesis build upon this work and further expand one of the system configurations, where a thin thermally evaporated

gold film is replacing one of the nanoflakes and acts as a mirror. The modification of the configuration include adding a spacer upon the mirror which leads to red-shift in the resonance modes of the Fabry-Pérot cavities and enable introduction of structural discontinuities, such as nanoholes in the spacer. The system is illustrated in Figure 2 (b).

The aim for this project is to experimentally study if lateral Casimir forces can be used to manipulate the self-assembly of the optical microcavities by introducing nanoholes in the spacer. The Casimir force is highly dependant on the permittivity of a material, a higher permittivity contribute to a higher Casimir energy potential. By introducing nanoholes in the spacer and potential variations are simultaneously introduced in the system, which in turn affect the self-assembly of the optical microcavities (illustrated in Figure 2 (a)). The nanoflakes will experience an attraction to the nanoholes because of the lower energy potential, induced by the lower permittivity of solution. The project was initialized by creating a nanofabrication method that resulted in a sample with a nanohole structure. Followed by observations of the nanoflakes on the fabricated mirror and measurements of the optical microcavities. Finally, calculations of the Casimir force was conducted.

1.3 Thesis outline

The thesis is structured in the following way: Chapter 2 describes the theoretical background, discussing the Casimir force, Lifshitz formalism, Electrostatic force and DLVO theory. The last part of Chapter 2 introduces optical Fabry-Pérot microcavity. The following Chapter 3 describes the methods that are used to conduct the project. The results are presented and discussed in Chapter 4. Finally, Chapter 5 concludes the thesis by a summation of the main results and present some ideas of future prospects for the project.

2

Theoretical Background

This Chapter is dedicated to theoretical background of which the project lean on. The forces governing the system are described, starting with an introduction of the Casimir force in section 2.1 and the attraction of perfectly conducting plates in vacuum, followed by an introduction to the Lifshitz formalism which is the model used for the calculations in section 2.1.1. This is followed by the introduction to the electrostatic forces in form of diffusive double layers in section 2.2. Section 2.3 is dedicated to the DLVO theory and section 2.4, briefly explain the origin of resonance modes in Fabry-Pérot cavities. The theoretical background is written to highlight the important theoretical concepts for the system and should be seen as a brief introduction. For readers interested in gaining a deeper insight in the theory are recommended to indulge in the following textbooks on the subjects [12, 10, 6].

2.1 The Casimir force

Attractive forces that rise between atoms and molecules in their ground state and where there should be no opportunity for chemical bonding are due to van der Waals interactions, which is a result of fluctuations in the atoms or molecules electromagnetic field [12]. The van der Waals interaction is highly dependant on distance and the attractive forces decrease rapidly when the distance between the atoms or molecules increase. The interaction was first described in a correction of the ideal-gas equation by van der Waals. Later, the interaction between two ground-state atoms was derived by London in 1930, using second-order perturbation theory applied to the electrostatic interaction between two dipoles. The approximation of the interaction, usually called the London dispersion interaction, is

$$V = - \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{3\alpha_A\alpha_B}{2r^6} \frac{I_AI_B}{I_A + I_B} \quad (1)$$

where α_A and α_B are the static polarizabilities, and I_A and I_B are the ionization potentials, r is the distance between the atoms and ϵ_0 is the vacuum permittivity. However, this result is only valid if the distance r is less than the wavelengths λ corresponding transition between the ground- and excited state of the atoms. For distances larger than r , retardation effects become significant[12].

In the work of Casimir and Polder from 1948, retardation effects were taken into account in the van der Waals dispersion interactions. In the limit of large distances r , the interaction between a perfectly conducting plate and an atom (or molecule), and two atoms (or molecules) with static polarizability

was given as

$$V = -\frac{3}{8\pi} \frac{\hbar c}{r^4} \quad \text{and} \quad V = -\frac{23}{4\pi} \frac{\hbar c}{r^7} \quad (2)$$

respectively. The same year Casimir published a paper, showing a simpler derivation of the interaction between two perfectly conducting plates in vacuum, using classical electrodynamics and the change of electromagnetic zero point energy[9, 12]. Figure 3 show the two plates in vacuum separated by a distance L , illustrated in Figure 3.

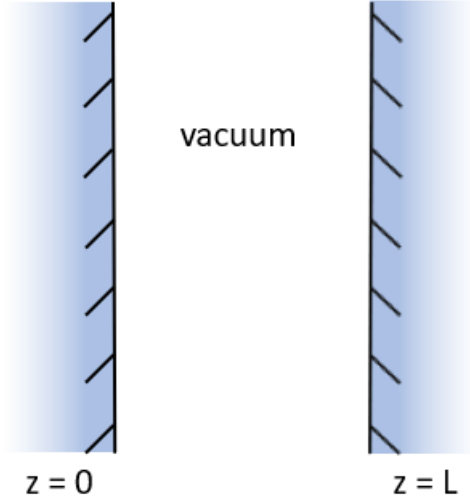


Figure 3: Perfectly conducting plates in vacuum experience an attractive force per unit area proportional to $1/L^4$.

By assuming a cubic volume bounded by perfectly conducting walls, and placing a square perfectly conducting plate in this cavity parallel to the xy -plane. Comparing the two situations where the plate is very close to the xy -plane, and very far from the xy -plane show that the summation over all possible frequencies in both cases, are divergent and lack any physical meaning. However, by calculating the difference between these two situations show a well defined value that may be interpreted as the interaction between the plate and the xy -plane, resulting in an expression of an attractive force

$$F = \hbar c \frac{\pi^2}{240L^4} \quad (3)$$

where L is the distance between the plates, c is the speed of light and $\hbar = \frac{h}{2\pi}$, where h is Planck's constant. This force, according to Casimir, can be interpreted as the zero point pressure of the electromagnetic waves[12].

An intuitive but quite superficial (and naive) explanation of the force on two perfectly conducting plates is the following: fields outside of the resonator reflect off it and push the plates together, while fields inside of the resonator reflect and push the plates apart. As all field frequencies are allowed outside the resonator, while the field frequencies between the plates are constrained by their boundary

conditions, results in the force pushing the plates together being much stronger than the force pushing them apart[12].

2.1.1 The Lifshitz framework for dielectric intermediate mediums

The system of interest is composed out of an aqueous solution of gold nanoflakes drop casted on a gold mirror in room temperature, conditions that are incomparable with the ones used to derive the original Casimir interaction. To accurately describe the system the Lifshitz formalism is used. Lifshitz generalized the Casimir interaction for system where intermediate mediums are included between two bodies, mediums such as water and SiO₂ that are present in this particular system.

To calculate the interaction between two bodies with intermediate mediums the Lifshitz framework assumes the bodies to be continuous, enabling a macroscopic approach to the system. By assuming that the distance between the bodies is much larger than the inter-atomic distance, the inter-atomic interaction may be neglected and in turn making it possible to regard the bodies as continuous [10, 13]. The interaction between the bodies is considered to be occurring through an electromagnetic field. A field always present in any medium as thermodynamic fluctuations, and at zero temperature as quantum fluctuations. The fluctuations regarded in this theory are those that have wavelengths in the order of size as the thickness of films and distance between the bodies. The properties of the fluctuations are specified by the electromagnetic permittivity at imaginary frequencies, $\varepsilon(i\xi)$ ($i\xi = \omega$, ξ are positive real numbers), of the bodies and intermediate mediums. Permittivity is a fundamental material property describing the propagation of electric fields and is a parameter that is known for the majority of materials, making the Lifshitz framework applicable for a vast range material combinations. The expression Lifshitz derived for real materials was done in support to the experimental measurements of attraction between solid bodies made by Deryagin and Abrikosova (in 1956) and their findings come to agree well with the theory [10, 13]. The force of interaction, between two bodies (media 1 and media 2) separated by a distance L which is occupied by medium 3, is expressed by the rather complicated equation

$$F = \frac{k_B T}{\pi c^3} \sum_{n=0}^{\infty} \varepsilon_3^{2/3} \xi_n^3 \int_1^{\infty} p^2 \left(\left[\frac{(s_1 + p)(s_2 + p)}{(s_1 - p)(s_2 - p)} \exp\left(\frac{2p\xi_n L \sqrt{\varepsilon_3}}{c}\right) - 1 \right]^{-1} \right. \\ \left. + \left[\frac{(s_1 + p\varepsilon_1/\varepsilon_2)(s_2 + p\varepsilon_2/\varepsilon_3)}{(s_1 - p\varepsilon_1/\varepsilon_3)(s_2 - p\varepsilon_2/\varepsilon_3)} \exp\left(\frac{2p\xi_n L \sqrt{\varepsilon_3}}{c}\right) - 1 \right]^{-1} \right) dp \quad (4)$$

where ε_1 , ε_2 and ε_3 are the permittivity for imaginary frequencies, T is the temperature, $s_1 = \sqrt{\varepsilon_1/\varepsilon_3 - 1 + p^2}$, $s_2 = \sqrt{\varepsilon_2/\varepsilon_3 - 1 + p^2}$, $\xi_n = 2\pi n k_B T/\hbar$, k_B is Planck's constant and p stem from the photon Green's function derived using quantum field theory[13]. For this project, the equation used for the calculation is slightly simplified, and is found in section 2.4.

2.2 Electrostatic forces - Diffusive double layer

Electrostatic interaction between two surfaces in a liquid solution rise due to ionization or dissociation of surface groups, or by absorption or binding of ions from the solution to an uncharged surface, resulting in a surface that is negatively (or positively) charged [6]. To the attractive van der Waals (or Casimir) forces in a solution are the electrostatic forces one of the counteracting repulsive forces, which hinder a solution of particles from coalescence. The co-ions, responsible for surface charge, are

balanced by counter-ions that are of equal but with an opposite charge to the co-ions. A part of the counter-ions are bound to the surface and this layer of counter-ions is called the Stern layer. Another part of the counter-ions form a diffusive double layer, where the ions are in a rapid thermal motion close to the surface[6]. In Figure 4 an illustration of a diffusive double layer of co- and counterions is shown.

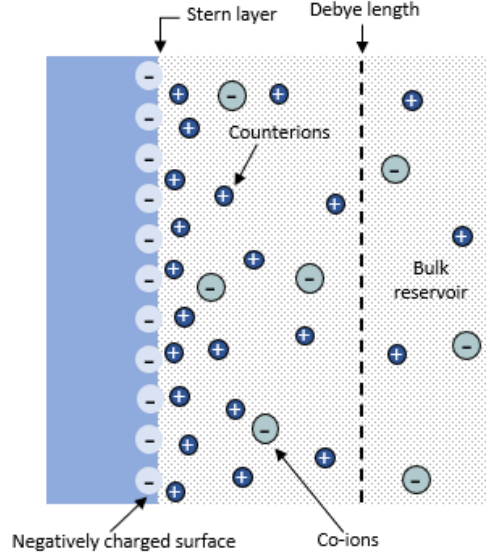


Figure 4: Illustration of the diffusive double layer in a 1:1 electrolyte solution. Close to the negatively charged surface there is a build-up of counterions with opposite charge to the surface and a depletion of co-ions. The surface charges is balanced by the Stern layer consisting of transiently bound counterions. The Debye length represent the thickness of the diffusive double layer and the border to the bulk reservoir.

