Bose–Einstein condensation in plasmonic lattices

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Aalto University
School of Science
Department of Applied Physics
Quantum Dynamics
Supervising professor
Prof. Päivi Törmä, Aalto University, Finland

Preliminary examiners
Prof. David Norris, ETH, Switzerland
Dr. Robert Nyman, Imperial College London, England

Opponent
Prof. Martin Weitz, University of Bonn, Germany

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Abstract

Plasmonics is the study of the interaction between light and metallic structures at the nanoscale. This dissertation explores metallic nanostructures which enable coupling photons to the electrons in the metal, thereby confining light in space smaller than the wavelength. This allows for observing macroscopic quantum-coherent phenomena at room temperature, such as the first Bose-Einstein condensate made of light and electrons observed in this dissertation.

The research focuses on periodic arrays (lattices) of gold nanoparticles that are overlaid with organic fluorescent molecules. The molecules can be excited optically by an external laser. The molecules emit photons into the lattice, exciting optical resonances supported by the array structure. When the concentration of molecules is sufficiently high, the lattice resonances can be strongly coupled with the molecules, which modifies the energy states of both. At strong coupling, the lattice resonances and the molecules form new type of quasiparticles with properties of both light and matter.

The dissertation consists of five research articles. In Publication I, we introduce the first Bose-Einstein condensate in a plasmonic system. The condensate is formed at room temperature in a picosecond timescale. In Publication II, we achieve the first plasmonic Bose-Einstein condensate at the strong coupling regime. The strongly coupled condensate is 100000 times more luminous than the first plasmonic condensate. Due to the room temperature operation and high luminosity, the strongly coupled plasmonic condensate provides a promising platform for fundamental studies of condensates of light and also for possible applications, for example, in the fields of sensing and optical communications.

In Publication III, we study spatial and temporal coherence of the strongly coupled plasmonic Bose-Einstein condensate in large arrays. The condensate studied in this work is half a millimeter long, making it reportedly the largest luminous condensate to date. In Publication IV, we report our observations on the phase and polarization properties of the strongly coupled plasmonic Bose-Einstein condensate. We observe a non-trivial phase distribution, which allows for creating different polarization textures. In Publication V, we present a new theoretical model for strongly coupled organic systems. With the new model we compute, for instance, lasing phase diagrams both at the weak and the strong coupling regime and pinpoint the origin of effective interactions in strongly coupled organic systems.

Keywords plasmonics, polariton, nanoparticle array, laser, Bose-Einstein condensate

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Preface

I am deeply grateful to Prof. Päivi Törmä for the opportunity to pursue the PhD degree in the Quantum Dynamics (QD) group and for her invaluable professional and personal mentoring. The journey began in 2015 when Päivi offered me a chance to do my MSc thesis studying the basics of nanoparticle arrays and the prerequisites for a plasmonic Bose-Einstein condensate. This laid the foundation for the PhD research started in 2017.

Ever since I entered the group, I felt very welcomed and supported by the senior scientists and colleagues: Drs. Tommi Hakala, Aaro Väkeväinen, Konstantinos Daskalakis, Aleksi Julku, Heikki Rekola, Jani-Petri Martikainen, Jami Kinnunen, Sebastiano Peotta, Rui Guo, Marek Nečada, and the other (former) members of QD. The productive and helpful spirit in the group remained as Jani Taskinen, Rebecca Heilmann, Drs. Javier Cuerda and Pavel Kliuiiev, and the other present QDs arrived. I want to thank all of you for those memorable times we spent both during and outside the working hours. I wish you all the best and hope to see you again.

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Above all, I want to thank my family and friends for their love and support I could rely on at all times. Eräreissu, (B)OYS, Corona cowboys: thanks for always being there. Finally, I thank Sofia for being in my life.

Masala, August 23, 2021,

Antti J. Moilanen
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List of Publications

This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


* The authors contributed equally to this work.
Author’s Contribution

Publication I: “Bose–Einstein condensation in a plasmonic lattice”


Publication II: “Sub-picosecond thermalization dynamics in condensation of strongly coupled lattice plasmons”

A.I.V., A.J.M., and K.S.D. conducted the experiments. A.J.M., A.I.V., P.T., and T.K.H. did the data analysis. A.I.V. fabricated the nanoparticle arrays. A.I.V. performed the rate-equation, A.J.M. the quantum model, and M.N. the T-matrix simulations. P.T. supervised the project. A.I.V., A.J.M., and P.T. wrote the paper with input from all authors.

Publication III: “Spatial and temporal coherence in strongly coupled plasmonic Bose–Einstein condensates”

A.J.M. built the Michelson interferometer setup under the guidance of K.S.D. who also did the LabVIEW programming. A.J.M. performed the experiments and did the data analysis. J.M.T. fabricated the nanoparticle arrays. P.T. supervised the project. A.J.M. wrote the manuscript with input from all authors.
Publication IV: “Polarization and phase textures in lattice plasmon condensates”

J.M.T. built the experiment, fabricated the samples and analysed the data. J.M.T. and A.J.M. did the measurements. P.K. performed the phase retrieval. J.M.T. and P.T. developed the theoretical model to describe the experimental findings. P.T. supervised the project. All authors discussed the results. P.T. and J.M.T. wrote the manuscript together with all authors.

Publication V: “Multimode organic polariton lasing”

K.B.A. and A.J.M. derived the second-order cumulant equations independently. K.B.A., A.S., and A.J.M. did the code implementation. J.K. and P.T. supervised the project. All authors discussed the results. K.B.A. and J.K. wrote the manuscript with input from all authors.

The author has also contributed to the following related publications that are not included in this dissertation:


Abbreviations

2D  Two-dimensional
BA  Benzyl alcohol
BE  Bose–Einstein
BP  Band pass
BS  Beam splitter
BEC  Bose–Einstein condensate
BKT  Berezinskii–Kosterlitz–Thouless
CCD  Charge-coupled device
CDA  Coupled dipole approximation
CMOS  Complementary metal–oxide–semiconductor
DBR  Distributed Bragg reflector
DMSO  Dimethyl sulfoxide
DO  Diffracted order
EBL  Electron-beam lithography
FWHM  Full width at half maximum
GPE  Gross-Pitaevskii equation
h.c.  Hermitian adjoint term
HW  Half width
KPZ  Kardar–Parisi–Zhang
LASER  Light amplification by stimulated emission of radiation
Abbreviations

LP  Long pass
LSPR  Localized surface plasmon resonance
MB  Maxwell–Boltzmann
NA  Numerical aperture
ND  Neutral density
OPA  Optical parametric amplifier
PMMA  Poly(methyl methacrylate)
RSP  Real space (image) plane
RMSE  Root-mean-square error
SEM  Scanning electron microscope
SLR  Surface lattice resonance
SPP  Surface plasmon polariton
TE  Transverse electric
TM  Transverse magnetic
Symbols

\( \beta \)  The exponent of stretched exponential function
\( \gamma_1 \)  Vibrational (thermal) excitation rate
\( \gamma_1 \)  Vibrational dissipation rate
\( \Gamma \)  The \( \Gamma \)-point of dispersion relation (k=0)
\( \Gamma^\pm \)  Absorption and emission rates
\( \Gamma_1 \)  Pump rate
\( \Gamma_1 \)  Spontaneous emission rate
\( \epsilon \)  Relative permittivity
\( \epsilon \)  Electronic transition frequency
\( \theta \)  Angle
\( \kappa \)  Cavity mode loss rate
\( \lambda \)  Wavelength
\( \lambda_{dB} \)  de Broglie wavelength
\( \lambda_i \)  Gell-Mann matrix of index \( i \)
\( \mu \)  Chemical potential / Index for molecular loss processes
\( \xi_{abs} \)  The energy where absorption probability becomes effectively zero
\( \rho \)  Density matrix or operator
\( \sigma^+, \sigma^-, \sigma^z \)  Pauli operators
\( \tau \)  Lifetime / Time delay
\( \phi \)  Phase
Symbols

\( \chi \) Universal roughness exponent
\( \psi \) Quantum state operator
\( \omega \) Angular frequency
\( \Omega \) Vibronic coupling constant
\( \Omega_R \) Rabi splitting
\( a^\dagger, a \) Bosonic creation and annihilation operators for photon modes
\( \text{a.u.} \) Arbitrary units
\( A_{H,V} \) Amplitudes of horizontal (H) and vertical (V) polarization components
\( b \) Power-law exponent
\( b^\dagger, b \) Bosonic creation and annihilation operators for vibrational modes
\( c \) Speed of light
\( [c] \) Concentration
\( C \) Amplitude of interference fringes
\( d \) Degeneracy
\( E \) Energy / Electric field
\( E_{H,V} \) Horizontally (H) and vertically (V) polarized components of electric field
\( f \) Frequency
\( f_{ijk} \) Symmetric structure constant
\( F_X \) Purcell factor
\( g \) Light-matter coupling strength
\( g^{(1)} \) First-order correlation function
\( g^{(2)} \) Second-order correlation function
\( G \) Reciprocal lattice vector
\( h \) Planck’s constant
\( \hbar \) Reduced Planck’s constant
\( H \) Hamiltonian operator
\( I \) Intensity
**k**  Wave vector

\( k_B \)  Boltzmann’s constant

\( L \)  System length

\( m_{\text{eff}} \)  Effective mass

\( n \)  Refractive index

\( n_k \)  Occupation number of state \( k \)

\( N_m \)  Number of molecules

\( N_{\text{ph}} \)  Number of photon modes

\( N_v \)  Number of vibrational states

\( N^* \)  Population inversion

\( p_e \)  Fraction of excited molecules

\( p_x, p_y \)  Lattice periodicity in \( x \) and \( y \)

\( \mathbf{p} \)  Momentum vector

\( P \)  Pump fluence

\( Q \)  Quality factor or Q factor

\( \mathbf{r} \)  Position vector

\( S \)  Huang-Rhys parameter

\( S_{1,2,3} \)  Stokes vector components

SU  Special unitary group

\( t_{ijk} \)  Antisymmetric structure constant

\( T \)  Temperature

U  Unitary group

\( V \)  Mode volume / Interaction term

\( \dagger \)  Hermitian adjoint

\( \mathcal{L} \)  Lindblad superoperator

Im  Imaginary part

Re  Real part

Tr  Trace operation; the sum of elements on the diagonal of a square matrix

\( \partial_t \)  Partial differential operator \( \partial / \partial t \)

\( d_t \)  Time derivative \( d / dt \)
1. Introduction

In the Standard Model, elementary particles are divided in two. Particles that make up matter are called fermions, whereas force-carrying particles are bosons. Fermions and bosons are distinguished by their spin, which is a measure of intrinsic angular momentum. Spin is quantized, meaning it can only take discrete values. The fact that fermions have half-integer spins and bosons have integer spins, causes a profound difference in their behaviour: whereas two identical fermions cannot be in the same place at the same time, bosons tend to bunch together [1]. In fact, unlimited number of bosons can share a quantum state. Particles with substructure, such as nuclei and atoms, also act as bosons or fermions depending on their constituents.

Albert Einstein and Satyendra Nath Bose predicted in 1924–1925 that a cloud of bosonic atoms could be driven into the same quantum state by lowering the temperature below a critical limit [2, 3]. This extraordinary phase of matter, called Bose–Einstein condensate (BEC), was realized in a laboratory in 1995 with atoms cooled down to almost \( 0 \text{ K} \) \((-273\,^\circ C)\) [4, 5, 6]. Since then, condensates have been created also from various types of quasiparticles [7, 8, 9, 10].

Quasiparticles refer to hybrids of different types of matter and field excitations, or collective disturbances in a medium, that behave particle-like. An everyday-life analogue of a quasiparticle is found from a glass of beer: a bubble rising from the bottom of the glass towards the surface can be viewed as a 'quasiparticle'. Though the bubble may look like an actual object, it is just a displacement of volume of the liquid by carbon dioxide gas. Nevertheless, the bubble holds observable particle-like properties such as location and speed. It can collide with other bubbles exchanging momentum but, as characteristic of quasiparticles, cannot occur outside the host system. As soon as it breaks through the surface, and the carbon dioxide escapes, the bubble ceases. Quasiparticles have a finite lifetime. The disturbances that make up quasiparticles can be, for instance, excitations or deformations of the medium, or simply restrictions in the allowed states of a particle. Examples of quasiparticles include phonons (vibrations...
in crystal structures), plasmons (collective oscillations of electrons), excitons (electrons paired with holes), and polaritons (light coupled to other quasiparticles). Before we can do physics beyond the beer glass with quasiparticles, let us recapitulate some of the basic properties of light, and how light can interact with matter.

Electromagnetic radiation (Box 1) is mediated by particles called photons. Photons, as all particles, possess both wave-like and matter-like characteristics. Exhibiting the rules of quantum mechanics, a photon that encounters a double slit flows through both the openings simultaneously like a sea wave hitting a breakwater. However, as soon as one measures which slit the photon passes through, the measurement will show that the photon only gets through one slit at a time. According to Heisenberg’s uncertainty principle, both the position and the momentum of a particle cannot be measured precisely: the more accurately one of the properties is measured, the more uncertain becomes determining the other [11]. The particle-like nature of photons manifests itself in that energy of electromagnetic radiation can only be transferred as discrete amounts. The quantum of energy carried by a photon with wavelength $\lambda$ is expressed as $E = \frac{hc}{\lambda}$, where $h$ is the Planck’s constant and $c$ the speed of light.

**Box 1. Electromagnetic spectrum**

The spectrum of electromagnetic waves can be divided into different regimes by the length of the waves, $\lambda$, ranging from ionizing radiation, i.e. gamma and X-rays, with $\lambda < 10$ nm to microwaves (1 mm...1 m) and radio waves (>1 m). In between lies a region of wavelengths that we generally call light, with wavelengths from ultraviolet to infrared (100 nm...100 μm). The part of the spectrum our eyes are sensitive to is within 400 to 700 nm. The different wavelengths of visible light are perceived as different colors in our brain. For example, light from a laser pointer has a certain color because it consists of a single wavelength only, but sun light appears "white" as it is a mixture of a wide range of wavelengths.
Consider a simple piece of matter – an atom with two distinct energy levels, $E_1$ and $E_2$. Let us assume $E_2 > E_1$ and that the atom is initially in the low-lying level 1, or the ground state. The atom will remain in the ground state unless external stimuli act on it. Suppose that a photon with energy equal to the level separation, $E_2 - E_1$, is incident on the atom. The photon may give away its energy to the atom, which then undergoes a transition from the ground state to the higher level 2, or the excited state. This process is called absorption. As time passes, the atom tends to undergo a transition from the higher energy level back to the lower one. Doing so, the atom releases an amount of energy equal to $E_2 - E_1$. If energy is released in the form of electromagnetic radiation, the process is referred to as spontaneous emission: a photon with energy $E_2 - E_1$ is emitted to a random direction and at a random phase. The atom may release energy also in some other form than electromagnetic radiation, such as thermal vibrations (phonons), in which case the process is called non-radiative decay.

Let us go back to the condition where the atom is still in the excited state and imagine that a photon with energy equal to the level separation $E_2 - E_1$ is incident on the atom. The atom can undergo a transition from level 2 to 1 and simultaneously release a photon with identical energy, momentum, and phase as the incident photon. The light waves travelling in phase are said to be coherent. This is the process of stimulated emission, a mechanism behind laser operation (Box 2).
**Box 2. Laser**

In light amplification by stimulated emission of radiation (LASER), light is reflected back and forth between two mirrors that form a cavity [12]. The ability of the cavity to provide resonant back-and-forth reflection is called feedback. Depending on the length of the cavity, only certain frequencies are resonant. One of the mirrors is highly reflective, while the other is partially transparent. The cavity is filled with a material that absorbs and emits light at the cavity frequencies. This gain medium can be atoms, fluorescent molecules, or a semiconductor material. The gain medium is excited optically or electrically. For laser action (lasing) to occur, it is important that the probability for a photon to trigger stimulated emission is larger than the probability of getting absorbed. To satisfy this, the gain material must be amenable to producing population inversion i.e. to have more atoms in the excited state than in the ground state. This would be difficult to achieve with two-level atoms, thus it is better to use three- or four-level atoms that have suitable lifetimes of the energy levels: for example, a three-level atom whose highest energy state decays rapidly but the second-highest state slowly.

As soon as population inversion is reached, the first (often spontaneous) photon incident to an excited atom may trigger an avalanche: due to photon multiplication by stimulated emission, the cavity mode gains more population at a rate that increases with the number of photons already in the mode. Consequently, the number of photons in the cavity mode increases non-linearly until out comes an intense, coherent, and highly directed beam of light at a single wavelength. Light with a single wavelength is called monochromatic.

Coherence enables focusing the laser beam onto a small surface area. Aside with tasks that utilize high power density, such as cutting and welding, lasers have proven useful in cooling a gas of atoms for experiments in quantum physics. Due to its abilities, laser light has found revolutionary applications such as the compact disc (CD), laser surgery, and fiber-optic communication that is the basis of the internet [13, 14]. Laser was undoubtedly one of the most significant inventions of the 20th century, enabling nothing less than the use of the internet in its present scale.

Emission and absorption are not the only ways by which light may interact with matter. The wave motion of photons can be described in terms of oscillation frequency $f = c/\lambda$. A two-level atom can be considered as an oscillator too: the optical transition between the levels 1 and 2 can be driven with a light field oscillating at the matching frequency given by $hf = E_2 - E_1$. 
Suppose now that these two 'oscillators' couple to each other like two weights that are attached to their surroundings with springs and further connected to each other with a third spring. By all odds, if one of the weights is being moved, the other will move as well. How much – depends on how stiff the springs are. The coupled system will oscillate at frequencies which depend on both its constituents as well as on the strength of the coupling. If the weights were free to move without any friction, the coupled system would continue to oscillate indefinitely. In analogue, strong coupling is a regime of light-matter interaction where an atom (or molecule, exciton, etc.) and a light field exchange energy coherently and reversibly [15, 16, 17, 18]. This leads to the hybridization of energy levels of the atom and the photon mode. Quasiparticles based on strong coupling are partly light but may effectively interact through the matter part. Strong coupling could be utilized, for example, in modification of chemical reactions [19, 20, 21, 22]. The coherent and reversible oscillation of energy is also a prerequisite for quantum information processing.

What other consequences may interaction with matter have on the properties of light? Photons are a rare type of particles in that they have no mass. This means that photons always travel at the speed of light in free space. However, if one finds a way to modify the potential landscape of the photon, the situation can be changed.

Imagine being a well-known scientist entering a room full of people in a conference cocktail event: you are determined to walk through the crowd to the other side of the room, where the bar is, but people tend to interact with you, grabbing onto your arm asking: "Can you make a condensate of light?" Your movement is slowed down, as if you had suddenly gotten heavier. One could calculate how 'massive' you should be in order to become as inert as now due to the external dragging interaction. In other words, you have gained effective mass. This very phenomenon occurs to conduction electrons moving in a metal: the positive ions jerk the sleeves of the electrons by attractive Coulomb force, giving the electrons an effective mass additional to their rest mass. Similarly, coupling to matter or quasiparticles gives a photon an effective mass.
Photons have integer spin (0 or 1) implying they are bosons, therefore it is only natural that the curious minds have been asking whether you can create a condensate of light. Before being able to give a definite answer, let us take a moment to reflect upon why atoms can collapse into the same quantum state when cooled down.

Atoms are in constant motion with their velocity proportional to thermal energy. As known by the Heisenberg’s uncertainty principle, if atoms are slowed down, their location becomes less well-defined. This means that the possible location where to find an atom, or its matter wave, becomes larger. Simplistically put, the heavier the atoms, the cooler the system must be for the matter waves of the particles to overlap – a prerequisite for Bose–Einstein condensation (Box 3). Once the matter waves overlap, an individual particle can no longer be distinguished from the others, and the cloud of atoms behaves in concert as a single large atom (Figure 1.1).

![Figure 1.1](image)

**Figure 1.1.** A cartoon of Bose–Einstein condensation. As the temperature is lowered, the energy of the particles decreases. This makes the particles slower and their matter waves extended. Once the critical temperature is reached, the matter waves merge, and the ensemble of particles acts as a single large particle with an enormous matter wave. Screenshots adopted with permission from [23].

Pure photons, on the other hand, cannot be cooled in the same way as atoms. A photon “gas” enclosed in a cavity can be brought to thermal equilibrium by interaction with the cavity walls at certain temperature (the black body radiation). However, if the cavity is cooled down with the aim of achieving a condensate, the number of photons is not conserved and at vanishing temperatures the photons disappear. Therefore, pure photons simply in contact with a thermal cavity cannot undergo Bose–Einstein condensation. However, there are systems where one can realize cooling and thermalization processes that do conserve the photon number.
Introduction

Box 3. Bose–Einstein statistics

Critical temperature to achieve Bose–Einstein condensation depends on the dimensionality and the potential landscape of the system. In a three-dimensional gas of non-interacting bosons, the critical temperature is proportional to the density $n$ and inversely proportional to the mass $m$ of the particles as $T \propto n^{(2/3)}/m$. Put the other way round, critical density for condensation depends on mass and temperature as $n \propto (mT)^{(3/2)}$ [24].

When the temperature is decreased below (or density increased beyond) the critical value, the matter waves ($\lambda_{dB}$) of the particles start to overlap, and the bosons may collapse into the same quantum state, forming a Bose–Einstein condensate (BEC). The de Broglie wavelength is given by

$$\lambda_{dB} = \sqrt{\frac{2\pi \hbar^2}{mk_B T}}, \quad (1.1)$$

where $k_B$ is the Boltzmann’s constant and $\hbar$ is the reduced Planck’s constant $\hbar = h/2\pi$. From Eq. (1.1) we see that to make the matter waves of particles overlap, it is helpful to have low temperature or small effective mass. If the effective mass is very small, the de Broglie wavelength can be large even at elevated temperatures.

The expected number of particles (mean occupation number) of energy state $k$ for a gas of non-interacting bosons in thermodynamic equilibrium is given by the Bose–Einstein (BE) distribution

$$n(E_k) = \frac{d_k}{e^{(E_k - \mu)/k_B T} - 1}, \quad (1.2)$$

where $E_k$ is the energy of state $k$, and $\mu$ is chemical potential, which corresponds to the amount of energy required to add a particle into the thermally isolated system. The energy levels can be degenerate, meaning that two or more different measurable states of the system yield the same energy: $d_k$ is the degeneracy of state $k$. At high temperatures, the significance of quantum statistics becomes negligible, and the BE distribution can be approximated by the Maxwell–Boltzmann (MB) distribution

$$n(E_k) = \frac{d_k}{e^{(E_k - \mu)/k_B T}}, \quad (1.3)$$

Also in case of a BEC, the population at higher energies follows the MB distribution. The graph below shows the shapes of the BE and MB distribution functions ($d=1, \mu=0, k_B T = 300$ K). The MB distribution is linear in the semi-logarithmic scale. The high-energy part of the BEC energy spectrum, which displays the MB distribution, is here called the thermal tail.
In 2010, Klärs, Weitz and co-workers trapped light between two very closely placed curved mirrors – a microscopic cavity [25]. Light in such a cavity forms a standing wave, which gives rise to a set of resonant modes that the photons can occupy. Each longitudinal mode hosts a manifold of transverse modes, and large frequency spacing between the longitudinal modes provides an effective lowest-energy mode of the system. The two-dimensional (2D) trapping potential imposed by the microcavity gave the photons a very small yet finite effective mass, approximately one millionth of an electron mass. Despite high-quality mirrors, photons may escape from the cavity, so an external "pump" laser is required to compensate for the loss. The cavity was filled with organic molecules in a liquid solution. Organic molecules are far from being simple two-level systems but have a complex structure and a large size (Box 4). Consequently, they tend to collide with other molecules and undergo vibrational and rotational conformation changes. When a photon from the cavity gets absorbed by a molecule, the molecule will lose some energy through vibrational dissipation before emitting a photon back to the cavity. Recurrent cycle of absorption and emission enabled the photons to thermalize from high energy into the lowest-energy mode of the cavity. Above critical density, all excess photons pumped into the cavity accumulated to the lowest-energy mode, and the first BEC of photons was realized. Owing to the very small effective mass of photons, the condensate was created at room temperature. Though this was the first BEC made up of photons, condensates of hybrid light-matter particles had been achieved earlier.

Exciton-polaritons (Box 5) – called polaritons hereafter – are quasiparticles of photons and excitons that are typically created in a microcavity filled with a semiconductor material. The photon part of the polaritons makes their effective mass small, allowing condensation at elevated temperatures. The exciton part, again, mediates interactions between polaritons, enabling a thermalization mechanism based on scattering. To initiate the process (in an incoherent excitation scheme\(^1\)), a population of excitons is created by optical or electrical pumping [26, 27]. Thermalization of polaritons takes place by two steps: first, polaritons scatter from the exciton reservoir, relaxing to a lower-energy polariton mode by dissipation of phonons. Then, the polaritons scatter from other polaritons such that some of them end up in the lowest-energy polariton mode. As the density of polaritons in the cavity is increased, a macroscopic population of polaritons accumulate to the lowest energy state by bosonic stimulation. Though polariton-polariton scattering is a stimulated phase-coherent process similarly to stimulated emission in a laser, there is a crucial difference that stimulated polariton scattering is not caused by population inversion in a gain medium.

\(^1\)There exist also coherent pumping schemes where an initial population is created directly to the lower polariton branch, from where the polaritons scatter resonantly to the condensing mode.
Box 4. Organic molecules

Organic molecules are made of chains of atoms (see an example below; the molecular structure of IR-792 dye [28]). The molecules may rotate, and the chemical bonds holding the molecule together vibrate. Each rotational and vibrational conformation corresponds to a different energy state. Therefore, the electronic states are surrounded by a large number of rotational and vibrational states [29]. In an ensemble, each molecule has a slightly different absorption and emission probability due to variations in the local environment within the liquid or solid. As a result, the absorption and emission spectra of the ensemble appear continuous and broad (inhomogeneous broadening).

Transitions of electrons, which may accompany absorption or emission of a photon, can occur between any of the states of the molecule. Some transitions are preferred over the others by the maximum overlap of the wave functions of different energy states i.e. a minimal change in the nuclear coordinates upon transition (Franck-Condon principle [30, 31]). The transitions within an organic molecule are described by Jablonski diagram [32], an example of which is shown below, where \( E \) is energy, \( R \) is a generic nuclear coordinate, and \( v \) \((v')\) stands for vibrational states of the ground (excited) electronic state; the rotational states that surround each vibrational level are not drawn. When a molecule is excited to one of the vibrational levels of the upper electronic state, vibrational relaxation takes place, leading to dissipation of energy. Hence, in the case of spontaneous emission, transition back to the ground state occurs from the lowest vibrational level of the upper electronic state (Kasha’s rule [33, 34]). Dissipation through vibrational relaxation is mediated by phonons (quasiparticles of vibrational motion). The energy difference between the absorbed and the emitted photon is called Stokes shift [35].

Some organic molecules obey Kennard-Stepanov relation which describes the scaling between emission and absorption rates [36, 37, 38]: the division of emission with absorption spectrum yields a thermal MB distribution with \( T \) equal to the environment temperature (or the so-called spectral temperature [39]). The higher the emitter’s quantum efficiency, the better its emission and absorption profiles follow the relation. The Kennard-Stepanov relation lays the foundation for thermalization of photons [40]. The right panel below depicts the Kennard-Stepanov relation at room temperature.
Introduction

Box 5. Exciton-polaritons

Exciton-polaritons (polaritons hereafter) form as a consequence of strong light-matter coupling between photons and excitons (bound electron-hole pairs). A typical system for studying polaritons is an optical microcavity filled with a layer of a semiconductor material that provides the excitons when activated optically or electrically. The mirrors of the microcavity can be, for instance, dielectric distributed Bragg reflectors (DBRs) or semi-transparent metal films. See an illustration below. The active layer can be in the form of a bulk material or consist of quantum wells.