For surfaces in an electrolyte solution, as for the system of interest where the aqueous solution contains the ions CTA^+ and Br^- , the bulk solution play a vital role for the electrostatic potential and the forces between surfaces. The thickness of the of the diffusive double layer is called the Debye length, which only depend on the properties of the solution, and is expressed by

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon k_B T}{2 \rho_\infty q^2 z}} \quad (5)$$

where ε is the static permittivity, k_B is Boltzman's constant, T is the temperature, ρ_∞ is the density of ions in the bulk solution with valence z and q is the elementary charge. The Debye length for the system of interest is approximately 23 nm in room temperature, with an ion concentration of ~ 0.35 mM [11]. The diffusive double-layer describe the variation of the electrostatic potential close to a charged surface in a solution[6]. The interaction between two surfaces in a dilute electrolyte, decay exponentially over a distance equal to the Debye length. The electrostatic potential between two charged planar surfaces opposite to each other is expressed by

$$U_e = \frac{2\sigma^2}{\varepsilon_0 \varepsilon \kappa} e^{-\kappa L} \quad (6)$$

where σ is the surface charge and L is the distance between the surfaces. The repulsive interaction between surfaces is highly dependant on concentration, where the interaction decrease with higher ion concentrations due to screening and increase with lower concentration[6].

The equilibrium distance of about $L_{eq} = \text{sim}100 - 200$ nm, between the bottom mirror and the gold flake, is much larger than the Debye length of ~ 23 nm. To explain this behaviour of the system it is in order to look closer at the condition for the equilibrium distance [11]. An assumption is made that the Casimir and electrostatic pressure cancel each other at a certain distance L_{eq} , that is $P_c + P_e = 0$ (the trivial solutions $L_{eq} = 0$ and $L_{eq} = \infty$ are not considered further). The Casimir and electrostatic pressure are evaluated as

$$P_C = -\frac{\pi^2 \hbar c}{240 L^4} \quad \text{and} \quad P_e = -\frac{\partial U_e}{\partial L} = \frac{2\sigma^2}{\varepsilon \varepsilon_0} e^{-\kappa L} \quad (7)$$

where the negative sign of P_C indicates an attractive pressure opposite to P_e , where the positive sign indicates a repulsive pressure. At the equilibrium distance the total pressure is zero $P_{tot} = P_C(L_{eq}) + P_e(L_{eq}) = 0$, by doing a Taylor expansion near L_{eq} for both pressures the following expressions are obtained

$$P_C = -\frac{\pi^2 \hbar c}{240 L^4} (1 - 4 \frac{\delta L}{L_{eq}} + o(\delta L)) \quad \text{and} \quad P_e = \frac{2\sigma^2}{\varepsilon \varepsilon_0} e^{-\kappa L} (1 - \kappa \delta L + o(\delta L)). \quad (8)$$

For positive δL the total pressure $P_{tot}(L_{eq} + \delta L)$ must be less than zero, which gives an additional requirement on the equilibrium distance such that

$$L_{eq} > 4\kappa^{-1}. \quad (9)$$

This provide an explanation of the much larger equilibrium distance for the system and an insight in how the Casimir and electrostatic balance each other, despite being based on rather rough assumptions[11].

2.3 The DLVO theory

The DLVO theory describes the interaction between two charged surfaces in a liquid quantitatively by a summation of all the forces acting in a system. There is a wide range of forces that can contribute to the total potential U_{tot} derived by the DLVO theory, such as the gravitational force or depletion forces like osmotic pressure and hydrophobic forces, but the most dominant forces are the Casimir (or van der Waals) force and electrostatic forces [6]. Henceforth, is the total potential a summation of Casimir U_C and electrostatic U_e potential as

$$U_{tot} = U_C + U_e \quad (10)$$

At small distances the Casimir potential exceeds the electrostatic potential, resulting in total aggregation of the particles in the solution[6]. This attractive well is usually denoted the primary minimum of the energy profile. As the distance between the particles increase the energy profile pass its maximum

called the energy barrier. For some cases where the electrolyte solution are of higher concentrations, the energy barrier is directly followed by a secondary local minimum. It is at this local minimum the stable equilibrium between the gold mirror and gold nanoflake is found. The height of the energy barrier indicate how stable the system is, the higher the barrier the more energy is needed for the system to become aggregated. For the system to get in a stable equilibrium the energy barrier must exceed the potential of the Brownian motion at room temperature[6].

2.4 Resonant optical cavity

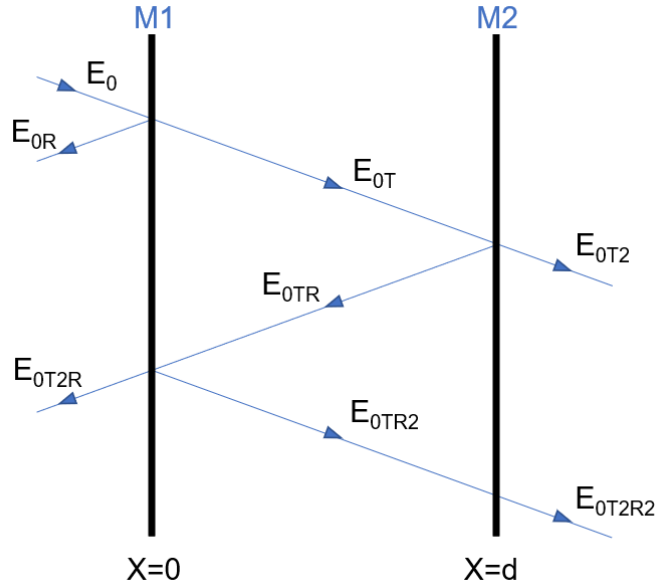


Figure 5: A Fabry-Pérot cavity consisting of two mirrors, $M1$ and $M2$, with a distance d between them. The incident light beam E_0 hit $M1$ and is reflected E_{0R} and transmitted E_{0T} . E_{0T} , then hit $M2$ and is reflected E_{0TR} and transmitted E_{0T2} . The same process then occur for E_{0TR} against $M1$, and again the pattern repeats itself indefinitely.

A resonant optical cavity is an arrangement of mirrors in which light may circulate. The Fabry-Pérot interferometer that was presented in 1899, is an optical cavity consisting of two parallel partially reflecting mirrors with a distance d between them [14]. In Figure 5, a multiple reflection between two reflective surfaces is illustrated, a beam of light is applied to one of the mirrors, here a part of the light is reflected and a part is transmitted. The transmitted light then travel until it hits the second mirror and a process of reflection and transmission occur again, but this time the reflected part of the light travels and hit the first mirror, this process of reflection and transmission then continues indefinitely. As the light is circulated in the cavity, interference of light rays occur. When the light rays are in phase with each other, there is an enhancement of light. The enhancement of light is independent of the specific values of frequency but depends on the frequency spacing

$$\Delta\nu = \frac{c}{2nd} \quad (11)$$

where c is the speed of light, n is the refractive index and d the distance between the mirrors. The wavelengths that enable the light enhancement is described by

$$\lambda_m = \frac{2nd}{m} \tag{12}$$

where m is an integer. The enhancement of the waves occurs every time a integer multiple of half-wavelength match the distance between the mirrors. These waves are said to exactly "fit" within the cavity, meaning that the electric vector of the electromagnetic wave is zero at the surfaces of the mirrors, creating standing waves called modes. The number of frequencies that can fit in a Fabry-Pérot cavity are infinitely many and the more frequency modes one want to measure the higher reflectivity of the mirrors is needed[\[14\]](#).

3

Methods

This Chapter introduces the methods used to realise and investigate the intended system. In section 3.1 the gold nanoflake synthesis is presented, followed by section 3.2 in which the nanofabrication is displayed. The setup for relectivity measurements is presented in section 3.3, together with laser tweezers. Section 3.4 is dedicated to the transfer matrix method, utilized as a tool to investigate the microcavities configuration. The theory behind the Lifshitz framework is explained in section 2.1.1. In section 3.5, the equations used to calculate the Casimir potential for this system is presented.

3.1 Synthesis of Gold nanoflakes

The gold flakes used for the experiments were synthesised for another project and were made using the recipe from ref. [15]. The gold flakes were synthesized by a rapid and seedless wet chemical method. First, 100 μL of 100 mM HAuCl_4 was added into 3 mL of 20 mM CTAB (aqueous) in a glass vial, this was then gently mixed and left undisturbed for several minutes. In the next step μL of 100 mM L-ascorbic acid was added to the mixture followed by a rapid inversion for 10 seconds. The resultant solution was directly put into a water bath at the temperature of 85 °C and left undisturbed for about an hour. The final product were washed by centrifugation at 4000 rpm for 10 minutes, and re-dispersed in de-ionized water for further use.

3.2 Nanofabrication

The fabrication process flow is illustrated in Figure 6, from cleaning of the glass substrate to finished sample. The samples are all prepared on 170 μm thin microscope glass coverslips. Before the fabrication of the sample, the coverslips are cleaned in acetone and isopropyl alcohol (IPA) for five minutes each at 50°C in an ultrasonicator. Thereafter, are coverslips rinsed in de-ionised water at 50 °C in the ultrasonicator for 1 minute to reduce risk of residues left on the substrates. Finally, the coverslips are dried with N_2 gas. To deposit a thin film of gold upon the substrate an electron-beam evaporator of model Lesker-PVD 225 was used. The deposition of thin films is a result of high energy electron bombardment of a gold target, the atoms that are transformed into a gaseous phase and travel trough the vacuum and precipitate to solid form and coat the chamber and the intended substrates. The mirror is made of a 30 nm thin film with a 2 nm adhesion layer. A 100 nm thin film of SiO_2 is deposited on the gold surface by reactive sputtering. This is done by using FHR MS 150 Sputter machine which is a computer controlled sputter tool, which can be used for both DC and RF sputtering. The process