When choosing the active material, it is necessary that both the exciton binding energy and the coupling strength exceed the thermal energy, which at room temperature \( T = 300 \text{ K} \) is \( E_{\text{thermal}} = k_B T = 26 \text{ meV} \). The exciton binding energy is inversely proportional to the relative permittivity of the material. Inorganic semiconductors typically have high permittivity whereas organic semiconductors have small. Consequently, the excitons in inorganic semiconductors (termed Wannier-Mott excitons) have small binding energies (e.g. 1–10 meV) and large radii, as opposed to organic semiconductors, where the excitons (Frenkel excitons) are smaller and more localized with higher binding energies (0.1–1 eV). Thus, excitons in organic semiconductors are more resistant to thermal dissociation.

Indeed, early demonstrations of strong coupling at optical frequencies in the 1990s required cooling the cavity, filled with an inorganic semiconductor material, to cryogenic temperatures to be able to resolve the Rabi splittings that were of the order 1–10 meV [41, 42]. The tables were turned in 1998, when Lidzey, Whittaker and co-workers achieved strong coupling in organic semiconductor microcavities which provided remarkably large Rabi splittings, exceeding 100 meV at room temperature [43]. Since then, various organic materials have been utilized in microcavity polariton experiments, including J-aggregates [44], perovskites [45], anthracene [46], fluorene (TDAF) [47], and conjugated polymers (MELPPP) [48]. Also many inorganic semiconductors with a wide band gap, such as GaN [49, 50, 51] and ZnO [52, 53], have proven suitable for high-temperature polariton systems. There exists also a line of polariton research where the active layer is a combination of inorganic and organic materials [54, 55, 56, 57]. Another interesting branch of polaritonics utilizes biological materials, where strong coupling to optical cavity modes [58] as well as polariton condensation has been demonstrated [59]. Exciton-polaritons are also investigated in the rapidly growing field of layered two-dimensional materials [60, 61].
The study of polariton lasing and condensation originates from the development of microcavity photon lasers (1988–1992) [62, 63]. In the end of the 1990s, the focus shifted towards establishing a coherent state of light at the strong-coupling regime [64, 65, 66, 67]. The first condensates of polaritons were realized in inorganic (GaAs, CdTe) semiconductor microcavities at cryogenic temperatures. Early evidence for condensation by the spontaneous appearance of coherence in 2002 [68] was followed by a complete description of polariton condensation in 2006–2007 [69, 70, 71]. Soon after, polariton lasing in inorganic microcavities was observed at room temperature by utilizing wide band gap materials (e.g. GaN) [50, 51, 74]. In parallel with the advancements in experiments in the late 2000s, significant theoretical efforts were made with the models of condensation kinetics, spin dynamics, and interactions [75, 76, 77, 78, 79, 80].

Excitons in organic materials can have very high binding energies, which makes them stable at ambient conditions. However, the integration of organic materials into high-quality optical cavities requires a considerable technological effort, and it took until the early 2010s before they started to arise as a feasible option to inorganic semiconductors. In 2014, the first organic polariton condensates were achieved at room temperature [48, 47]. Since then, room-temperature polariton lasing and condensation has been studied with various materials [81, 7].

Compared to atomic BECs, condensates of light have the advantage that the energy and the in-plane momentum are preserved by the photons that leak out of the cavity, carrying information that is directly accessible by optical spectroscopy and quantum optical measurement techniques. Within the past decade, the understanding of the properties of condensates of light has been pushed forward in many fronts.

Since the first realization in 2010 [25], photon BECs in dye-filled microcavities have been created and their properties studied by several research groups [82, 83, 84]. BECs have been formed even with a very small number of photons [85, 86]. First-order [87, 88] and second-order correlations in photon BECs have been investigated [89, 90, 91, 92], and thermalization dynamics probed by time-resolved measurements [93]. Critical behaviour of thermodynamic quantities at phase transition, as known e.g. for liquid helium [94], have been studied in photon BECs [95]. Note that, apart from BEC, so-called 'classical' (also Rayleigh–Jeans) condensation of light waves has been studied in optical fiber and photorefractive crystal systems [96, 97, 98, 99]. Recently, photon BECs have been reported in an erbium-ytterbium doped optical fiber [100] and an electrically pumped semiconductor microresonator [101].

It should be noted that while polariton lasing has been distinguished from polariton condensation by the absence of thermal equilibrium [72, 73], the line between the two phenomena remains blurred and the terms 'polariton lasing' and 'polariton condensation' are often used interchangeably.
Interactions in photon BECs are reportedly weak, which could be expected due to the intrinsically non-interacting nature of photons [102, 103, 104, 105, 91, 90]. In polariton condensates, interactions are stronger given by the high exciton content of the quasiparticles [72, 7]. Inorganic systems provide the strongest interactions, mediated by direct Coulomb forces between excitons [106, 107]. Weaker, yet notable, interactions are also found in organic polariton condensates, predominantly given by saturation effects [47, 48, 108, 109]. Consequently, polaritons may show intriguing phenomena such as superfluidity – the ability of particles to flow without friction [110, 111]. Topological defects, such as quantized vortices and solitons, have been observed in density and phase measurements [112, 113, 114, 115, 116], and by the creation of polarization textures [117, 118, 119, 120, 121]. The polarization state of polaritons acts as a ‘pseudospin’ in analogue to solid state systems [122], liquid crystals [123], ultracold gases [124], and liquid helium [125], where complex topological defects, e.g. skyrmions, merons, half-vortices, and magnetic monopoles, have been investigated before.

As opposed to atomic BECs, polariton condensates are typically far from equilibrium conditions due to the short lifetime of polaritons versus their thermalization time. A quasi-equilibrium state can be obtained by a dynamical balance of pump and dissipation [7, 126]. The non-equilibrium nature of polariton condensates provides a platform to study unique physical phenomena [127], but it also raises fundamental questions about the definition of a BEC [112, 128]. For instance, while equilibrium BEC is conventionally defined as the macroscopic occupation of the ground state, it has been shown that in driven-dissipative systems condensation may occur to several modes at distinct energies [129, 130]. Ultimately, whether a system may reach a thermal equilibrium depends on the relative duration of different processes in the system. Sufficiently long lifetimes with respect to thermalization times have been reached in both photon [25] and polariton [131, 132] condensates so as to discuss an equilibrium-like state. Yet even in the equilibrium case, categorizing condensates of light in the context of “textbook” BECs is controversial; the existence of true long-range order in dimensions below three is a subtle issue [133], and even more so in non-equilibrium systems [134] (Box 6).

Various theoretical approaches have been developed to model lasing and condensation in the driven-dissipative\(^3\) light-matter systems [135, 136, 137, 138, 139, 140, 105, 141, 142, 126]. While many of the models focus on the properties of the condensate wave function (mean-field theory), multimode description is important in order to properly model processes involving several modes such as thermalization and multimode lasing and condensation [109, 129, 130].

\(^3\)A lossy system that is pumped externally is called driven-dissipative.
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Box 6. Berezinskii–Kosterlitz–Thouless transition

In quantum mechanics, a physical system is described by a Hamiltonian function or operator. A broken symmetry refers to a situation in which a particular state does not exhibit all the symmetries that the system Hamiltonian has. Bose–Einstein condensation is associated with spontaneous breaking of the U(1) symmetry through the occurrence of a well-defined global phase [24]. The fact that a whole ensemble of particles can be described by the same wave function is equivalent to the occurrence of off-diagonal long-range order [143, 144, 145, 146].

Three-dimensional BECs in thermal equilibrium exhibit long-range order of spatial correlations. In two dimensions, “true” long-range order is prohibited at a finite temperature [147, 148, 149]; thermal fluctuations give rise to vortices and anti-vortices which disrupt the long-range ordering of correlations. However, it has been shown that quasi-long-range order may persist through the Berezinskii–Kosterlitz–Thouless (BKT) transition [150, 151]. In the BKT transition, below a critical temperature, vortices and anti-vortices are paired such that their phases cancel out allowing algebraic decay of spatial and temporal correlations with power-law exponent below 0.25. In non-equilibrium condensates, quasi-long-range order could be restored by the dynamical phase ordering of Kardar–Parisi–Zhang (KPZ) [152]. The KPZ equations describe the stochastic dynamics of driven interfaces in non-equilibrium processes, such as the growth of bacterial colonies [153] and the burning of paper [154]. The KPZ equations predict decay of both spatial and temporal correlations as a stretched exponential function with universal roughness exponents. A crossover between the equilibrium-like BKT and the KPZ dynamics has been proposed, dependent on pumping conditions and anisotropy of the system [134, 141, 155].

Spatial and temporal coherence of polariton condensates has been studied in both non-equilibrium and equilibrium-like conditions. Early reports on spatial correlations in microcavity polariton condensates indicated algebraic decay [156, 157], whereas temporal correlations have been shown to decay as an exponential or a Gaussian [158, 159, 160, 161, 162, 163], similar to a usual laser [12] or non-ordered phase. There have been very few studies that include both spatial and temporal correlations, thus the nature of long-range order in non-equilibrium polariton condensates has not been fully characterized. At equilibrium-like conditions, with polariton lifetime exceeding the other characteristic timescales of the system, observation of the BKT transition has been reported [132].

One of the distinctive features of condensates of light is the small effective mass of photons and polaritons, which enables condensation at elevated temperatures. This not only makes the experiments simpler compared to atomic BECs, but is beneficial for practical applications. In fact, various polariton devices have already been proposed [164], including polariton light-emitting diodes [165, 166, 167, 168], amplifiers [169], spin switches [170], and polariton transistors [171, 172]. Lattices of photon and polariton condensates offer an intriguing option for quantum simulation of interacting many-body systems [173, 174, 175, 176, 177, 178, 179, 180, 181, 182], which to date have been mostly considered in superconducting electrical circuits [183, 184], ultracold atomic gases [185], and trapped-ion systems [186]. While most of the studies of polariton condensates have been based on optical excitation, electrical injection of polariton lasers has been...
demonstrated [187, 188, 189, 190, 191], marking an important milestone towards integration to electronics.

Considering applications of photonic (or polaritonic) devices in information processing (Box 7), converting electronic signals to optical ones and back poses a bottleneck for the speed of information transfer. All-optical integrated circuits could enable exchanging information between optical signals without involving intermediate electronics, but one of the challenges is the non-interacting nature of photons.

Box 7. Towards optical information processing

Digital computers have changed our lives in many ways, but the electronics they are built on begins to approach the end of its journey, as the density of transistors on a chip is reaching its physical limits [192]. Ever increasing amount of data is being transferred over the web as we stream high-definition media for remote work, social interaction, and entertainment. Also virtual and augmented reality is making its entry to our lives along with wearable technology, with demands for capacity and speed of data processing as well as for the physical size of the devices [193]. Moreover, emerging applications that utilize machine learning require vast sets of training data [194]; artificial intelligence is anticipated to help out in solving and inhibiting global crises such as natural disasters and pandemics. At the same time, energy consumption must be significantly reduced.

Photonic integrated circuits based on manipulating light instead of electricity could revolutionize the future of information technology, enabling orders of magnitude faster operation and lower energy consumption than electrical circuits [195]. Photonic circuits have been considered in a variety of platforms, from which silicon and InP have become the most popular choices. Silicon provides compatibility with the current complementary metal-oxide–semiconductor (CMOS) fabrication technology and integration with transistor based electronics, whereas InP allows integration of semiconductor laser light sources on the same chip [196, 197, 198, 199]. Photonic crystals with a band gap are the photonic version of semiconductor in electronics. In addition to conventional lithography and patterning techniques, photonic crystals can be formed through self-assembly, which could be one route to mass production [200, 201, 202].

The advantages of both electronic and photonic devices are potentially combined in the field of plasmonics: the study of the interaction between light and metallic structures at the nanoscale [203, 204, 205]. Coupling photons to electrons in metal enables confining light into a space smaller than the wavelength. While preserving interactions given by the electronic nature, operational speeds of plasmonic systems are of the same order as in photonics [206]. Plasmonics promises groundbreaking applications in optical communications [207, 208, 209, 210, 211], biosensing [212, 213, 214], solar energy harvesting [215, 216], and ultrahigh-resolution imaging [217, 218], and it could be the facilitator of room-temperature quantum information technology [219, 220, 221, 222, 223].

Whereas the starting point for electronics integration was the invention of the transistor in 1948, the starting point for photonic circuitry was the
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In a similar fashion, establishing integrated plasmonic circuits calls for the development of coherent light sources in the nanometer scale [224, 225]. Lasing in plasmonic systems has been studied extensively since the creation of the first plasmonic nanolasers in 2009 [226, 227, 228, 229, 230, 231, 232, 233, 234]. Another possible mechanism to produce coherent light is through a phase transition into a BEC. Condensation also provides a framework for other fascinating quantum-coherent phenomena such as superfluidity and superconductivity.

This dissertation introduces the first plasmonic BECs, created at room temperature in a system consisting of periodic arrays of nanoparticles overlaid with organic fluorescent molecules. As compared with conventional plasmonic systems, such as metal films, an array structure provides higher quality factors with longer lifetime of the modes. Nanoparticle arrays can be fabricated 'on chip' with direct-write methods such as electron-beam lithography (EBL) [204]. The first plasmonic BEC (Publication I) was achieved at weak light-matter coupling regime. In the follow-up work (Publication II), we established a plasmonic BEC at strong coupling regime. Furthermore, we characterized first-order spatial and temporal correlations in the strongly coupled plasmonic BEC (Publication III), and demonstrated the formation of polarization textures (Publication IV). In addition, we introduced a novel theoretical model for strongly coupled organic polariton systems (Publication V). The model also lays a foundation for theoretical description of plasmonic polariton BECs: some features the model can already predict such as the blue shift of polariton dispersion related to effective interactions, which we observed in Publication II. The research work summarized in this dissertation has been carried out by a combination of theoretical work and optical measurements.