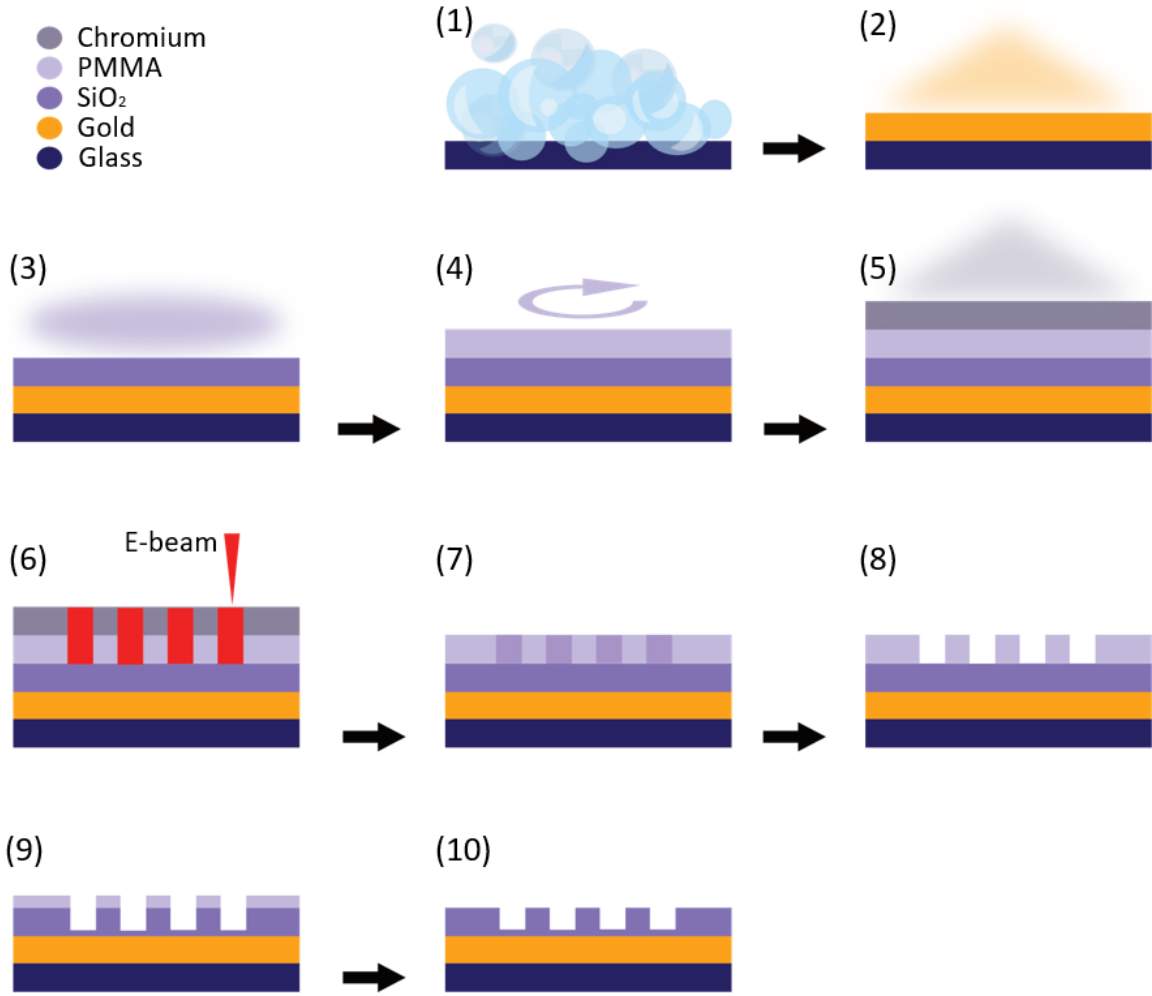


Figure 6: Process flow for sample fabrication; (1) The glass substrate is thoroughly cleaned in an ultrasonicator (2) A 30 nm thin gold film is deposited by thermal evaporation (3) A 100 nm thin film is deposited by reactive sputtering (4) PMMA is spin coated on the SiO₂ as a resist (5) A 20 nm thin film of chromium is deposited as a conductive layer for EBL (6) The pre-designed pattern is exposed in the EBL machine (7) The chromium film is removed (8) The exposed pattern is developed (9) The SiO₂ is etched by reactive ion etching (10) The excess PMMA is removed and the sample is done

gasses are Argon, O_2 and N_2 . To deposit SiO_2 a reactive sputtering process is performed. The O_2 gas, the reactive gas, is introduced into the Argon plasma causing a reaction between the target material, in this case silicon, and the O_2 gas. The material is then deposited on the gold surface of the sample.

Electron-beam lithography (EBL) system of model JEOL JBX 9300FS was used to create the etching mask. EBL utilize a focused electron beam to expose a prepared pattern on a resist, which is an electron sensitive film. The solubility of the exposed areas of the resist change, making it possible to remove the exposed or unexposed parts of the resist by immersing it in a solvent (development). For this project the mask design was prepared in a CAD software called Klayout 0.26. Figure 7 show the design of the pattern in the Klayout 0.26 interface with a magnification of a nanohole area. The design consists of a 2 by 2 matrix with circular holes of varying diameters from $0.5 \mu m$ to $10 \mu m$. The holes are enclosed by a $2 \mu m$ square trench. The crosses at the corners of the design are separated with $500 \mu m$. The size of the holes are chosen to have a similar diameter as the lateral size of the flakes, and be both bigger and smaller. By doing this it is possible to examine if observations and measurements of the flake vary with different size of the holes. The trenches are there to act as a barrier that hinder flakes to diffuse into the area of the holes, enabling more control over the flakes that are under examination.

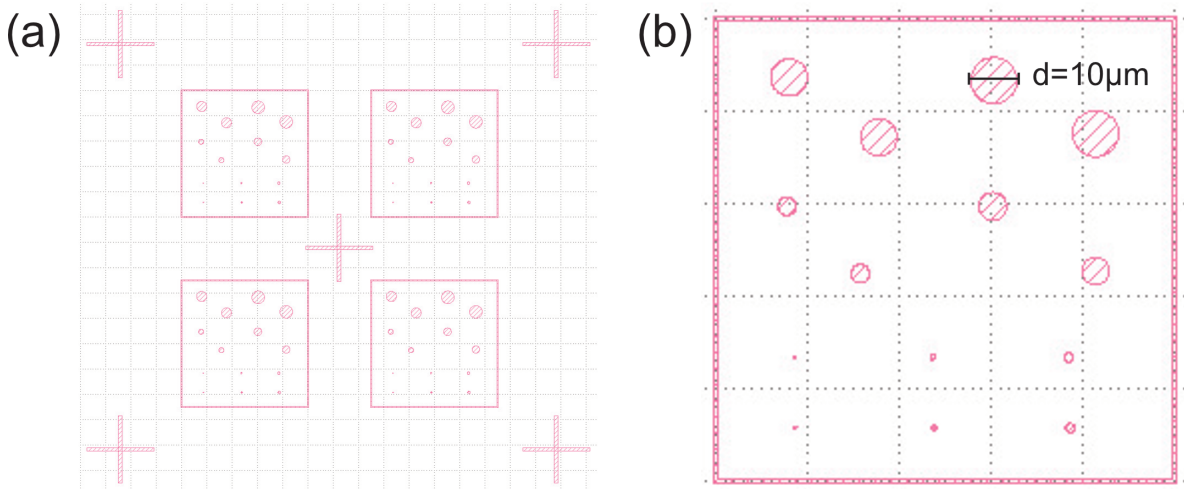


Figure 7: The mask design in the Klayout 0.26 interface shown in (a) and a magnification of a trench confined nanohole area in (b).

After the gold and SiO_2 deposition the sample is prepare for the EBL. First, a resist, PolyMethyl-Methacrylate (PMMA), with a thickness of ~ 220 nm was spin coated on top. PMMA is a positive resist, meaning that the exposed areas of pattern are removed during the development process. The resist was then baked for 5 minutes at $180^\circ C$. Thereafter, a 20 nm thin layer of chromium was deposited on top of the resist by thermal evaporation. As SiO_2 is a non-conducting material there is a risk of charging effects in the resist, which result in bad resolution of the exposed areas. By adding the chromium, the risk of charging effects is reduced. The sample is now ready for the electron-beam exposure. The design was exposed in a 2 by 2 matrix, resulting in total of 16 trench enclosed nanohole areas. The electron dose was changed as a matter of optimization of the process, to reduce the risk of resist residues remaining in the exposed structures after the development. For the first batch of fabricated samples the electron dose was $900 \mu C/cm^2$ and for the second batch of sample the electron dose was increased to $1200 \mu C/cm^2$.

After the EBL exposure the chromium was removed using wet-etching. The chromium was removed using ceric ammonium nitrate, which is a standard etchant for chromium removal. After one minute

of etching, the sample was rinsed in an abundance of water. After, the samples are dried with N_2 gas. The development of the PMMA was done by two different methods, as for the increase of electron dose was the reason for changing the development a way to optimize the process to get as clean development as possible. The first development method was made in MIBK:IPA (1:3) for 2 minutes and 30 seconds with a 30 second rinse in IPA and then dried with N_2 gas. The second development method is more aggressive than the first. Here, the removal was made in H_2O :IPA (1:4) for 1 minute and afterwards directly dried with N_2 gas.

The next step is to etch the design pattern in to the SiO_2 . This was done by Reactive Ion Etching (RIE), using an Oxford Plasmalab 100 Inductively Coupled Plasma / Reactive Ion Etcher (ICP/RIE). RIE is a dry-etching method where chemically reactive plasma interact with the surface of the sample and remove material. For this process CHF_3 gas was used. The CHF_3 interact with the plasma and becomes ionized due to removal of electrons. The electrons interact with the CHF_3 molecules and creates free radicals, which are then absorbed on the surface of the sample. The CHF_3 ions, on the other hand, bombard the surface of the sample and creates sites by breaking chemical bonds where the absorbed radical has created a volatile product. The volatile product comes off the sample together with SiO_2 . The ion-assisted etching of the surface enable anisotropic etching. The normal incident direction of the ions result in vertical or near vertical walls of the etched structure and a good resolution. Ion-assisted etching also give a very low selectivity between the PMMA and SiO_2 , resulting in both being etch at almost the same rate. Henceforth, is the PMMA mask much thicker than the SiO_2 film (and the desired depth of the structure), 220 nm and 100 nm respectively. For this process it was important that the SiO_2 was not completely etched to the gold surface. The reflectivity of the gold mirror is important for the measurements and the gold surface must be protected by a thin layer SiO_2 to avoid losses due to scattering. The etching rate was assumed to be 10 nm per minute, and the samples was etched for 8 minutes, 9 minutes and 10 minutes with CHF_3 and with an additional 20 or 45 seconds of O_2 plasma. After the etching process the samples were cleaned from any remaining residues of PMMA, by immersing the sample in acetone for five minutes, then quickly rinsed in IPA and finally, dried with N_2 gas.

To evaluate the sample and the quality of the etched nanoholes, atomic force microscope (AFM) was used. AFM is a technique which measure the topography of a sample with a very high resolution. AFM utilize a sharpened probe to scan the surface of the sample, and deliver a 3 dimensional image of the surface topography. For these particular measurements tapping mode was used, in this mode the cantilever is oscillating at a certain frequency close to the surface and utilizes the short-range forces to scan the surface.

3.3 Reflection Spectroscopy and Laser Tweezing

To measure the reflectivity spectra of the Fabry-Pérot cavities, the solution with gold nanoflakes were drop-casted on the sample. The solution was then sealed on the sample by using PMDS as an O-ring and cover glass as a lid to prevent evaporation. Figure 8 (b) show an image of one of the samples used for the project.