The dissertation folds as follows. Chapter 2 provides an introduction to the plasmonic resonances in a nanoparticle array and summarizes the theoretical tools: non-equilibrium model of photon condensation used to simulate the plasmonic BEC in Publication I and multimode model of strongly coupled organic systems presented in Publication V. Chapter 3 contains a brief description of sample fabrication and experimental techniques used in Publications I–IV. In Chapter 4, the main results of Publications I–V are presented and discussed. Finally, Chapter 5 closes the dissertation with a summary and outlook of the present research. The original journal articles of Publications I, II, IV, V and the manuscript of Publication III are provided as appendices.
2. Theoretical framework

This Chapter presents the theoretical concepts and tools used in this dissertation. Section 2.1 provides an introduction to the dispersive properties of electromagnetic waves travelling in free space and those coupled to metallic nanostructures. Modelling of organic systems is discussed in Section 2.2, and the theoretical models applied and developed in this dissertation are described in Sections 2.2.1–2.2.2. The non-equilibrium model of photon condensation in Section 2.2.1 was applied to describe the first plasmonic BEC in Publication I. Section 2.2.2 presents the strong coupling extension of the model, which we introduced in Publication V.

2.1 Plasmon resonances

2.1.1 Electromagnetic waves

Electromagnetic waves are periodically changing electric and magnetic fields that carry energy and momentum as they propagate through space. The energy $E$ of an electromagnetic wave is related to its wavelength $\lambda$, which can be converted to frequency $f$ or angular frequency $\omega$ through the relations

$$E = \hbar \omega = \hbar f = \frac{hc}{\lambda}. \quad (2.1)$$

The momentum is given by $p = \hbar k$, where $k$ is the wave vector that describes the direction of propagation for a homogeneous wave. Note that because $p$ and $k$ are directly proportional through the constant $\hbar$, it has become a convention to use the terms wave vector and momentum as synonyms [235, 236]. The absolute value of the wave vector is the (angular) wave number $|k| = k = \frac{2\pi}{\lambda}$. Substituting this into Eq. (2.1) gives the relation between energy and wave number of a wave travelling in a medium with refractive index $n = \sqrt{\epsilon_1}$ (non-magnetic material) i.e. the dispersion relation

$$E = \frac{\hbar ck}{\sqrt{\epsilon_1}}, \quad (2.2)$$
where $\epsilon_1$ is the relative permittivity of the material. The dispersion relation of electromagnetic waves in free space, also known as the light line, is presented in Figure 2.1(b). In Cartesian coordinates and three dimensions $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$. For light waves travelling in the $xy$-plane, the $k_z$ component is 0, and the dispersion relation is presented by a conical surface which forms when the light line rotates 360 degrees around the $E$-axis. Such a light cone is presented in Figure 2.1(a). Only the modes that are on the surface of the cone correspond to a wave propagating in the $xy$-plane, whereas outside the cone $k_z$ becomes imaginary, and the wave is evanescent.

### 2.1.2 Surface plasmon polaritons

Optical properties of metals are described by the dielectric function (relative permittivity) $\epsilon(\omega)$. While $\epsilon(\omega)$ is real and positive constant for many dielectric materials such air or glass, metals can have a complex $\epsilon(\omega)$ with a negative real part [235, 237]. Consequently, interesting resonance effects can be induced in metals.

When a light beam encounters a piece of metal, it is mostly reflected by the surface. Part of the electromagnetic field is transmitted into the metal where it quickly attenuates. Free electrons near the surface of the metal may interact with the field, yielding coupled electron-light modes called surface plasmon polaritons (SPPs) [238, 239, 240]. SPPs can propagate along the interface between a metal and a dielectric but decay exponentially in the perpendicular direction. Confinement of the modes to the interface leads to a highly enhanced electromagnetic field, which can be utilized in, for example, sensing applications [241, 242, 243, 244]. Metal thin films suitable for SPPs can be fabricated with commonly available technologies, and their structural and optical properties can be tailored [240, 245, 204].

Dispersion relation of SPPs with in-plane momentum $k_{SPP}$ is given by

$$E_{SPP} = \hbar ck_{SPP} \sqrt{\frac{\epsilon_1 + \epsilon_2}{\epsilon_1 \epsilon_2}}, \quad (2.3)$$

where $\epsilon_1$ and $\epsilon_2$ are the relative permittivities of the two media. As the dispersion relations in Figure 2.1(b) depict, the SPP modes have higher momentum than light propagating in free space, implying they cannot be directly excited by light. Momentum of light can be increased by a prism or a grating coupler to match with the momentum of the SPPs. A diffraction grating is a periodic structure that diffracts light into rays travelling in different directions depending on the wavelength. Each angle of incidence $\theta$ corresponds to a wave vector component $k_{0,\|} = k_0 \sin \theta$ parallel to the plane. The grating increases the in-plane wave vector by an amount determined by the period $p$, giving the light a 'momentum kick' $G$ (reciprocal lattice vector), as illustrated in Figure 2.1(c). Photons with in-plane momentum
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Figure 2.1. Dispersion of light and surface plasmon polaritons. (a) Dispersion relation of light is presented by a conical surface on $k_x-k_y$-plane. (b) Dispersion relations of light and surface plasmon polaritons (SPP) are shown by blue and red lines, respectively. The SPP dispersion is calculated for silver with the values of $\varepsilon_2(\omega)$ obtained from Ref. [249]. Red dashed line denotes the plasmon energy $E_p$. (c) Schematic of coupling photons into SPPs on a metal film by a grating coupler. Parallel grooves on a metal film can be used to match the wave vectors by increasing the in-plane component $k_{0,||}$ given by the grating period $p$.

increased beyond the light line may couple into SPPs. Grating couplers can be formed by patterned surfaces or periodic arrangements of sub-wavelength scatterers such as holes or particles [246, 247, 248].

Besides the surface of a bulk material, SPPs can be bound to the surfaces of sub-wavelength scatterers such as metal nanoparticles. In analogue to antennae for radio waves, nanoscale scatterers act as antennae for light [250, 251, 252, 253, 254]. SPPs confined to the surfaces of nanoparticles are called localized surface plasmon resonances (LSPRs). They form when an electromagnetic field interacts resonantly with a nanoparticle, displacing negative (electrons) and positive (holes) free charge carriers from each others, and the restoring Coulomb force leads to oscillation of the carriers. Due to the collective oscillation of the electron cloud, the nanoparticle absorbs and transmits different wavelengths of light with different efficiency. The resonant wavelengths are determined by the material, size, and shape of the nanoparticle as well as the refractive index of the environment [255].

The plasmon resonance is responsible for the formation of colors in stained glass – one of the early "applications" of nanoparticles by medieval artisans [256] – and in the Lycurgus Cup – a 4th-century Roman glass chalice which appears to change color depending on whether light passes through it [257]. More recently, nanoparticles of metals and dielectrics have found applications in fields such as photocatalysis [258, 259, 260, 261], photosynthesis [262, 263, 264], solar energy conversion [265, 266, 267, 216, 215], targeted photothermal cancer therapy [268, 269, 270, 271], and plasmonic color displays [272].
2.1.3 Surface lattice resonances

Plasmon resonances can be further enhanced by assembling nanoparticles into a periodic array: a plasmonic lattice, see Figure 2.2(a). Namely, when the distance between the nanoparticles is of the order of the wavelength, incident light diffracts to the lattice plane inducing far-field radiative coupling between the nanoparticles. This gives rise to collective modes called surface lattice resonances (SLRs), which are hybrids of the LSPRs (i.e. electron oscillations) of individual nanoparticles and the diffracted orders (DOs) of light [273, 274, 275, 276]. An excitation of the SLR is a bosonic quasiparticle with an effective mass of $10^{-7}–10^{-5}$ electron masses [10, 277]. SLR modes have been studied in various geometries including triangular, hexagonal, honeycomb, and Lieb lattices [278, 279, 232], and also using dielectric nanoparticles [280]. In this dissertation, the research is focused on rectangular lattices of gold nanoparticles.

Dispersion relation of the SLR modes can be derived starting from the empty lattice approximation, which considers an infinite 2D periodic structure with periodicities $p_x$ and $p_y$ [281, 282]. The lattice is called ‘empty’ as it assumes an infinitesimally small periodic variation to the refractive index of the medium. When light diffracts to the lattice plane, the lattice provides momentum kicks equivalent to $G_x = \pm 2\pi/p_x \hat{x}$ and $G_y = \pm 2\pi/p_y \hat{y}$. According to Bloch’s theorem [283], the resulting waves with wave vectors shifted by $sG_x + qG_y$ ($s, q$ are integers $0, \pm 1, \pm 2, \ldots$), have equal energies. Thus the light cone is simply repeated on the $k_xk_y$-plane. The first DOs in $k_y (0, \pm 1)$ and in $k_x (\pm 1, 0)$ are presented in Figure 2.2(b-c). Figure 2.2(d) shows a close-up of two intersecting DOs $(0, \pm 1)$ with the cross sections along $k_{x,y} = 0$ highlighted with dashed and solid lines. The modes in the cross sections are denoted as transverse electric (TE) and transverse magnetic (TM) given by the direction of propagation and the polarization vector. The TE modes have electric field polarization perpendicular to the propagation direction ($E_x, k_y$ and $E_y, k_x$), whereas for the TM modes the polarization is parallel to the propagation direction ($E_x, k_x$ and $E_y, k_y$). The modes in the intersection are given by

$$E = \frac{\hbar c}{\sqrt{\epsilon_1}} \sqrt{(k_x \pm G_x)^2 + (k_y \pm G_y)^2},$$

which gives the dispersion relations of the TE and TM modes in Figure 2.2(d) ($G_x = 0$) with $k_x = 0$ and $k_y = 0$, respectively.

In a real nanoparticle array, the scatterers are of finite size, and therefore the empty lattice approximation does not provide a complete description of the dispersion. Due to the strong coupling between the DOs and the LSPRs [284], close to the single particle resonance the dispersion is bent similarly as for the SPPs in Figure 2.1(b). Far away from the single particle resonance, the SLR modes are mostly photonic, and the dispersion follows that of the DOs. Around $k = 0$ (Γ-point), however, counter-propagating
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Figure 2.2. Nanoparticle array and dispersion of light in a 2D periodic structure. (a) Schematic of a nanoparticle array. (b) The first diffracted orders in \( k_y \): \((0, \pm 1)\). (c) The first diffracted orders in \( k_x \) and \( k_y \): \((\pm 1, 0)\) and \((0, \pm 1)\). (d) Intersection of the DOs \((0, \pm 1)\) with the modes along \( k_x = 0 \) and \( k_y = 0 \) highlighted: the solid line shows the mode which we denote transverse electric (TE) and the dashed line transverse magnetic (TM). For the TE mode, polarization of light is perpendicular to the wave vector \((E_x, k_y)\). For the TM mode the polarization is parallel to the wave vector \((E_y, k_x)\). Note that for clarity only the DOs \((0, \pm 1)\) are shown here; corresponding TE and TM modes exist at the intersection of cones for \( E_y \) polarization.

Modes with momentum \( \mathbf{k} = \pm \mathbf{G}_x = \pm 2\pi/p_x \hat{x} \) backscatter to each other via coupling to the DOs \((\pm 2, 0)\) (correspondingly in \( y \)), which leads to the formation of two hybrid modes, symmetric and antisymmetric, and the opening of a photonic band gap in the dispersion [285, 231]. The symmetric and antisymmetric modes correspond to standing waves with nodes either at the nanoparticle sites or between the sites, respectively. The symmetric mode is associated with a dipolar and the antisymmetric with a quadrupolar excitation in the nanoparticle. The quadrupolar mode is often called ‘dark’ because in an infinite lattice it does not radiate to the far field, owing to its zero net dipole moment. The features of the dispersion around the band gap depend on the size and shape of the nanoparticles: typically with large (small) particles the upper (lower) branch becomes bright. The size and shape of the nanoparticles also determine the width of the band gap. Examples of measured SLR dispersions around the \( \Gamma \)-point are presented in Fig. 2.3. Small nanoparticles can be considered as point dipoles, which radiate predominantly in directions perpendicular to their polarization.

The SLR modes in an array of small nanoparticles can be modelled using coupled dipole approximation (CDA) [231, 286, 287]. Larger nanoparticles may obtain higher-order multipolar excitations, leading to more complex radiation patterns. In this case, the array can be modelled by T-matrix method [288].

Given by the high photonic content and thus lower losses, SLRs have longer lifetimes (~ 100 fs) as compared with LSPRs (~ 10 fs). Lifetime of
modes in a cavity is obtained from the spectral linewidth $\Delta \omega_0$ as

$$\tau = \frac{Q}{2 \pi f_0} = \frac{1}{\Delta \omega_0},$$  \hspace{1cm} (2.5)$$

where $Q = f_0/\Delta f_0$ is the quality factor of the cavity. Plasmonic lattices typically have $Q$ factors of around 100 – 700 [273].

The electromagnetic field of SLRs is confined to the lattice plane, and the LSPRs provide further field enhancement in field 'hot spots' close to the nanoparticles (an example is shown in Section 4.1 Figure 4.1(d)). The field is accessible by emitters, such as quantum dots or fluorescent molecules, placed in the vicinity of the array. The field hot spots lead to an increase of the local optical density of states, which can dramatically modify the probability of spontaneous emission of emitters. The enhancement of spontaneous emission rate is called Purcell effect, and the (Purcell) factor by which the rate is increased is given by [289]

$$F_P = \frac{3}{4\pi^2} \left( \frac{\lambda_0}{\n} \right)^3 \frac{Q}{V},$$  \hspace{1cm} (2.6)$$

where $\lambda_0$ is the wavelength of light in vacuum and $n$ is the refractive index of the medium. Clearly, the enhancement is higher when light is confined into a small mode volume $V$, or when the $Q$ factor is high.

High field confinement enforces coupling between light (cavity modes) and matter (emitters). Strong coupling leads to the hybridization of the energy levels of the emitters and the cavity modes, manifested as the anti-crossing of exciton and photon dispersion energies [15, 16, 17]. The formation of an energy gap in the dispersion of the hybrid modes is called Rabi splitting, and the coherent temporal oscillation of population between

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**Figure 2.3.** Measured TE mode dispersions of typical nanoparticle arrays. (a) Dispersion relation obtained by white-light transmission measurement for an array of large rod-shaped gold nanoparticles. In transmission spectrum, the dips (blue) correspond to the mode locations. (b) Measured extinction of an array consisting of small cylindrical silver nanoparticles. In extinction spectrum, the peaks (yellow) correspond to the mode locations. The dashed lines are the DOs and the circle denotes the location of the dark mode.
the emitter and the mode is termed as Rabi oscillation. The Rabi splitting \( \Omega_R \) is proportional to the coupling strength \( g \) and the square root of the density of emitters \( N_m/V \) as \( \Omega_R = 2g \sqrt{N_m/V} \). Strong coupling regime is reached when the rate of the Rabi oscillation exceeds the decay rates of the light and matter components. This is typically evidenced by comparing the observed Rabi splitting to the linewidths of the photonic modes and the exciton by transmission or extinction measurements.

Despite that plasmonics suffer from relatively high losses, strong coupling has been achieved in various plasmonic systems [15, 290] by using high density of emitters with high oscillator strengths. In the recent years, strong coupling has been achieved even at the single emitter limit [291, 292]. The quasiparticles formed by excitons and plasmonic modes are called plasmon-exciton polaritons [284, 293, 228, 294]. In the works presented in this dissertation, organic fluorescent molecules are employed as emitters, applying them on the nanoparticle arrays in a liquid solution. Whereas the number of emitters \( N_m \) and the mode volume \( V \) are unknown or difficult to determine, we can tune the density \( N_m/V \) (concentration) in a controlled way. SLRs in nanoparticle arrays have been coupled also with other emitters than organic molecules such as quantum dots [295, 296] and transition metal dichalcogenides [297].

The past decade has seen significant progress in the development of plasmonic lasers in various architectures [234]. In a nanoparticle array, the standing waves that are formed at the dispersion band edges provide feedback for lasing. Plasmonic lattices combined with various types of emitters have shown lasing [228, 229, 230, 298, 231, 299, 232, 233, 300, 301, 302, 303, 304] and polariton condensation/lasing [294, 305, 306]. Publication I in this dissertation was the first realization of a BEC in a plasmonic lattice [10], extended to the strong coupling regime in Publication II [277]. Characteristic of plasmonic lattice lasers and condensates is ultrafast, (sub-)picosecond timescale, dynamics [307, 308, 306, 277] and large extent of spatial coherence [299, 309].

### 2.2 Modelling lasing and condensation in organic systems

Organic systems have many features that make their theoretical and computational modelling challenging [310, 311]. Polariton lifetimes in organic microcavities are usually of the order 0.1–1 ps, which is shorter than the typical relaxation or thermalization time of polaritons. Moreover, since organic fluorescent materials tend to suffer from long triplet-state lifetimes and photobleaching [34, 35], pulsed excitation is often required. Consequently, organic systems are often far from equilibrium conditions. However, a quasi-equilibrium state can be achieved by a dynamical balance of the pumping and dissipation [7].
Organic systems can be operated at elevated temperatures, which in turn means that dissipative effects are enhanced: the emitters are in thermal contact with other emitters and the solvent or host medium, which leads to efficient dissipation of energy through vibrational and rotational relaxation. The electronic states can be strongly coupled to the vibrational modes, yielding large Stokes shifts and inhomogeneously broadened linewidths of absorption and emission spectra. Moreover, typical platforms such as microcavities and nanoparticle arrays host a continuum of cavity modes, which sets further demands for modelling. An accurate model of an organic polariton system would be immensely complicated given by the large number of degrees of freedom. To limit the complexity, while still preserving the essential physics, one needs to resort to deliberate approximations.

Several approaches have been introduced to model lasing and condensation in organic light-matter systems. The first approach includes phenomenological kinetic models based on coupled rate equations, analogous to conventional laser theory [12]. Rate equations have been used to describe condensation of polaritons that occurs through stimulated scattering between an initial state (polaritons close to an exciton reservoir) and a final state (the mode that becomes macroscopically occupied) [312, 313].

The second approach involves mean-field descriptions focused on modelling the condensate wave function. In the mean-field theory, interactions imposed to a particle by all other particles are replaced by an average interaction field. A typical model is constructed starting from the (non-linear) Gross-Pitaevskii equation (GPE) which describes the time evolution of the condensate wave function. The GPE can be further coupled to a rate equation for the reservoir population. Such models can describe the state of the macroscopically occupied mode but not the other modes such as those that take part in the thermalization process. Linearizing the mean-field model around a steady-state solution or a homogeneous state can be done to estimate two-time correlators and the effect of quantum fluctuations [77, 314, 47].

The third and more elaborate approach includes microscopic models starting from a quantum mechanical description [126, 7]. The models often build on density matrix formalism which is routinely used in modelling coupled light-matter systems [315, 135, 136, 138, 316, 317]. These models are especially powerful for organic materials because they can explicitly involve strong exciton-phonon coupling. Finding exact solutions to the system's quantum states or directly solving the master equation [318, 139, 319, 320, 321] quickly becomes computationally too costly for a realistic system. Drive and dissipation play a significant role in organic systems and can be conveniently included by the Lindblad formalism [322, 323]. Derivation from the master equation has been proceeded to first and second-order cumulants [324, 135, 136, 138, 109, 325, 105]. This
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approach stems from the semiclassical theory of lasing [326], and has been utilized e.g. in studying the different regimes of lasing and condensation in the Dicke model [327, 324], and Rabi oscillations in strongly coupled light-matter systems [325]. Second-order cumulants have also proven useful in modelling photon condensation, where higher-order correlations arising from coherences between photons and excitons can be neglected due to weak coupling [135, 136]. Considering strongly coupled systems, many of the recent models have still restrained to the mean-field approximation, considering a single cavity mode and neglecting all but first-order cumulants [138]. The multimode extension of a microscopic strong coupling model up to second-order cumulants was introduced in Publication V of this dissertation. It should be noted that in addition to those mentioned here, many other microscopic frameworks for coupled light-matter systems have been developed based on e.g. Keldysh formalism [328, 329, 330, 331] and quantum Langevin equations [332, 333].

Let us begin the formulation of models for non-equilibrium photon condensation (Section 2.2.1) and multimode polariton lasing (Section 2.2.2) by considering a system of \( N \) homogeneously distributed emitters coupled to \( N_{ph} \) photon modes in a 2D cavity. The emitters consist of two electronic states that are coupled to vibrational modes. This very general system is described by the extended Tavis-Cummings-Holstein Hamiltonian in the rotating wave approximation [334, 335, 323, 336] (\( \hbar = 1 \))

\[
H = \sum_{k} \omega_{k} a_{k}^{\dagger} a_{k} + \sum_{n} \left[ \frac{\varepsilon}{2} \sigma_{n}^{z} + \omega_{v} \left( b_{n}^{\dagger} b_{n} + \sqrt{S} \sigma_{n}^{z} \left( b_{n}^{\dagger} + b_{n} \right) \right) \right] + \sum_{n,k} \left( g_{n}(k) a_{k} \sigma_{n}^{+} + g_{n}(k)^{*} a_{k}^{\dagger} \sigma_{n}^{-} \right),
\]

(2.7)

where \( a_{k}^{\dagger} (a_{k}) \) is the bosonic creation (annihilation) operator describing the photon mode of momentum \( k \), \( \sigma_{n}^{\pm} \) are the Pauli operators corresponding to the two electronic states of molecule \( n \), and \( b_{n}^{\dagger} (b_{n}) \) is the bosonic creation (annihilation) operator of the vibrational ladder of molecule \( n \). Moreover, \( \omega_{k} \) is the frequency of the photon mode \( k \), \( \varepsilon \) is the electronic transition frequency of the molecules, and \( \omega_{v} \) the vibrational frequency. The Huang-Rhys parameter connected to the spectral broadening of emission and absorption linewidths due to the vibrational degrees of freedom is denoted as \( S \), and \( g_{n}(k) \) describes the coupling strength between molecule \( n \) and photon mode \( k \). In an \( L \times L \) square with periodic boundary conditions, the photon modes may be approximated as plane waves with \( k = (2\pi/L)(K_{x}, K_{y}) \), where \( K_{x} \) and \( K_{y} \) are integers. The coupling constant \( g_{n,k} \) can be written as \( ge^{-ik\cdot r_{n}} \), where \( r_{n} \) is the location vector of molecule \( n \).

The Hamiltonian in Eq. (2.7) describes an isolated system without interactions with the environment. Driven-dissipative systems interact with the environment through losses of the cavity modes and the emitters and excitation by a pump. Open quantum systems are routinely treated in the
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context of density matrix formalism [337]. A density operator $\rho$ describes a probability distribution of all possible states $|\Psi_n\rangle$

$$\rho = \sum_n p_n |\Psi_n\rangle \langle \Psi_n|,$$  \hspace{1cm} (2.8)

where $p_n$ is the classical probability that the system is found in the quantum state $n$. The expectation value of an observable $A$ is obtained as $\langle A \rangle = \text{Tr}[\rho A]$. Applying the Schrödinger equation $H|\Psi\rangle = i\hbar \partial_t |\Psi\rangle$, we obtain the equation of motion for the density matrix [337]

$$\partial_t \rho = \partial_t |\Psi\rangle \langle \Psi| + |\Psi\rangle \partial_t \langle \Psi| = -i[H, \rho],$$  \hspace{1cm} (2.9)

which describes the time-evolution of the system. Eq. (2.9) is also known as the von Neumann-Liouville equation. Here we have assumed the so-called coarse-grained time derivative: $d_t \rho(t) \approx \partial_t \rho(t)$ [323, 338], given that the time step $\partial t$ is small compared to the time evolution of the system density operator. Taking dissipative processes into account yields the complete master equation for the system in the Lindblad form [323, 337]

$$\partial_t \rho = -i[H, \rho] + \sum_k \kappa \mathcal{L}[a_k] + \sum_{\mu, n} \mathcal{L} \left[ \gamma^{(\mu)} C^{(\mu)}_n \right],$$  \hspace{1cm} (2.10)

where $\mathcal{L}[X] = X \rho X^\dagger - \frac{1}{2} (X^\dagger X \rho + \rho X^\dagger X)$ is the Lindblad superoperator [322], $\kappa$ is the cavity mode loss rate, $n$ runs over the $N_m$ molecules, and $\mu$ refers to the driven-dissipative processes acting on the molecules, described by the corresponding jump operators $C$. The relevant processes in our system are excitation of the molecules by a pump, non-radiative decay, dephasing, and vibrational excitation and dissipation with rates given by $\gamma^{(\mu)}$.

It should be noted that to arrive at the master equation in the form Eq. (2.10) requires applying the standard Born-Markov approximations for the external reservoirs [339, 337]. The main assumptions are that the correlation time of a reservoir is much faster than the timescale of interactions with the system; in other words the reservoir has no memory on the past interactions with the system. The reservoir is also taken to be stationary at all times, regarding the system as a negligible perturbation. The density matrices of the system and the environment remain separable throughout the time evolution, $\rho_{\text{tot}}(t) \approx \rho(t) \otimes \rho_{\text{env}}$. The assumptions are valid as long as the interaction is weak and the environment is large compared to the system.

The Hamiltonian in Eq. (2.7) and the master equation in Eq. (2.10) serve as a starting point for both models presented next.
2.2.1 Non-equilibrium photon condensation model

The model of non-equilibrium photon condensation developed by Kirton and Keeling [135, 136] has been widely adopted in the research of photon BECs in dye-filled microcavities [93, 105, 130]. In Publication I, we applied the model to study the dynamics of a plasmonic BEC under weak light-matter coupling. Our system consists of a 2D periodic nanoparticle array overlaid with dye molecules. The photons occupying the SLR modes are considered to act as a non-interacting gas of bosons. The molecules have two electronic states surrounded by a large number of vibrational levels forming a reservoir which is in thermal equilibrium with environment. In a real system the thermal contact is established by frequent collisions with solvent molecules [340]. The molecule population is excited by a laser pulse. We apply the Born-Markov approximation for the reservoirs that account for drive and dissipation: SLR loss, non-radiative decay of excited electronic state, and external pump [135, 136, 341].

Loss rate for SLR modes. The environment reservoir related to radiative and ohmic losses of the plasmonic excitations is assumed to consist of a large number of harmonic oscillators in thermal equilibrium. The rate of change of the system density operator due to the loss rate \( \kappa \) of mode \( k \) is

\[
\frac{\partial}{\partial t}\rho = \kappa \mathcal{L}[a_k].
\]  

(2.11)

In general, the loss rate could depend on frequency and wave vector of the modes, but here it is taken constant.

Loss processes for molecular excitations. Similarly, we can derive the rate of change of the density operator due to non-radiative decay of the molecular electronic state

\[
\frac{\partial}{\partial t}\rho = \Gamma_{\downarrow} \mathcal{L}[\sigma^-],
\]  

(2.12)

where \( \Gamma_{\downarrow} \) is the spontaneous decay rate of the molecules. This includes the effects of spontaneously emitting photons to the far field without exciting any SLR modes and quenching induced by other molecules [235, 342].