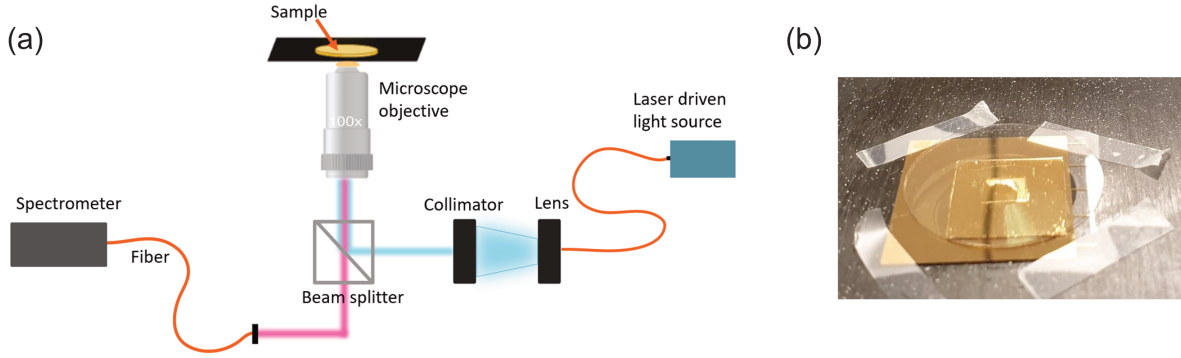


Figure 8: Schematics of the setup used for the reflection spectroscopy is visualized in (a). A photo of the sample with a sealed chamber containing the solution with nanoflakes attached to the sample carrier of the microscope is shown in (b).

Figure 8 show a schematics of the setup used for measurements. The reflection spectra of the Fabry-Pérot cavities were collected using an inverted microscope at normal incidence (numerical aperture (NA) = 0.5). The microscope was equipped with an oil-immersion 100x objective with a switchable NA = 0.5 - 1.3. The reason for using oil-immersion is to reduce scattering of light due to refractive index difference between the glass and the air. By using an oil that has the same refractive index as the glass, less light is lost to the environment, which result in a higher resolution image than without the oil. To measure the reflection spectra the microscope was fibre coupled to a spectrometer (Andor Shamrock SR-303i, equipped with a CCD detector Andor iDus 420). The measurements were conducted under collimated illumination with a laser-driven white light source (LDLS, EQ-99FC, high-brightness, flat-broadband spectrum).

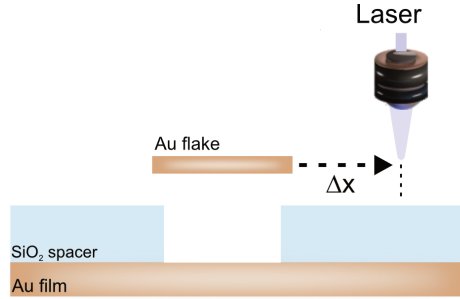


Figure 9: Laser tweezers attract the nanoflakes from a distance ΔX by inducing a strong electromagnetic field in the system.

To gain real-time control over system (i.e. enable to collect and move the flakes on top of the sample) a continuous wave (CW) laser ($\lambda = 455$ nm) was fiber coupled to the microscope. Figure 9 show an illustration of the laser tweezers used to gain real-time control over the system. The laser beam is focused by the 100x oil-immersion objective with NA = 1.3 on to the sample. The focused laser beam induce a strong gradient of an electromagnetic field and in the middle of the focused laser beam is the intensity the strongest and the potential energy at its minimum [16]. The gold nanoflakes feel an attraction to the laser beam and becomes optically trapped, which enable moving them in and out of the nanoholes in the spacer, for example.

3.4 Transfer Matrix Method

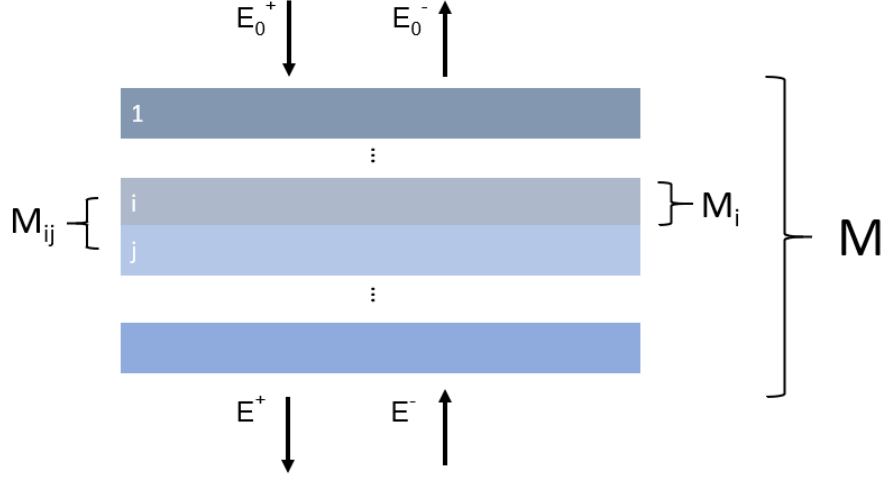


Figure 10: Illustrate a stack of materials in one dimension, $\mathbf{E}^+$ and $\mathbf{E}^-$ represent the the backward and forward propagation of the $\mathbf{E}$ field. $\mathbf{E}_0^+$ and $\mathbf{E}_0^-$ indicate an illumination from the top. The scattering matrix is shown for layer i and the interface ij .

To obtain the optical response from a multilayered system of thin films the Transfer Matrix Method (TMM) is used. TMM utilize matrices to explain the propagation of light, electromagnetic waves, though a medium or a series of mediums stacked in one dimension, illustrated in Figure 10. The reflection and transmission of light at the interface of a medium is described by the Fresnel equations [17]. The light, or the electric field $\mathbf{E} = \mathbf{E}^+ + \mathbf{E}^-$, is related through a matrix $\mathbf{M}$ as

$$\begin{pmatrix} \mathbf{E}^+ \\ \mathbf{E}^- \end{pmatrix} = \mathbf{M} \begin{pmatrix} \mathbf{E}_0^+ \\ \mathbf{E}_0^- \end{pmatrix} \quad (13)$$

where $\mathbf{E}^+$ and $\mathbf{E}^-$ represent electromagnetic waves propagating forward and backwards, respectively. Every layer in the system has a scattering matrix of propagation $\mathbf{M}_i$, and for the interface $\mathbf{M}_{ij}$. $\mathbf{M}$ is the product of the scattering matrices for all the layers multiplied. The calculation was made for normal incidence assuming 30 nm thin gold mirror and 30 nm thin gold flake, the refractive index for gold was calculated using the Drude model

$$n_{Au} = \sqrt{8 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}} \quad (14)$$

where $\omega_p = 8.6$ eV is the plasma frequency and $\gamma = 0.07$ eV the damping factor [18, 11]. The SiO_2 is assumed to be 100 nm on the spacer and $\sim 10 - 20$ nm in the holes, the refractive index for the SiO_2 is set to be $n_{\text{SiO}_2} = 1.45$ and the refractive index for the solution is assumed to be $n_{\text{sol}} = 1.38$.

3.5 Lifshitz Calculations

In section 2.1.1 the Lifshitz formalism is explained and equation 4 represent the Casimir force between two parallel mirrors with an intermediate medium. For the calculations in this thesis, the expression of the force is derived using scattering theory and is equivalent to the one presented in section 2.1.1 [19]. The force per unit area is expressed by reflection amplitudes, r_i^{ab} , at the interface of the object ($i = 1, 2$ and represent the mirrors in the system) and the vacuum. The reflection amplitude r_i^{ab} is the ratio of a reflected electromagnetic wave (with polarization a) by the incoming wave (with polarization b) [20]. The a and b stands for electric (p) and magnetic (s) waves. As described in section 2.1.1, are the frequencies imaginary ($\omega = i\xi$). The expression used for the calculations is

$$U_C = \frac{\hbar}{2\pi} \int_0^\infty \int \frac{d^2 \mathbf{k}_\parallel}{(2\pi)^2} \ln \det \mathbf{G} \quad (15)$$

where $\mathbf{k}_\parallel$ is the in-plane part of the wave vector in the gap between the bodies with the distance L [11]. $\mathbf{G}$ relate to the reflection operator $\mathbf{R}$ as $\mathbf{G} = 1 - +\mathbf{R}_1 \mathbf{R}_2 e^{-2K_0 L}$ and

$$\mathbf{R} = \begin{pmatrix} r_i^{ss} & 0 \\ 0 & r_i^{pp} \end{pmatrix} \quad (16)$$

where $i = 1, 2$ represent side of the system and r_i^{ss} and r_i^{pp} are the Fresnel reflection coefficients for s and p polarized light. $K_0 = \sqrt{\mathbf{k}_\parallel^2 + \xi_n^2/c^2}$ and represent the z -part of the wave vector in between the two bodies. The Drude model was used to calculate the permittivity of gold as

$$\varepsilon_{Au} = 8 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (17)$$

for imaginary frequencies [11]. For water the permittivity was calculated as

$$\varepsilon_{H_2O} = \varepsilon_\infty + \frac{\varepsilon_D - \varepsilon_\infty}{\omega^2 - i\omega\tau} + \sum_{i=1}^3 f_i \frac{\omega_{p,i}^2}{\omega_{0,i}^2 - \omega^2 - i\gamma_i\omega} \quad (18)$$

and evaluated at imaginary frequencies with a static Debye contribution and a series of Lorentzian transitions. In the expression of ε_{H_2O} is $\omega_{p,i}$ the plasma frequency of the i -th resonance mode, ω is the frequency, γ_i is the linewidth and f_i is the oscillator strength. In the Debye contribution is ε_D the amplitude and τ is the Debye relaxation of permanent dipoles [11].

4

Results and Discussion

The main results are displayed and discussed in this Chapter. The effect the nanoholes have on the self-assembly of the Fabry-Pérot cavities is first treated in section 4.1. In section 4.2 the results from reflection spectroscopy together with calculations done by transfer matrix method are looked at, whereas the last part is dedicated to the nano-fabrication process in section 4.3.

4.1 Nanoholes and self-assembly

The process where the nanoflakes are drop-casted on the gold mirror was observed in real-time through the microscope for all the samples used for reflectivity measurements. Figure 11 show two photographs of a sample directly after the flakes are drop-casted and 15 minutes after that. The sample was left undisturbed during this period. By comparing Figure 11 (a) and (b) it is clear that after some time the nanoflakes go from being randomly distributed on the sample to form microcavities in the areas of the nanoholes.

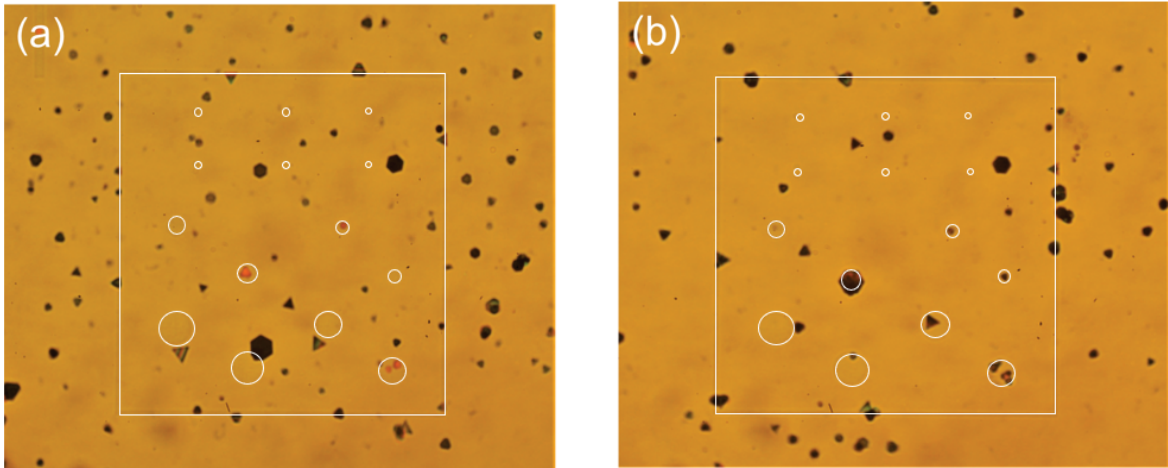


Figure 11: Image of a sample (a) directly after drop-casting the nanoflakes and (b) 15 minutes after the flakes were drop-casted.