Excitation of molecules by external pump. According to the Markov approximation, energy flow from the system to an external reservoir is irreversible. To model energy flow into the system by an external pump, we can define a reservoir of inverted harmonic oscillators. The effect of the pump on the system density operator can be written as [339]

\[
\frac{\partial}{\partial t}\rho = \Gamma_{\uparrow} \mathcal{L}[\sigma^+],
\]  

(2.13)

where \( \Gamma_{\uparrow} = \Gamma_{\uparrow}(t) \) is the time-dependent pump rate.

Master equation. The Hamiltonian in Eq. (2.7) contains three quantum operators; \( a \), \( b \), and \( \sigma \). To reduce the complexity of the model, we apply
polaron transformation \([343, 344, 345, 136]\) to the coupling between two-level systems and vibrational modes;

\[
U = \exp \left[ \sum_n \sqrt{S} \sigma^z_n (b_n - b_n^\dagger) \right], \tag{2.14}
\]

which allows to write the Hamiltonian in the form \(\mathcal{H} = U^{-1} H U = H_0 + V\) with

\[
H_0 = \sum_k \omega_k a_k^\dagger a_k + \sum_n \left( \frac{\xi}{2} \sigma^z_n + \omega_v b_n^\dagger b_n \right),
\]

\[
V = \sum_{n,k} \left( g_n(k) a_k^\dagger D_n e^{ik\cdot r_n} + g_n^*(k) a_k^\dagger D_n^\dagger e^{-ik\cdot r_n} \right). \tag{2.15}
\]

Here \(V\) describes all the interactions, with contribution of vibrational modes included in the combined operators \(D_n = \exp \left[ \frac{2}{\sqrt{S}} (b_n^\dagger - b_n) \right]\) and \(D_n^\dagger = \exp \left[ -\frac{2}{\sqrt{S}} (b_n^\dagger - b_n) \right]\). As we are dealing with weak coupling, i.e. \(g_n(k)\) is much smaller than the optical and vibrational frequencies, we may treat the interaction term \(V\) as a perturbation to the system, which now consists of the photon modes and the electronic states only. The phonon ladders represented by the operators \(b\) are treated as reservoirs within the Born-Markov approximation. It should be emphasized that this implies a significant restriction to the vibrational relaxation time, which is hereby assumed to be smaller than the other timescales in the system.

The perturbative treatment of \(V\) is conducted in the interaction picture, see Refs. \([341, 135, 136]\) for details of the derivation. As a result, the operators \(b\) are traced out, and the contribution of vibrational reservoirs is included in coefficients \(\Gamma^\pm(\delta_k) \equiv \text{Re} [S(\pm \delta_k)]\), where \(S(\omega) = \int_0^\infty dt \langle \tilde{D}(t) \tilde{D}(0) \rangle e^{i\omega t}\). Absorption and emission rates are described by the two coefficients \(\Gamma^\pm(\delta_k)\), where \(\delta_k = \omega_k - \epsilon\) is the detuning between frequencies of the SLR modes \(k\) and the molecular transition. Taking into account the Lindblad terms for pump and dissipation, master equation for the system density matrix becomes

\[
\frac{d}{dt} \rho = -i[H'_0, \rho] + \sum_k \kappa_k \mathcal{L}[a_k^\dagger a_k] + \sum_n \left( \Gamma^1 \mathcal{L}[\sigma^+_n] + \Gamma^1 \mathcal{L}[\sigma^-_n] \right)
+ \sum_{n,k} 2|g_n(k)|^2 \left( \Gamma^+(\delta_k) \mathcal{L}[a_k^\dagger \sigma^+_n] + \Gamma^-(\delta_k) \mathcal{L}[a_k^\dagger \sigma^-_n] \right), \tag{2.16}
\]

where the free Hamiltonian \(H'_0\) is renormalized according to \([135, 136, 341]\).

**Rate equations.** Time evolution of the SLR mode occupations \(n_k = \langle a_k^\dagger a_k \rangle\) and the fraction of excited molecules \(p_e = \langle \sigma^z_0 \sigma^-_0 \rangle\) can be solved by proceeding to second-order cumulants:

\[
\frac{d}{dt} \langle a_k^\dagger a_k \rangle = \text{Tr} \left[ a_k^\dagger a_k \frac{d \rho}{dt} \right],
\]

\[
\frac{d}{dt} \langle \sigma^+_n \sigma^-_n \rangle = \text{Tr} \left[ \sigma^+_n \sigma^-_n \frac{d \rho}{dt} \right]. \tag{2.17}
\]
As coupling between the molecules and the SLR modes is assumed weak, we can decompose higher-order correlators as 
\[ \langle a_k^+ a_k \sigma_n^+ \sigma_{\bar{n}}^\sigma \rangle \approx \langle a_k^+ a_k \rangle \langle \sigma_n^+ \sigma_{\bar{n}}^\sigma \rangle. \]
Furthermore, we assume that the system is homogeneous in terms of molecular absorption and emission rates: population inversion \( p_e \) and coupling strength are the same for all \( N_m \) molecules. The coupling strength is assumed to be independent of \( k \). The rate equations become

\[
\frac{d}{dt} n_k = -\kappa n_k + 2N_m |g|^2 \left[ \Gamma^-(k)(1 + n_k)p_e - \Gamma^+(k)n_k(1 - p_e) \right],
\]
\[
\frac{d}{dt} p_e = \Gamma^+(1 - p_e) - \Gamma^-p_e + \sum_k 2|g|^2 \left[ -\Gamma^-(k)(1 + n_k)p_e + \Gamma^+(k)n_k(1 - p_e) \right].
\]

These can be expressed in the frequency space by taking into account the dispersion relation \( E = \hbar \omega(k) \):

\[
\frac{d}{dt} n_\omega = -\kappa n_\omega + 2N_m |g|^2 \left[ \Gamma^-(\omega)(1 + n_\omega)p_e - \Gamma^+(\omega)n_\omega(1 - p_e) \right],
\]
\[
\frac{d}{dt} p_e = \Gamma^+(1 - p_e) - \Gamma^-p_e + \sum_\omega 2|g|^2 d(\omega) \left[ -\Gamma^-(\omega)(1 + n_\omega)p_e + \Gamma^+(\omega)n_\omega(1 - p_e) \right].
\]

The SLR modes are discretized and their energies follow the TE band dispersion relation described in Section 2.1.3. Degeneracy of states \( d(\omega) \) of the modes is numerically obtained from the dispersion relation [286].

After the molecules are excited by a laser pulse, they may exchange photons with the SLR modes. Subsequent absorption and emission processes eventually lead to thermalization of the SLR excitations, and the thermal distribution of the vibrational states (Kennard-Stepanov relation) becomes imprinted on the SLR mode population. Above a critical photon density, the population follows the BE distribution, that is, macroscopic occupation of the ground state followed by a thermal tail at energies above the ground state. Figure 2.4 presents some early simulations of a plasmonic BEC with parameters that could be achieved experimentally. The results nicely illustrate how the BE distribution is established only after a certain time from the beginning of the simulation; at early times the thermalizing population contributes highly to the distribution. In this example, the time until the BE distribution is complete (~thermalization time) was 1.8 ps and the BE distribution was maintained for at least half a picosecond. The simulations laid the foundation for experiments towards achieving the first plasmonic BEC [286, 341, 346, 10]. Particularly, the results indicated that one needs to find a way to look at the later times of the system and not time-integrate over whole time evolution. We will return to this discussion in Section 4.1 with the experimental results.
2.2.2 Multimode organic polariton lasing model

Extending the model of non-equilibrium photon condensation to the strong coupling regime is not straightforward, because the light-matter interaction was treated as a perturbation to the system and the vibronic coupling as a dissipative reservoir. At strong coupling, the Rabi splitting becomes comparable to the linewidths of the original modes of the system, and one can no longer treat the coupling merely as a perturbation. Motivated by this, we aimed at formulating a multimode model which preserves both the light-matter coupling and the vibronic coupling in the system Hamiltonian.

**Master equation.** Our model of a microcavity filled with organic molecules is depicted in Figure 2.5. The model takes $N_m$ two-level systems homogeneously distributed in a planar cavity which supports multiple photon modes. The photon modes can be strongly coupled to the emitters, whose electronic states can be strongly coupled to vibrational modes. The Hamiltonian in Eq. (2.7) is the starting point for modelling such a system. Drive and dissipation are taken into account by the Lindblad formalism similarly as for the weakly coupled system in Section 2.2.1. Here the interactions are kept part of $H$, and the thermal excitation, and dissipation of vibrational modes are included by the corresponding Lindblad terms. The master equation reads [347]

$$
\dot{\rho} = -i[H, \rho] + \sum_k \kappa \mathcal{L}[a_k] + \sum_n \left( \Gamma_{\uparrow} \mathcal{L}[\sigma_n^+] + \Gamma_{\downarrow} \mathcal{L}[\sigma_n^-] \right) + \Gamma_z \mathcal{L}[\sigma_n^z] + \gamma_{\uparrow} \mathcal{L}[b_n - \sqrt{\mathcal{S}} \sigma_n^z] + \gamma_{\downarrow} \mathcal{L}[b_n - \sqrt{\mathcal{S}} \sigma_n^z], \quad (2.20)
$$

where $\Gamma_z$ accounts for dephasing, that is, the rate at which phase coherence of the electronic states lost. Directly solving Eq. (2.20) for a realistic system would require unbearable computational resources, therefore we proceed to second-order cumulant equations to solve the photon mode occupations and the molecule population inversion.
Generalized Gell-Mann basis. To simplify the formulation, we combine the two electronic states ($\sigma$) and the $N_v$ vibrational states ($b$) into $2N_v$-level operators. For this we deploy Gell-Mann matrices, $\lambda$, which have previously been used e.g. in describing the strong interaction in particle physics [348, 349]. They obey the following relations:

$$\lambda_i = \lambda_i^\dagger, \quad \text{Tr} \lambda_i = 0, \quad \text{Tr}[\lambda_i \lambda_j] = \delta_{ij},$$

$$[\lambda_i, \lambda_j] = 2i f_{ijk} \lambda_k, \quad \lambda_i \lambda_j = \zeta_{ijk} \lambda_k + \frac{2}{N_\lambda} \delta_{ij},$$

where $\zeta_{ijk} = i f_{ijk} + t_{ijk}$ and $N_\lambda$ is the dimension of the matrices. The tensors $f_{ijk}$ and $t_{ijk}$ are the symmetric and antisymmetric structure constants, respectively [350]. Gell-Mann matrices allow for expanding any linear $N_\lambda \times N_\lambda$ operator in this basis as

$$A = \frac{1}{N_\lambda} \text{Tr}[A] \lambda_i \lambda_i + \frac{1}{2} \text{Tr}[A \lambda_i] \lambda_i. \quad (2.21)$$

As a practical example, a complete set of $3 \times 3$ Gell-Mann matrices are shown in Figure 2.6. In our model, we utilized generalized, $2N_v \times 2N_v$, Gell-Mann matrices. By the change of basis, the Hamiltonian is cast into the form

$$H = \sum_{\mathbf{k}} \omega_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \sum_{n} \left[ A_i + \sum_{\mathbf{k}} (B_i a_{\mathbf{k}}^\dagger e^{-i \mathbf{k} \cdot \mathbf{r}_n + \text{h.c.}}) \right] \lambda_i^{(n)}, \quad (2.22)$$
where the vectors $A_i$ and $B_i$ combine the terms in the original Hamiltonian in Eq. (2.7). Note that tensor sums that run over Gell-Mann operator indices $i$ are implicit. In the new basis, the master equation in Eq. (2.10) takes the form

$$\frac{\partial}{\partial t}\rho = -i[H, \rho] + \sum_k \kappa L[a_k] + \sum_{\mu, n} L[\gamma^\mu L^{(n)}_i],$$

(2.23)

where $\mu$ refers to the dissipative processes related to molecules: (1) pump, (2) decay, (3) dephasing, and vibrational (4) excitation and (5) decay.

**Second-order cumulant equations.** To fully exploit the symmetry invoked by the rotating wave approximation, i.e. the conservation of number of excitations, we divide the operators $\lambda_i$ into three groups that either increase ($+$), decrease ($-$), or conserve ($z$) the electronic excitations. When deriving the second-order cumulants, expectation values of operators that do not conserve the number of excitations ($\langle a_k \rangle, \langle a_k^\dagger \rangle, \langle \lambda_i^+ \rangle, \langle \lambda_i^- \rangle$) become zero. We split higher-order expectation values into products of first and second-order cumulants: third-order correlators are taken to be zero, i.e. we make an assumption that the correlations between three operators is captured by the second-order cumulants, allowing to decompose the third-order terms as $\langle ABC \rangle = \langle A \rangle \langle BC \rangle + \langle B \rangle \langle AC \rangle + \langle C \rangle \langle AB \rangle$ [351].

Spatial homogeneity allows for approximating the phase factors as $\sum_n e^{i(k-k')\cdot r_n} = N_m \delta_{k,k'}$, conserving momentum. For the number-conserving Gell-Mann operators we then obtain $\ell_i = \langle \lambda_i^{(n)} \rangle$. Likewise, the coherence terms can be written as $d_{ij}^k = \sum_{n,m \neq n} e^{i(k-k')\cdot r_n} \langle \lambda_i^{(n)} \lambda_j^{(m)} \rangle / N_m^2$ and $\xi_i^k = \sum_n e^{i(k-k')\cdot r_n} \langle a_k \lambda_i^{(n)} \rangle / N_m$. Photon mode occupations are given by $n_k = \langle a_k^\dagger a_k \rangle$.

The equations of motion for these quantities become:

$$\frac{\partial}{\partial t} n_k = -\kappa n_k - 2N_m \text{Im}\left[ B_i c_i^k \right],$$

$$\frac{\partial}{\partial t} \ell_i = \xi_{ij} \ell_j + \phi_i - 8\text{Re}\left[ \beta_{ij} \sum_k c_k^j \right],$$

$$\frac{\partial}{\partial t} c_i^k = \left[ X_{ij} - \left( i\omega_k + \frac{\kappa}{2} \right) \delta_{ij} \right] c_j^k + 2\beta_{ij} \ell_j n_k - iB_j d_{ij}^k - \frac{i}{N_m} \left( \xi_{ij} \ell_j + \frac{B_i}{2N_m} \right),$$

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\begin{equation}
\partial_t a_{ij}^k = X_{ij}^* a_{ip}^k + X_{jp} a_{ip}^k + 2\ell_p (\beta_{ip} c_j^k + \beta_{jp}^* c_i^k), \tag{2.24}
\end{equation}

where \(\hat{c}_i^k = c_i^k - \sum_q c_i^q/N_m\), and the coefficients are given by
\[
\phi_i = \frac{2i}{N_v} f_{ip} \sum_{\mu} \gamma_{ip}^{\mu*}, \quad \beta_{ij} = \frac{1}{2} B_p (f_{ij}^{ip} - i f_{ij}^{jp}), \quad X_{ij} = \xi_{ij} + i \xi_{ij},
\]

\[
\dot{\xi}_{ij} = 2 f_{ij} A_p + i \left( f_{ips} \xi_{spj} + f_{ris} \xi_{sjp} \right) \sum_{\mu} \gamma_{ip}^{\mu*}. \tag{2.25}
\]

Equations (2.24) describe the strongly coupled multimode system and capture the effect of fluctuations, which is not possible in mean-field approaches.

**Photoluminescence spectrum.** Strong coupling modifies the original resonances of the system such that the hybrid mode energies are no longer those of bare photons and excitons. The resulting polariton dispersion bands are separated by Rabi splitting. The energies of the polaritons are found by computing the photoluminescence spectrum:
\[
S_k(\nu) = \int_{-\infty}^{\infty} dt \langle a_k^\dagger(t) a_k(0) \rangle e^{i\nu t}. \tag{2.25}
\]

Here, we utilize the quantum regression theorem to calculate the two-time correlations[352]. Solving \(S_k(\nu)\) requires the steady-state density matrix \(\rho_{ss}\) which is used to construct Ca\(\rho(0) = a_k^\dagger \rho_{ss}\). In other words, the steady-state solution to the problem is taken as the starting point for evaluating the photoluminescence spectrum. Time-evolving the effective density matrix \(\tilde{\rho}(t) = e^{t\mathcal{L}} \rho(0)\) and evaluating Tr\([a_k^\dagger \tilde{\rho}(t)\)] gives the coupled differential equations for the two-time correlators [353]:
\[
\partial_t \langle a_k^\dagger(t) a_k(0) \rangle = \left( i\omega_k - \frac{K}{2} \right) \langle a_k^\dagger(t) a_k(0) \rangle + i N_m B_i^* c_i^k(t),
\]
\[
\partial_t c_i^k(t) = \xi_{ij} c_j^k(t) + 2 f_{ip} B_j \ell_p \langle a_i^\dagger(t) a_k(0) \rangle, \tag{2.26}
\]

where \(c_i^k(t) = 1/N_m \sum_n e^{-ikr_n} \text{Tr}\left[ \lambda(n) \tilde{\rho}(t) \right]\) and
\[
\langle a_k^\dagger(t) a_k(0) \rangle = \text{Tr}\left[ a_k^\dagger e^{t\mathcal{L}} a_k \rho_{ss} \right].
\]

Here, \(\ell_p\) becomes constant in the steady state. Because the equations are linear, they can be written in a matrix form as \(\partial_t \mathbf{C}_k = \mathcal{M} \mathbf{C}_k\) where the vector \(\mathbf{C}_k = [\langle a_k^\dagger(t) a_k(0) \rangle, \langle c_i^k(t) \rangle]^T\) and the matrix \(\mathcal{M}\) are obtained from Eqs. (2.26). The Fourier transform can be written analytically as
\[
S_k(\nu) = \int_{-\infty}^{\infty} e^{i\nu t + \mathcal{M} t} \mathbf{C}(0) dt = (i\nu + \mathcal{M})^{-1} \mathbf{C}(0) = \sum_i \frac{\alpha_i}{\mu_i + i\nu} \langle r_i \rangle, \tag{2.27}
\]

where \(\mu_i\) is the eigenvalue of \(\mathcal{M}\) that corresponds to the right \(\langle r_i \rangle\) and left \(\langle l_i \rangle\) eigenvectors. The coefficient \(\alpha_i\) is then given by \(\alpha_i = \langle l_i | \mathbf{C}(0) \rangle / \langle l_i | r_i \rangle\).
3. Experimental methods

This Chapter gives an overview of the sample fabrication and experimental techniques used in Publications I–IV. In Section 3.1, the nanofabrication and sample preparation procedures are briefly described. Section 3.2 presents the experimental setups used for angle- and spatially resolved photoluminescence measurements (3.2.1), transmission and reflection measurements (3.2.3), and pump-probe spectroscopy (3.2.4). Section 3.2.5 describes the Michelson interferometer setup built for the experiments in Publication III, and explains the method to extract first-order correlation function from the measurement data.

3.1 Sample fabrication and preparation

Nanoparticle arrays are fabricated using standard EBL and lift-off methods [204]. The process consists of four steps: 1) borosilicate glass substrates are spin-coated with a poly(methyl methacrylate) (PMMA) resist layer which is solidified on a hot plate, 2) the PMMA layer is exposed to an electron beam creating an inverse pattern of the desired array configuration, and developed in a solution of 1:3 (methyl isobutyl ketone) : (isopropanol), 3) an adhesion layer (2 nm of titanium) and a layer (50 nm) of gold is evaporated on top of the patterned PMMA, followed by 4) lift-off in acetone. Figure 3.1 shows zoomed-in scanning electron microscope (SEM) images of typical rod and cylinder nanoparticle arrays. For the experiments presented in this dissertation, gold was chosen as the nanoparticle material because it is more resistant to oxidation than, for example, silver which we have also used before [231]. Also, gold has relatively low losses (almost as low as silver) in the near-infrared wavelengths (750–950 nm) where the experiments were conducted [249]. The near-infrared regime is favorable because the plasmonic modes have less losses (longer lifetimes) at longer wavelengths.

After the fabrication, the nanoparticle arrays are covered with a solution of fluorescent dye. The dye solution is prepared by dissolving molecules
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into a mixture of 1:2 dimethyl sulfoxide (DMSO) : benzyl alcohol (BA). The refractive indices of DMSO and BA are 1.479 and 1.540, respectively, and the 1:2 mixture has a refractive index of 1.52, compatible with glass. We chose IR-792 perchlorate C_{42}H_{49}ClN_{2}O_{4}S as the dye because 1) we wanted to work in the near-infrared regime: IR-792 has absorption maximum at around 800 nm and emission maximum at around 855 nm; 2) after trying out several dyes, IR-792 was found out to dissolve well up to high concentrations; 3) IR-792 is resistant to photobleaching as compared with many other infrared laser dyes that were tested in our group (e.g. IR-783, IR-806 [354]). As a downside, infrared dyes generally have rather low quantum yields. At high concentrations, the photoluminescence efficiency of dyes is reduced due to aggregation and fluorescence quenching of the molecules [355]. For example, at 100 mM the quantum yield of IR-792 is reduced to about 1.4% of the yield at 1 mM [354]. The choice of the dye has not been optimized; practically we chose the first infrared dye that performed well in the lasing and BEC experiments.

In Publication I we applied a drop of a 50 mM dye solution on the nanoparticle arrays and added another glass slide on top to seal it. This created a thin (approximately 10–15 μm) layer of dye between the glasses. In Publications II–IV the glass with nanoparticle arrays was attached to another glass slide with thick (0.8 or 1 mm) silicon seals, see Figure 3.1 for schematics. No adhesives are needed to attach the silicon seals to glass, but the assembly was secured by paper clamps placed at the ends of the glass slides. Then the chamber formed between the two glasses and the middle seal was filled with an 80 mM dye solution. When injecting the dye through the silicon seal (with a 0.5 mm needle), it is important to use an additional needle to vent the chamber during filling. A sample prepared in this way can be used for several months without having to replace the dye. We found that the large molecule reservoir helps the samples to sustain measurements at high pump powers for a longer time, likely because the dye can replenish between consecutive measurements through Brownian diffusion. Note that the active region, in which the dye molecules may interact with the SLR modes, lies only within a few hundred nanometers from the arrays [231, 308, 356, 357].

3.2 Measurement techniques

Optical characterization of the plasmonic lattices presented in this dissertation include transmission and reflection measurements, angle- and spatially resolved luminescence measurements, pump-probe spectroscopy, and spatial and temporal coherence measurements. Photoluminescence of the sample is collected by a 10x Nikon objective lens with 0.3 numerical aperture (NA). In transmission, reflection, and angle- and spatially
resolved measurements we introduce the sample luminescence to a spectrometer with a charge-coupled device (CCD) camera. In Publications I–III we used Princeton Instruments Acton SP2500i spectrometer with PIXIS 400F CCD camera. In Publication IV the spectrometer was Princeton Instruments IsoPlane SCT-320 and the CCD camera PIXIS 2048BRX. Additionally, two CMOS cameras (Point Grey Grasshopper 3) are used to record \( k \)-space and real space images. All moving components of the setup, such as shutters, are controlled by a dedicated LabVIEW program. The program controls the exposure and data acquisition times of the spectrometer CCD and the CMOS cameras such that it is possible to conduct various types of measurements simultaneously.

In the lasing and condensation experiments, the dye is optically excited by femtosecond laser pulses generated by Coherent Astrella ultrafast Ti:Sapphire amplifier. The laser pulses have 800 nm center wavelength, 30 nm bandwidth, 1 kHz repetition rate, and less than 35 fs duration at the output of the amplifier. In Publications II–IV we used the pulse directly from Astrella, while in Publication I we guided the pump beam through an optical parametric amplifier (OPA) (TOPAS Prime by Light Conversion) to shift the center wavelength to 750 nm. Pump pulse duration is measured using a commercial autocorrelator (APE pulseCheck 50). The initially 35 fs pulse becomes slightly elongated due to travelling through all the optics; the shortest available pulse duration at the sample location is 50 fs. In Publication II we altered the pulse duration by tuning the stretcher-compressor of the amplifier.
The pump beam is cropped spatially by an iris and directed onto the sample either from the side of the objective at about 45° angle (Publication I) or through the objective at normal incidence (Publications II–IV). Imaging the iris that crops the pump beam onto the sample yields a flat-top spatial intensity profile of the pump spot. The energy of the pulses, i.e. the pump fluence, is controlled by a continuously variable neutral-density filter wheel.

The experimental setup and its variations used in Publication I are described in Figure 3.2, and the setup used in Publication II is presented in Figure 3.3. The setups are almost identical except for the aforementioned change in the pump path. The setup used in Publication III (Figure 3.4) is the same as in Publication II, except for the added Michelson interferometer with a delay line. The setup used in Publication IV was built based on the setup in Publication II such that we had two setups with otherwise identical optical components but with new spectrometer and CCD camera. In Publication IV the polarization state of the pulses was controlled using quarter-wave and half-wave plates on the pump path and there was an optional polarizer in the detection side. This setup is not repeated here but can be found from Supplementary Information of Publication IV.

3.2.1 Angle-resolved luminescence measurement

Back focal plane (Fourier plane) of the objective contains angular information of the collected light. Taking an image of the back focal plane with a CMOS camera provides the angular distribution of luminescence intensity in two dimensions i.e. the 2D k-space image. For angle-resolved measurement, the image of the back focal plane is focused onto the entrance slit of the spectrometer. Each vertical location on the slit corresponds to an in-plane momentum \( k_y = 2\pi/\lambda_0 \sin \theta_y \) on the sample, where \( \lambda_0 \) is the free-space wavelength. The wavelengths of the incoming light are resolved by the spectrometer and projected to the pixel columns of the CCD array. The pixel rows (index \( p \)) of the CCD are mapped to the angle \( \theta_y \) at the entrance slit according to

\[
\theta_y(p) = \arctan \left( \frac{p - p_0}{p_r} \tan(\theta_{\text{max}}) \right) - \theta_{y,\text{tilt}},
\]

where \( p_0 \) and \( p_r \) are the center and the radius of the back focal plane image at the CCD, respectively. \( \theta_{\text{max}} = \arcsin(\text{NA}/n) \) is the maximum collection angle, which for our objective with NA 0.3 (air \( n = 1 \)) gives 17.5°. The sample tilt in vertical direction is given by

\[
\theta_{y,\text{tilt}} = \arctan \left( \frac{p'_0 - p_0}{p_r} \tan(\theta_{\text{max}}) \right),
\]

where \( p'_0 \) is the pixel row of normal incidence of the sample luminescence (\( \Gamma \)-point of the dispersion at \( \mathbf{k} = 0 \)). The entrance slit width determines
Figure 3.2. Schematic of the experimental setup used in Publication I. The excitation beam from the output of the OPA (750 nm central wavelength) is cropped by a pinhole (P) and directed to the sample using a lens (L) and a mirror (M) at an angle of about 45°. (a) For angle-resolved measurements, the back focal plane (BFP) of the objective (Obj.) is imaged to the entrance slit of the spectrometer. Transmission measurement is done by using a halogen white light (WL) source. An adjustable iris is used to spatially crop the sample image. For the double slit experiment, the iris is replaced with a double slit. A beam splitter (BS) is used to guide the sample luminescence to a CMOS camera for a real space image taken simultaneously with the spectrometer measurement. (b) For spatially resolved luminescence measurements, an additional lens is used to focus the real space image of the sample onto the entrance slit of the spectrometer. (c) Michelson interferometer with an L-shaped mirror (R) that flips the image along its horizontal axis. The inverted image is overlapped with the non-inverted one at a CMOS camera. (d) Pump-probe experiment. The detection side is the same as in (a), but the excitation side is modified to accommodate a delay line. The probe pulse is temporally delayed with respect to the pump pulse, and their spatial location can be controlled independently. Figure reproduced with permission from Publication I (© 2018 Springer Nature).
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Figure 3.3. Experimental setup used in Publication II. The excitation pulse is retrieved directly from the Astrella output (800 nm central wavelength) and spectrally limited by a band-pass (BP) filter centered at 785 nm (bandwidth 61 nm). A polarizer is used to maintain linear polarization of the excitation. The pump is guided to the sample through the objective at normal incidence. Pump fluence is controlled by a continuously variable neutral-density (ND) wheel. In the detection path there is a long-pass (LP) filter with a cutoff at 834 nm to block the pump laser. A lens is denoted by L, a mirror by M, and a beam splitter by BS with a marked fraction of reflectivity vs. transmission. The setup allows simultaneous recording of real space image, 2D $k$-space image, and angle-resolved luminescence spectrum. For spatially resolved measurement, an additional lens was placed before the $k$-space lens to focus the real space image onto the entrance slit of the spectrometer. Transmission and reflection measurements are possible with the two optional light sources. Figure reprinted with permission from Publication II (© CC BY 4.0).

the range of angles in $k_x$ that are collected; a narrower slit gives better resolution, but reduces the total intensity of collected light. For example, a slit width 500 μm corresponds to ± 0.16 μm⁻¹ or ±1.3° at 880 nm (1.41 eV).