The behaviour the nanoflakes showed in Figure 11 is consistent for every sample. For the nanoflake to

diffuse towards the nanoholes, they need to be within a range of 10-20 μm . The nanoflakes are attracted to each other as well, resulting in dimers and even multimers being created. It is not unusual that these dimer and multimers are formed inside the nanoholes. Through observations of the nanoflakes and their attraction towards the nanoholes, it is obvious that the nanoholes that are larger and much larger than the flakes are more attractive than the nanoholes smaller than the flakes. However, if the flake is dragged to a nanohole much smaller than the flake, it feels an attraction and tries to enter. The difference is that the flake must be in a very close range to the small nanoholes to feel the attraction. When the nanoflakes are in the immediate vicinity of the nanohole they encounter a sort of energy barrier. This energy barrier occur at the edges of every nanohole, no matter its size. This require that a flake must inhibit enough kinetic energy to pass this barrier into the nanohole. From observations it is clear that the energy that the flakes inhibit always overcomes this barrier; a flake will never approach a nanohole without eventually entering it (even though it sometimes take longer time, especially for larger flakes). This shows that energy barrier is smaller than the kinetic energy of the nanoflakes. The origin of this energy barrier is unknown, but a reasonable assumption would be that it is an accumulation of surface charge due to the structural variation of the spacer.

If a nanoflake enters a nanohole completely (i.e. a nanohole larger than the flake), the flake will remain inside the hole and only leave if pulled out by the laser tweezers, or if the there is turbulence in the solution near the hole. It is also more probable that a small flake leaves a nanohole than a larger flake, as the smaller flakes are more affected by the thermal energy in the system. When a sample is

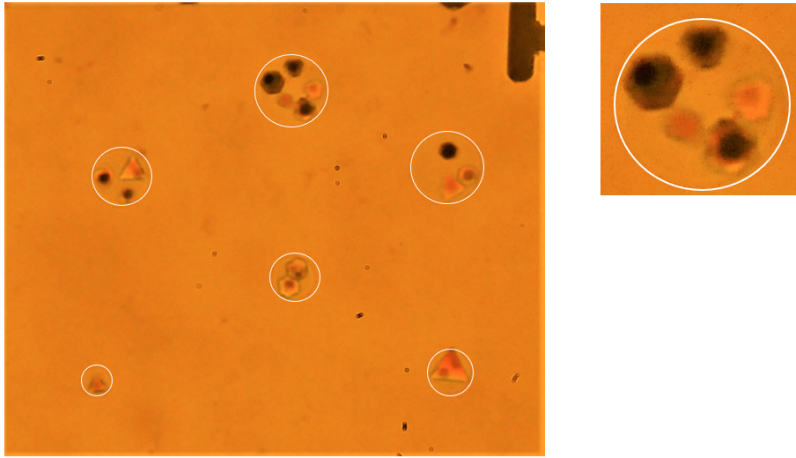


Figure 12: Image of a sample left untouched for several hours, showing nanoholes with many flakes inside (right). Magnification of the top most nanohole (left).

left untouched for several hours or days, the area around the nanohole structures (upon the spacer) is very clean from flakes as almost all of them are inside the nanoholes. Usually, there are many flakes inside every hole, which can be seen in Figure 12. Dimers and multimers are also seen inside the nanoholes. In Figure 12 these dimers and multimers are the flakes that has a brighter color with a dark spot on them. When observing the flakes in a microscope, they can appear in different ways. If a flake is completely dark they can either be dimer/multimer or being thicker, meaning that less light is transmitted through the material. The different colours seen through the microscope may also indicate different resonance modes of Fabry-Pérot cavities. However, reflectivity measurements need to be done to establish the resonance modes.

4.1.1 Laser tweezers

The laser tweezers is used to move the nanoflakes to desired areas on the spacer or to pull a flake out of a nanohole. The laser power needed to move the flakes are quite small and range from about 2 mWatt to 8 mWatt. The amount of power needed to move a flake upon the spacer compared to the power needed to drag a flake out is smaller. The reason for this may be the energy barrier the flake experience around the edges of the nanoholes, due to this the power needed execute this is the power to attract a flake combined with the power for overcoming the energy barrier on the edges. The quality of the nanoholes (discussed and evaluated in section 4.3) is also an important contributor in how much laser power is needed to drag a flake out. If there are irregularities on the surface in the nanoholes, such as spikes, less power is needed to drag out a flake in comparison with a nanohole that has a very smooth surface.

Smaller nanoflakes are easily and faster attracted to the laser tweezers, leading to formations of flake-clusters were the laser is focused. This sometimes result in trouble moving one specific flake without accidentally creating a dimer or a multimer, which are very hard to separate. There are flakes in the solution which are very small (a SEM image of a cluster of these flakes can be seen in last image in the photo series in Figure 19) and attracts to the laser extremely fast, after which they stick to the larger flake that is moved. These contaminating smaller flakes may then may then cause noise in the reflectively measurements. Another impact that the laser tweezers has on the system is that it creates turbulence in the solution, most likely due to thermal effect induced by the laser. This is something that contribute to a higher Brownian motion of the flakes and contribute to flakes-clusters and dimer/multimer formations.

To minimize these effects of the laser, several methods can be utilized. By only open the shutter for the laser at very short moments at the time, flakes further away from the area do not feel the attraction towards the laser as strong. Furthermore, by diluting the solution the amount of flakes per volume is less and fewer flakes are attracted to the laser. The nanohole design can also incorporate features that ease the use of the laser tweezers. In Figure 7 the trench around the nanoholes is such feature, this trench stop many of the flakes to enter the area of the nanoholes even though the laser is on. The trench has worked well during the experiments. However, for very small flakes, and if there is a lot of turbulence in the solution, the energy barrier created by the trench is less than the Brownian motion of the flakes and they are able to pass over it.

4.1.2 Calculation of the Casimir potential

Figure 13 show calculations done by the Lifshitz formalism described in section 3.5. In Figure 13 (a) the Casimir potential is calculated for water and SiO_2 in $\text{eV}/\mu\text{m}^2$, for distances between the flake and mirror varying from 50 -190 nm. Comparing the potential for the two mediums, the potential for the water is consistently lower than the potential for the SiO_2 . As previously mentioned in section 2.1.1, the only material parameter needed to calculate the Casimir force by the Lifshitz formalism is the permittivity for imaginary frequencies. The permittivity for SiO_2 is larger than the permittivity for water, which is the reason for the lower Casimir potential for water. Looking closer at the distance of 50 nm, the U_C for water is $-5.785 \text{ eV}/\mu\text{m}^2$ and the U_C for SiO_2 is $-5.452 \text{ eV}/\mu\text{m}^2$. The difference in potential between water and SiO_2 is not constant, which can be seen in Figure 13 (b). The difference is larger for smaller distances, and increases as the distance between the bodies get larger. Comparing the the two extremes in distance, at 50 nm the difference is $332 \text{ meV}/\mu\text{m}^2$ and at 190 nm, the difference is only $\sim 6 \text{ meV}/\mu\text{m}^2$. To indicate if the difference in potential can have an impact on the nanoflakes in the system, the thermal energy $k_B T$ for room temperature is included in the graph. This, because the thermal energy can be regarded as the limit of what amount of energy can affect the system. The intersection of the thermal energy and the potential difference is found at about 120 nm, indicating

that at above 120 nm there is no significant potential difference between water and SiO₂ that can affect the flakes.

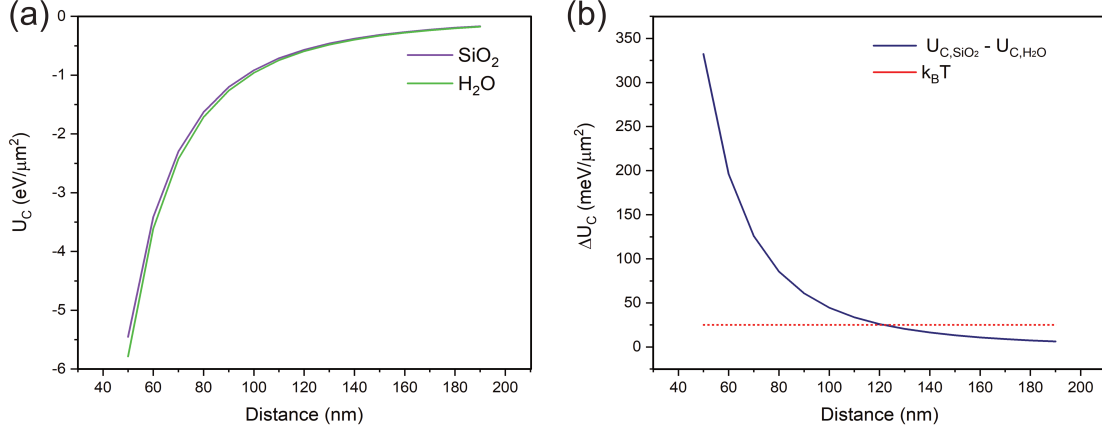


Figure 13: Calculations of the Casimir potential is shown in (a), using the Lifshitz formalism between two gold plates where the intermediate medium is H₂O (in green) and SiO₂ (in purple). The graph in (b) shows the potential difference between H₂O and SiO₂, compared with the thermal energy $k_B T$ in room temperature, which is set to 25 meV.

The calculated Casimir potentials in Figure 13 do not represent the system perfectly, but it indicates the potential difference a flake might experience due to the nanoholes in the spacer. Self-assembly of colloidal systems, such as the system in this study, is driven by the system trying to order itself in a way that minimize the over all energy. When the nanoholes are introduced in the spacer, areas of lower potential are introduced with it and this affect where the optical microcavities form. Instead of randomly form all over the spacer, the nanoflakes diffuse towards the nanoholes and this behaviour can be connected to the Casimir potential being lower inside the nanoholes. Arguably, the self-assembly is manipulated by lateral Casimir forces that stem from pointedly placed nanoholes on a surface. Worth pointing out is that the nanoholes only are about 80 - 90 nm deep, and it is still enough difference for the flakes to experience the attraction towards them.

The results shown in Figure 13 also indicate that the closer the flake is to the mirror, the more substantially it experience the potential difference between water and SiO₂. The quality of the nanoholes affect, as previously mentioned in section 4.1.1, how much laser power is needed to drag a flake out. A flake inside a nanohole with a smooth surface requires more laser power. The smooth surface of the nanoholes, enables the flakes to get closer to the to the mirror. Here, the potential difference is much larger and the flakes become more reluctant to move from the nanoholes. This peculiarity may arise from the Casimir force acting stronger on the nanoflakes due to the absence of surface roughness. Another possible explanation is that the SiO₂ film is thicker (although in an appearance of spikes, further discussed in section 4.3) which also can suppress the Casimir force. A combination of the surface roughness and the thicker layer of SiO₂ is an additional potential explanation. From observations, the flakes appear more attracted to larger nanoholes. This may also be connected to the lateral Casimir forces. If a nanohole is big the potential difference occur on a larger area, which increases the probability of the flake feeling it, as the total energy is given by an integration of the potential energy

per unit area of the flake.

4.2 Reflectivity spectra of the microcavities

Figure 14 (a) show the reflectivity spectra of two nanoflakes with a solution concentration of $C = 0.35$ mM. The line in blue show measurement made on flake inside a nanohole, the resonance mode of this microcavity appear at about 625 nm. The red line is measured on a flake upon the spacer, here the resonance mode appear at about 810 nm. Normalisation of the reflectivity spectra was done with a reflectivity spectra taken on the spacer without any flakes present. As the bottom mirror of the system is partially transparent, the normalised spectra for the microcavity reached above 1. However, this does not affect the placement on the x-axis for the resonance mode.

From Figure 14 (a), it is evident that the resonance mode for the microcavity measured inside a nanohole is blue-shifted with ~ 190 nm. This is an expected result as ~ 80 nm of the SiO_2 is removed. For all measurements made during the project, the blue-shift of the resonance modes for flakes inside the nanoholes is consistent. However, difference in the magnitude of the blue-shift compared to the resonance modes of the flakes upon the spacer have occurred. This can be traced to where on the flake the reflectivity was measured. The nanoflakes are very thin (see the second image in the series of Figure 19), which result in them being rather ductile and do not appear completely flat in the solution. They may appear in a concave or convex shape when they form the microcavities. This means that the resonance mode of the microcavity is not homogeneous; if the flake is measured on the edge or in the middle of the flake. As a flake inhibit kinetic energy and constantly moves slightly, measurements made on the same flake directly after each other can result in different resonance modes with an offset of 10-20 nm. Therefore, it is very important to be consistent where on a flake the measurements are taken. The offset of resonance mode for flakes inside of the nanohole are usually smaller than for flakes upon the space. This is likely due the flakes being confined in the nanoholes, with the walls hindering them to move around.

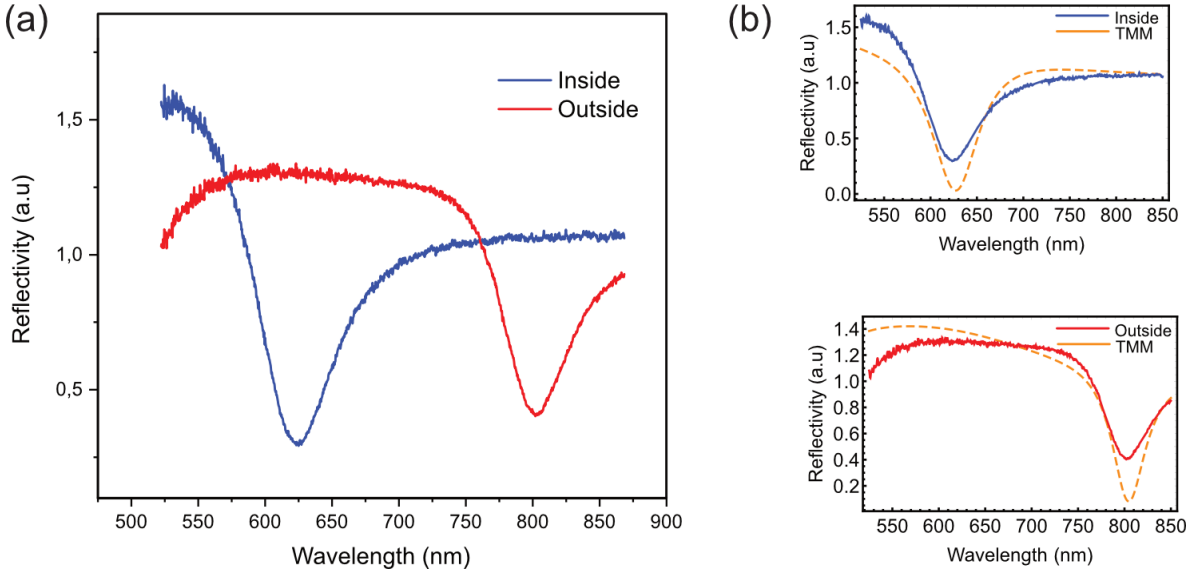


Figure 14: (a) Reflectivity spectra of a nanoflake inside (blue) of a nanohole and of a nanoflake on the spacer, outside (red) of a nanohole. (b) Reflectivity spectra of a flake inside and outside of a nanohole together with a reflectivity spectra (orange) calculated by the transfer matrix method.

Figure 14 (b) show the reflectivity spectra for the flake inside a nanohole and outside upon the spacer, together with a calculation of the resonance mode done with the transfer matrix method (introduced in chapter 3). The calculations were done using the material properties disclosed in section 3.4. The thickness of the flake, gold mirror and SiO₂ were fixed to be able to extract the thickness of the water layer in the microcavity and also consequently find the distance between the flake and the gold mirror. To mimic the real system as much as possible, the normalisation is calculated with semi-transparent gold mirror with a SiO₂ spacer of 100 nm. Therefore, the calculated reflectivity spectra is exceeding 1 as well. To calculate the resonance mode for a microcavity inside a nanohole, the thickness of the flake is 30 nm, the mirror is 30 nm and the SiO₂ spacer is 20 nm. The resulting thickness of the water layer could then be found to be 140 nm resulting in a total cavity length to 160 nm. For a microcavity assembled on the spacer, the thickness of the flake is 30 nm, the mirror is 30 nm and the SiO₂ spacer is 100 nm. The resulting thickness for the water layer could then be found to be 125 nm, resulting in a total cavity length to 225 nm. As predicted, the size of the microcavities assembled on the spacer is larger than the distance of the microcavities in the nanoholes, which agrees with the measurements. A more red-shifted resonance mode indicate a longer cavity distance. However, the thickness of the different materials are only assumptions and variations may occur.

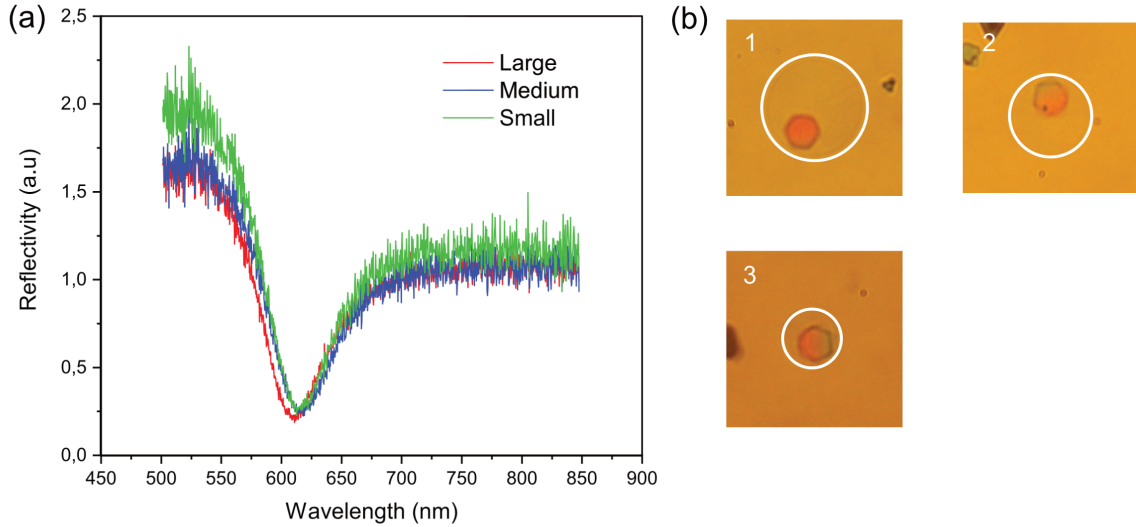


Figure 15: (a) Reflectivity spectra of one nanoflake moved between three different sized nanoholes, going from large to medium to small. (b) Photographs of the measured flake in the three different nanoholes. *Photo 1* show the nanoflake in the large nanohole (diameter = 10 μm), in *photo 2* the nanoflake is in the medium sized nanohole (diameter = 8 μm) and *photo 3* show the nanoflake in the small nanohole (diameter = 5 μm).

Figure 15 shows reflectivity spectra and pictures of one flake being measured in three different nanoholes, with diameters of 10 μm , 8 μm and 5 μm . This experiment was conducted to study if the size of the nanohole affect the placement of the resonance mode. The flakes were moved between the nanoholes using the laser tweezers. To reduce risk of unwanted flakes disturbing the measurements, the solution was diluted with water. Figure 15 show that the resonance mode of the microcavity is not affected by the size of the nanohole, as long as the flake can enter it completely. The large nanohole is twice the size of the smallest nanohole. Nevertheless, is the resonance mode offset only about 5 nm. This may indicate that the above mentioned energy barrier around the edges, is restricted to the very edge

of the nanohole and do not extend inwards. However, if the flake is larger or of equal size as the nanohole the resonance modes may differ. For nanoholes smaller than the flake, a good measurement of the reflectivity spectra is difficult to achieve as the flake is bending much more than flakes usually do in the system. For nanohole with a similar size as the flake, the edge effects may play a role of what distance the flakes is from the mirror. If the energy barrier on the edges is an accumulation of counterions, the flake would feel a stronger repulsive force than in other places of the sample. This in turn, could force the flake upward, resulting in a larger cavity and more red-shifted resonance modes.

4.3 The nanofabrication process

Figure 16 show an AFM image and height profile of a sample, which was fabricated through the original process using an electron dose of $900 \mu\text{C}/\text{cm}^2$ in EBL with the developer MIBK:H₂O. The depth of the nanohole is 80 nm, which correspond well with the assumed etching rate of $\sim 10 \text{ nm}/\text{min}$. The sample was etched for 8 minutes, which resulted in nanoholes of 80 nm. From Figure 16 it is obvious that the fabrication process of the nanohole do not deliver a good quality nanohole. The height profile shows a significant amount of spikes in the bottom of the hole, an analyse of the spikes revealed a height variation from 10 nm to 80 nm. In the AMF image in Figure 16 the colour variation indicates the different height of the spikes, the brightest dots are the spikes with a height of about 80 nm. A nanohole with this amount of spikes inside will definitely affect the distance between the gold mirror and the flake.

In addition to the way the spikes can affect the formation of the microcavity discussed in section 4.2, co-ions and counterions would assemble on the spikes and contribute to electrostatic repulsion. The reason why the spikes appears, is most probably due to residues of the PMMA being left on the spacer in the areas where the nanoholes are etched. Two possible causes for this that was investigated. The first being the development procedure, the mask may have been under developed. To solve this issue, the recipe for development were changed to a more aggressive one. From MIBK:H₂O to H₂O:IPA. The second being underexposure during the EBL, to solve this the electron dose was change from $900 \mu\text{C}/\text{cm}^2$ to $1200 \mu\text{C}/\text{cm}^2$.

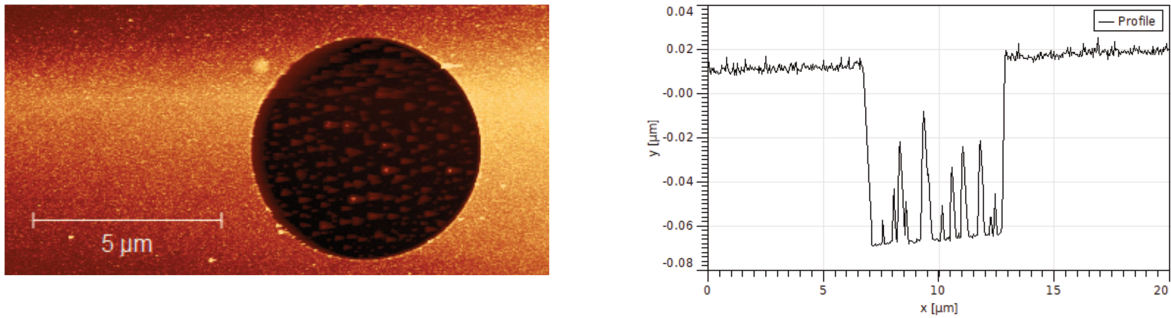


Figure 16: AFM image of a nanohole with a diameter of $5 \mu\text{m}$, together with the height profile of the nanohole.

Figure 17 show an AFM image of a sample where the nanofabrication process was optimized by an increase in the electron dose during the EBL. The same development recipe was used as for the sample shown in Figure 16. The quality of the nanohole is substantially improved for the sample in Figure 17. Here, the bottom of the nanohole hole appear smooth, except for a few places where irregularities are present. The smooth appearance is shown in the even colour of the AFM image, but most distinctly from the height profile.

As the same development is used for the two samples, underexposure seems to be reason for the spikes in Figure 16. However, there are height irregularities also in the sample of Figure 17, but their origin does not stem from PMMA residues. They appear all over the sample, even in areas not etched. This indicate that they are a product of fabrication problems earlier in the process. It can either come from the cleaning process, the deposition of gold or from the deposition of SiO_2 . The irregularities, which have a height of about 40 nm, are not affected by the etching. The height of these are the on same inside as on the outside of the nanoholes. These structural irregularities, or hillocks, can appear for different reasons, for examples due to thermal stress in the gold film or due to foreign particles on surface during sputtering [21, 22]. Even tough the hillocks are present in the sample in Figure 17, they are much fewer and not as tall as the spikes in Figure 16. Therefore, are the nanoflakes expected to form microcavities that have more blue-shifted resonance modes in nanoholes created with the higher electron dose.

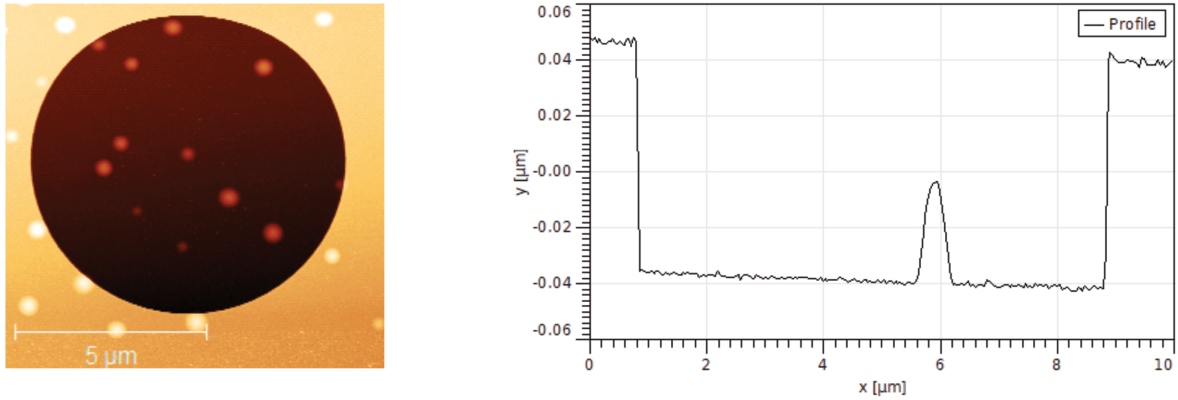


Figure 17: (right) AFM image of a nanohole with a diameter of 8 μm , and (left) the height profile of the nanohole.

Figure 18 displays the reflectivity spectra from a microcavity measured before (red) the change in electron dose and after (blue). It is evident that the spectra measured on the sample fabricated with the higher electron dose, is considerably more blue-shifted than the spectra from the other sample. The difference is about 70 nm, which is much more than the difference that can be obtained due to alignment errors on the nanoflake during measurement. This indicate that spikes in the nanoholes do affect the measurements, and removing them by optimizing the nanofabrication process generate a more blue-shifted resonance mode of the microcavity.

This result show the importance of the nanofabrication process and how much the quality of the sample can affect the measurements. It is therefore important to consider that the methods used to deposit the different materials of the sample can influence the material properties, such as permittivity and refractive index. Another important property that can be altered, especially during the etching procedure, is the surface charge. During etching different atoms are introduces on the surface of the sample, for this project the gas used for etching is CHF_3 and O_2 plasma, that can affect the surface charge. This may lead to a different surface charges in the nanoholes and on the spacer. Something that could be an additional mechanism for the flakes behaviour, that they rather form microcavities inside the nanoholes, rather than outside.

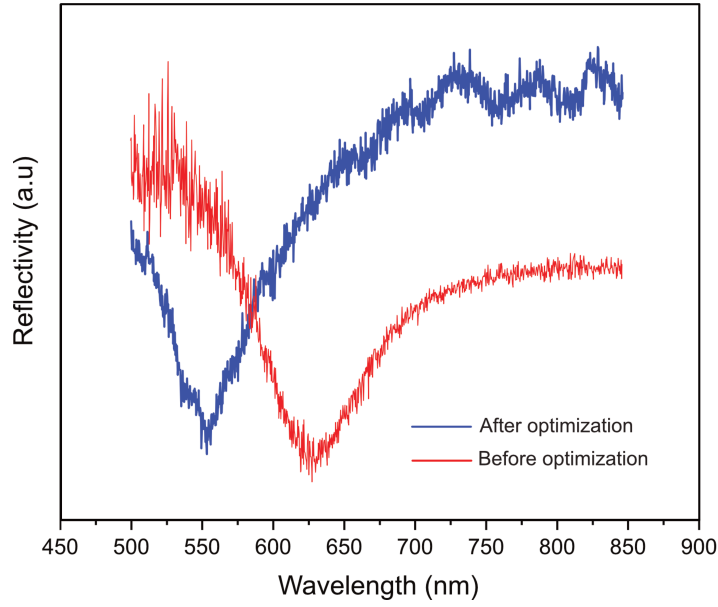


Figure 18: The reflectivity spectra from microcavities inside a nanohole. The blue line is the reflectivity spectra take on a sample were the electron dose used is $1200 \mu\text{C}/\text{cm}^2$, and for the red spectra an electron dose of $900 \mu\text{C}/\text{cm}^2$ was used.

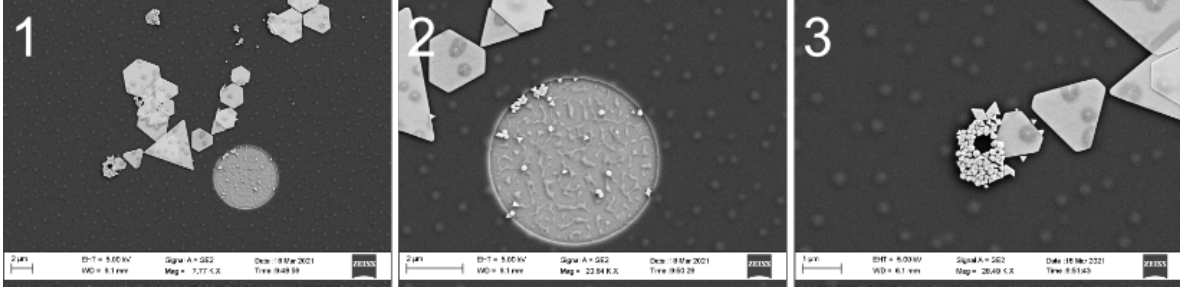


Figure 19: A series of images taken using scanning electron microscopy (SEM), showing a nanohole together with nanoflake on a sample fabricated before optimization.

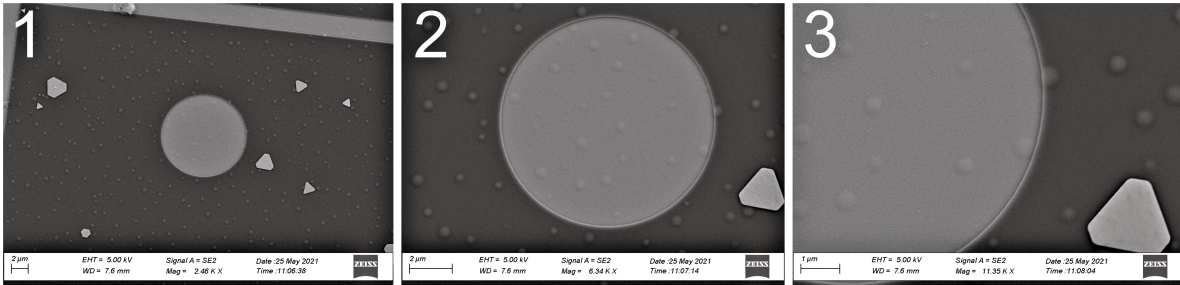


Figure 20: A series of images taken using SEM. Here, a nanohole on a sample fabricated after the optimization is visualized for three different magnifications.

Figure 19 shows a nanohole on a sample that was fabricated using the first EBL process, with an electron dose of $900 \mu C/cm^2$. The second image of the series show a very uneven surface in the nanohole. It agrees with the results generated by the AFM, shown in Figure 16. The difference is how sharp the spikes appear, in Figure 19 the irregularities are more soft and have a more organic appearance than the spikes in Figure 16. The sample, of which the image is taken, has been used for measurements and then only been cleaned in tap water afterwards. This is the most probable cause for the smooth and organic appearance of the spikes. Figure 21 shows similar spikes as in Figure 16 and has been subjected to the same treatment. Figure 20 shows a nanohole on a sample fabricated using the optimized EBL process, with an electron dose of $1200 \mu C/cm^2$. Here, the surface of the nanohole is smooth, except for the hillocks that are distributed over the entire sample. The sample was previous to the SEM, used for measurements and then afterwards cleaned using the cleaning method presented on section 3.2. Comparing Figure 19 and Figure 21 with Figure 20 there is a clear difference in the quality of the nanoholes, which further confirms the results from the AFM.

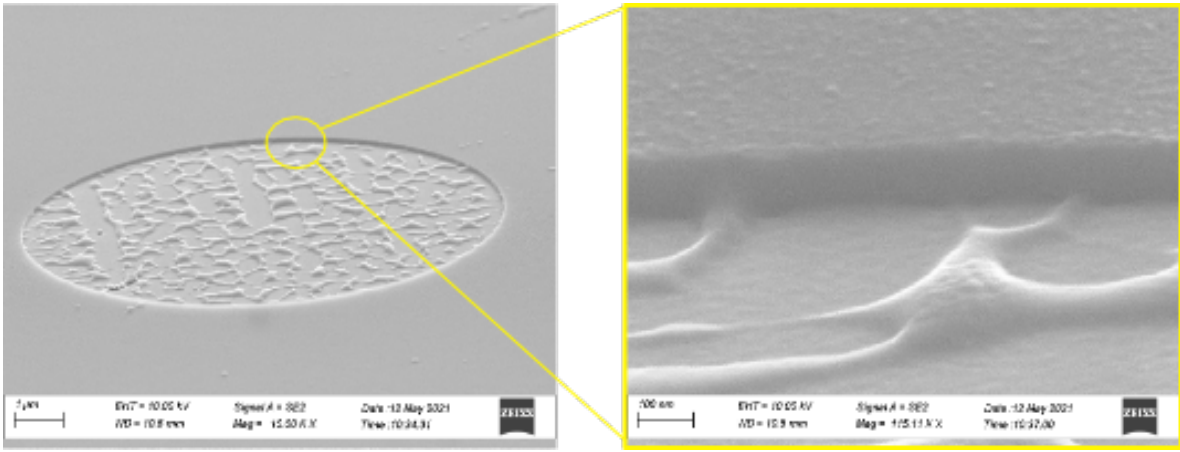


Figure 21: Image of a nanohole take using tilted SEM. The sample displayed is fabricated before optimizing the fabrication process.

Figure 21 shows a nanohole using tilted SEM. Here, it is possible to evaluate the anisotropic nature of the etching procedure. Despite the sample being previously used for measurements and the insufficient cleaning afterwards, the walls of the nanohole appear vertical. This result confirms that this type of etching is suitable for structures as the nanoholes.

5

Conclusions and Outlook

In this Chapter, the results presented and discussed in Chapter 4 are summarized to highlight the main content of the study, followed by a conclusion with the most important findings. The summary and conclusion are presented in section 5.1. The prospects for the examined configuration is lifted in 5.2, together with possible applications and future developments of the system.

5.1 Summary and conclusions

In this thesis, a system consisting of self-assembled microcavities on a SiO_2 covered gold mirror, containing a nanohole-structure was studied. The main objective was to investigate if lateral Casimir forces can affect the self-assembly of the microcavities. Due to the difference in the permittivity of water and SiO_2 , the nanoflakes was expected to be attracted to the nanoholes where SiO_2 had been removed. The nanoholes lead to formations of areas on the mirror where the potential energy is lower, as water has a lower permittivity.

To realise the system, the SiO_2 covered gold mirror was fabricated in the cleanroom facility at Chalmers. The fabrication process's most important parts contained deposition of gold and SiO_2 , creating a mask using EBL and reactive ion etching of the nanoholes. The process was evaluated using AFM and SEM, which showed poorly etched nanoholes. Thereafter, an optimization of the fabrication process was conducted, in the form of using a more aggressive developer of the etching mask and increase the electron dose during EBL. Results showed that underexposure was the main contribution to the bad quality of the nanoholes, and by increasing the electron dose the problem was sorted.

The nanoflakes was drop-casted upon the mirror and observed with an inverted microscope. The observed tendency of the nanoflakes, in all the studied samples, showed that they were attracted towards the nanoholes in the spacer. Confirming the assumed nature of the system based on the potential variations introduced by the nanoholes, due to different permittivity of the SiO_2 and water. To further investigate this, calculation was conducted using Lifshitz formalism. The results shows that the Casimir potential for the water, is consistently smaller than for SiO_2 for the distances investigated. The difference in potential vary with distance between the bodies, for smaller distances the difference is larger. At a distance of about 120 nm, the difference between water and SiO_2 is not substantial enough to affect the system. Even though the calculations do not represent the system to its fullest, it give a good indication the difference in the potential variation a nanoflake experience.

The nanoflakes also encountered resistance in the form of some sort energy barrier, when trying to enter the nanoholes. The kinetic energy of the flakes always overcame the barrier and entered the nanoholes.

A possible reason for this barrier, could be an accumulation of surface charge in the structural change of the spacer, leading to the edges of the holes being more repulsive than the rest of the system.

The reflectivity spectra was measured on nanoflakes inside and outside of nanoholes and compared. For flakes measured outside the nanoholes, the Fabry-Pérot resonance mode was found at about 810 nm. For flakes inside the nanoholes, the resonance mode appear around 625 nm, which is a blue-shift of about ~ 190 nm from the resonance mode of the flakes measured on the spacer. Reflectivity spectra taken on the same flake in three different sized holes, confirmed that the spectra is not affected by the energy barriers at the edges as long as the flake completely can enter the hole. For measurements of microcavities in nanoholes smaller or of the same size as the flake, the energy barrier will impact the placement of the resonance mode.

To estimate the thickness of the water layer and the cavity distance, calculation of resonance mode, using transfer matrix method, for system with similar parameters was conducted. A cavity distance of 225 nm, with a corresponding water layer of 125 nm was calculated for a microcavity upon the spacer. For a microcavity assembled inside a nanohole, the cavity length and water layer was calculated to be 160 nm and 140 nm, respectively. However, the parameters used in the calculation were estimated and not measured from the experimental system, leaving room for improvements in the transfer matrix method model of the system. The quality of the nanoholes highly affected the placement of the resonance mode. A nanohole with a smooth surface generated a resonance mode at about 550 nm, which is blue-shifted by about 70 nm from a sample with nanoholes of lesser quality. The quality of the nanoholes also affected how much power was needed to move a flake out of a nanohole with laser tweezers. A stronger power is needed for nanoholes with better qualities. The laser tweezers is a good tool for real-time control of the system, but must be handled carefully as it is easy to form unwanted multimeres.

In conclusion, the nanoholes introduced in the spacer do affect the self-assembly of the microcavities, in spite of their modest depth of ~ 80 nm. Calculations of the Casimir potential show that water as an intermediate medium results in a lower potential, indicating that Casimir forces may play a role in the microcavities self-assembly. Furthermore, the nanofabrication of the SiO_2 covered mirror, has a significant impact on the distance between the mirror and nanoflake in microcavities formed in a nanohole.

5.2 Outlook

The effortlessly self-assembled microcavities enables the study of fundamental quantum forces, in the form of Casimir forces, which in itself is quite remarkable and there is more insights to gain from it. To further extend the understanding of the system is of interest, as it would lead to a more accurate model of the system and better understanding of the forces acting in it. The natural progression of the project is to make a more extensive investigation of the Casimir force in the system. By modifying the system through adding salt to the solution, the distance of the microcavities can be tuned and the attraction towards the mirror can be examined. There are several directions one can take to extend the knowledge about the system. One involves improvements and investigation of the nanofabrication process. A process where all samples created having the same surface roughness, without hillocks, would generate better and more uniform results. By investigating the impact the fabrication process has on the material properties is advised, as this would improve the accuracy of the models used. A particularly interest should be appointed to the presumed affects the etching process can have on the surface charge in the nanoholes. A system feature that possibly can contribute the self-assembly of microcavities inside the nanoholes. To start with, one should compare the experimental results of the cavity distance with a model generated using DLVO theory. If a significant difference of the cavity distance is found, one should consider additional forces affecting the self-assembly.

Another important part of the system is the synthesis of the nanoflakes, as there are uncertainties in what part CTAB play in the system. As a suggestion, a replacement of CTAB to a more predictable molecule to gain a better insight in possible ligand formations, for example. To have a more homogeneous size distribution of the nanoflake, is also an attractive improvement of the system. As this also contributes to a more uniform system, which would contribute to consistency in the results and more control over the system.

The self-assembled Fabry-Pérot microcavity can lead to discoveries in many exciting directions. The system provide the perfect condition for strong light-matter interactions, also known as polaritons. By introducing an active medium, for instance plasmonic nanoparticles, on the spacer it is possible reach strong coupling with the resonance modes of the cavity. Strongly coupled light and matter emerge to a new entity, which exhibits hybrid characteristics of both light and matter. Consequently, modifications of both the material and optical properties can be achieved [23]. Furthermore, utilizing the aqueous state of the system and its tunability may enable realization of vibrational strong coupling (VSC), a fascinating concept that has, for instance, shown possibility to alter the kinetics of chemical reactions [24]. The corner stones of such setup is optical Fabry-Pérot cavities in contact with molecules in a liquid phase. The possibility to actively control the optical modes has advantage over fixed cavities as they can be adjusted to a variety of vibrational modes and molecules. This may open up for applications in detection and characterization of chemicals and medical diagnostics.

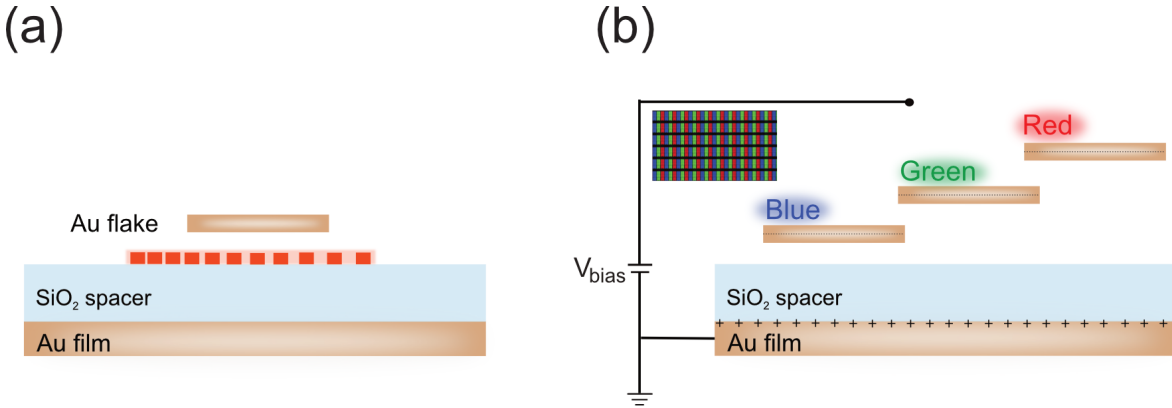


Figure 22: Schematic visualisation of (a) a microcavity with an active medium (b) electric control over the flake to spacer distance.

Combining area controlled self-assembly and active tuning of the Fabry-Pérot modes, which lies in the visible spectral regime, could result in a pixel-arrangement where colour change may be observed directly by the naked eye. One interesting direction this system open up for is to develop an electrically controlled active tuning of the flake to spacer distance. By applying voltage to the gold mirror, control over the surface charge of the substrate is enabled. The charged surface create an attraction (repulsion) of the nanoflakes, which in turn affect the resonance mode of the cavities. This examples of future prospects, shows a greatly versatile system that can provide both fundamental insights of the Casimir force and develop future technologies.

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