3.2.2 Spatially resolved luminescence measurement

Spatial luminescence intensity distribution is provided by a real space image of the sample, which we record with a second CMOS camera. In spatially resolved measurements, the real space image is focused onto the spectrometer slit, and each pixel row of the CCD corresponds directly to a $y$ position on the sample. The wavelengths are resolved and projected to the pixel columns of the CCD. The magnification of the real space image is ×4 at the entrance slit, and the slit width determines how wide spatial region of the sample in $x$ is imaged: for example, a slit width 300 μm corresponds to a 75 μm wide slice of the sample. We use also an adjustable iris to spatially crop the sample image. In a plasmonic lattice, resolving the luminescence spectrum spatially provides an indirect access to the dynamics of the system, because the distance that light travels along the array can be converted into time via the group velocity of SLR modes.
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3.2.3 Transmission and reflection measurements

Transmission and reflection measurements are standard tools for determining the dispersion relation of a periodic structure. The sample is illuminated by a white light source, and the spectrometer is used to capture angle-resolved luminescence. As the light source, we use a halogen lamp that covers wavelengths from visible to near-infrared. Due to the periodicity of the array, certain wavelength–$k$-vector pairs are diffracted to the plane of the array. Therefore, the resonant modes of the lattice will show up as dips (peaks) in the transmission (reflection). Transmission measurement is possible for a bare nanoparticle array (Publications I,II,IV) and for an array overlaid with a thin layer of dye solution (Publication I). A thick layer of dye prevents light from passing through the sample, in which case reflection of the sample is measured instead (Publication II).

3.2.4 Pump-probe experiment

Pump-probe technique utilizes the non-linearity of luminescence intensity emerging at lasing or condensation threshold. The basic idea of the measurement is that in the non-linear regime even a small change in the energy brought to the system yields a massively amplified response. In the pump-probe experiment, the pump pulse is divided to two and the energy of one of the pulses, called the 'probe', is strongly attenuated. The ratio of energies is typically of the order $P_{\text{probe}} = 0.05P_{\text{pump}}$. Time delay between the pump and the probe pulse is controlled by a motorized linear stage. When the time delay is varied, a drop or a sharp increase of the luminescence intensity is observed depending on whether the pulses arrive to the sample simultaneously. This allows for probing the temporal dynamics of the system. Optionally, the pulses can be spatially separated to different locations on the sample, as was done in Publication I.

3.2.5 Michelson interferometer

Lasing and Bose–Einstein condensation are associated with increased spatial and temporal coherence of the sample luminescence. In Publication I and Publication II, spatial coherence was measured with a Michelson interferometer equipped with an L-shaped mirror that inverts the real space image around one axis. The fringe contrast was analyzed from single interferograms recorded at around zero time delay. To measure the spatial coherence more rigorously, a new Michelson interferometer setup was built for the experiments in Publication III. The setup includes a cube retroreflector which inverts the image along both the horizontal and vertical axes, see Figure 3.4 for a schematic of the setup. On one arm, a flat mirror stands on a motorized translation stage (Thorlabs TZ200),
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Figure 3.4. Experimental setup used in Publication III. The setup is overall the same as in Publication II (Figure 3.3) except for the added Michelson interferometer with a delay line. An additional beam splitter (BS2) is placed to the left side of the pump beam splitter (BS1) to deviate the sample luminescence from the main beam line towards the Michelson interferometer. In the interferometer, the luminescence is divided to the two arms of the interferometer by another 50:50 beam splitter (B3). On one arm, a delay mirror (M2) stands on a motorized linear stage controlled with a LabVIEW program. On the other arm, a cube retroreflector (R) is on a fixed mount. The retroreflector inverts a real space image along both the horizontal and vertical axes, and returns the inverted image back to the beam splitter (BS3). The inverted and the non-inverted image are focused to a CMOS camera by a $f = 450$ mm bi-convex lens (L4), which, together with the 10x objective, gives a total magnification of 22.5x. Long pass and band-pass filters may be placed at the first entrance of the beam splitter (BS3) as needed. In all measurements, a long pass filter (834 nm or 850 nm) is used to block the pump laser (not shown in the schematic). The iris placed at the real space image plane (RSP) after the tube lens (L1) is used to crop the sample luminescence spatially. Lens L2 focuses the back focal plane of the objective to the spectrometer entrance slit for angle-resolved spectra. Lens L3 focuses the RSP to the second CMOS camera for a real space image.

while on the other arm, the retroreflector is placed on a fixed mount.

In the interferometer, a real space image of the sample is divided to two: one image is inverted in the retroreflector and combined with the non-inverted image at a CMOS camera. Longitudinal position of the delay stage defines the time-delay $\tau$ between the image planes. If the sample emits coherent light, the two images produce an interference pattern at the combined image plane. The interferometer can be operated simultaneously with the spectroscope and the real space camera, which allows for monitoring the stability of the sample throughout the measurement and recording angle-resolved spectra and real space intensity distributions to support the analysis. The disadvantage is that the intensity is reduced to half by an extra beam splitter.

Contrast of the interference fringes is directly proportional to the first-order correlation function $g^{(1)}(r, r'; \tau)$ between two centrosymmetric points separated by $|r - r'|$. The fringe contrast is extracted by recording a series interferograms at fixed steps closely around the zero time delay ($\tau = 0$). The delay is swept over three cycles of light frequency oscillation, in total $\sim 9$ fs, divided to 21 discrete steps. Each interferogram is normalized with
corresponding non-interfered images ($I_1$ and $I_2$) obtained by blocking one arm of the interferometer at time. Background counts are subtracted from each recorded image. The intensity of a normalized interferogram is given by $I = (I_{\text{raw}} - I_1 - I_2)/(2\sqrt{I_1I_2})$ [358]. The amplitude $C$ and phase $\phi$ of the interference fringes are obtained by fitting a sinusoidal function, $C\sin\left(\frac{2\pi}{\tau_0} r + \phi\right) + C_0$, through each pixel of the stack of normalized interferograms, see Figure 3.5. The fringe contrast $C$ is directly proportional to the absolute value of the first-order correlation function $|g^{(1)}(r, -r; \tau)|$ as [359]

$$C(r, \tau) = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}} = \frac{2\sqrt{I(r)I(-r)}}{I(r) + I(-r)} |g^{(1)}(r, -r; \tau)|. \quad (3.3)$$

Under optimal conditions and symmetric condensate with $I(r) = I(-r)$, the fringe contrast $C$ is equal to $|g^{(1)}(r, -r; \tau)|$. This is rarely the case in experiments, hence the maximum attainable $|g^{(1)}| < 1$. This method of extracting the fringe contrast is robust against artifacts produced by spatial intensity variations, such as stripes that may occur due to lasing of individual columns or domains of nanoparticles in arrays, as seen e.g. in Refs. [277, 305].

Temporal coherence is obtained by scanning the longitudinal position of the delay mirror. The fringe contrast reaches its maximum when the time delay between the arms is $\tau = 0$. When moving the delay stage sufficiently far from the $\tau = 0$ position to either positive or negative delay, the interference fringes disappear. Therefore, recording interferograms over a long-range sweep of delays and extracting the fringe contrast provides the functional form of $|g^{(1)}(\tau)|$. In the temporal coherence measurements of Publication III, the fringe contrast was extracted by directly fitting the spatial fringes in the normalized interferograms to a sinusoidal function. This method is naturally much faster than the one described above for spatial correlations, but not as robust against spatial intensity variations. Temporal coherence is analyzed over small spatial regions on the sample, as described further in Section 4.3.2.
This Chapter summarizes the results obtained in Publications I–V, each in a dedicated Section. Section 4.1 starts by describing the experiments and simulations that led to the observation of the first plasmonic BEC (Publication I). Section 4.2 introduces the strongly coupled plasmonic BEC (Publication II), the properties of which are studied further in the two subsequent Sections. Section 4.3 characterizes the first-order spatial and temporal correlations of the strongly coupled plasmonic BEC (Publication III), and Section 4.4 presents polarization textures invoked by a non-trivial phase of the condensate (Publication IV). Finally, Section 4.5 presents results obtained by the multimode model of strongly coupled organic systems introduced in Publication V.

4.1 Plasmonic Bose–Einstein condensate

Excitations of SLRs in a plasmonic lattice are mostly photonic, however due to the strong coupling between light and the collective electron oscillations in metal nanoparticles, they possess a finite effective mass of the order of $10^{-7}$–$10^{-5}$ electron masses [10, 277]. The small effective mass of these bosonic quasiparticles hinted to the possibility of achieving a plasmonic BEC at elevated temperature [346, 341, 286]. Preliminary simulations with the non-equilibrium model of photon condensation (presented in Section 2.2.1) indicated that with typical parameters of a plasmonic lattice, thermalization and BEC could occur in a picosecond timescale. The simulations suggested that in order to observe the BEC, one should measure the SLR populations after a certain time has passed from the onset of the process, that is, after the system has thermalized. Any attempts to measure the population distributions by time-integrated photoluminescence spectroscopy would yield a mixed spectrum of both the incompletely thermalized population and the BEC. Moreover, due to the high losses of the plasmonic modes, the total intensity at the times when BE distribution occurs could be orders of magnitude lower than in the beginning of
the process. Likewise, other signatures of BEC, such as the increase of spatial coherence, might be obscured by the presence of the incompletely thermalized population at early times.

Experimentally the main question was: how could one access the later-time dynamics when dealing with such short timescales? There were no technologies readily available for time-resolved ultrafast spectroscopy, which studying population distributions would require. Key to the observation of the first plasmonic BEC was to start resolving the luminescence spectrum as a function of distance travelled along the array [10]. Converting the distance to time by the group velocity of SLR modes provided indirect access to the underlying dynamics.

In Publication I, we studied periodic arrays of gold nanoparticles overlaid with a drop of IR-792 dye solution. The arrays were $100 \times 300 \mu m^2$ in $x \times y$ dimensions, and the periodicity was varied from 580 nm to 610 nm. The nanoparticles were rod-shaped with height of 50 nm, a short axis of 100 nm, and a long axis of 65% of the periodicity. An SEM image of a typical rod sample is shown as the inset of Figure 4.1(a), and a dispersion relation in Figure 4.1(c). The curvature of the band edge corresponds to an effective mass of approximately $10^{-7}$ electron masses. The linewidth of the SLR mode around the band edge is 5.5 meV. With 50 mM dye concentration, coupling between the SLR modes and the molecules remains weak, thus we may discuss SLR excitations rather than plasmon-exciton-polaritons. The absorption and emission profiles of IR-792 are shown in Figure 4.1(e). An important spectral location (marked as a solid line) is the energy $\xi_{\text{abs}}$ at which the absorption rate is effectively zero, that is, lower than the losses of the system.

A schematic of the experiment is shown in Figure 4.1(a-b). We pumped the molecules at one edge of the array by 100 fs laser pulses (1 kHz repetition rate, central wavelength 750 nm). The molecules emit light to the array, exciting SLR modes at high energy and momentum $k$. The SLR excitations propagate along the array $y$-axis due to the finite momentum, and the photon part of the SLR excitations leaks out to the far field, conveying information about the mode populations.

### 4.1.1 Three regimes as a function of periodicity

We resolved the luminescence spectrum spatially along the $y$-axis of the array: each row in the graphs in Figure 4.2(a-c) corresponds to a distance $y$ from the top edge of the array and shows the energy spectrum. Periodicity of the array determines the location of the band edge in energy. We observed three regimes with distinct characteristics, depending on whether the band edge was set to energy above, below, or matching $\xi_{\text{abs}}$.

**Thermalization process.** When the band edge located at energy higher than $\xi_{\text{abs}}$, we observed a gradual shift of luminescence from higher energy
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1.32 1.34 1.36 1.38 1.4 1.42

-0.5 0 0.5

k (1/μm)

Energy (eV)

0 0.2 0.4 0.6 0.8 1

Normalized spectrum

Emission Absorption

ȟ

Pump

Detection (y, λ)

Propagation along y-axis

IR-792

Figure 4.1. Experimental scheme for observing BEC in a plasmonic lattice. (a) Artistic view of a gold nanoparticle array and dye molecules pumped at one edge of the array. An SEM image of a part of the array is shown in the inset (the scale bar is 300 nm). (b) Experimental scheme. Only a very small proportion of the pump spot was spatially overlapped with the array, as illustrated in the left side of Figure 4.2. (c) Dispersion relation of the nanoparticle array obtained by a white-light transmission measurement. Dashed blue line marks the maxima of the dispersion, and the white dashed line shows a parabolic fit at the band edge for extracting the effective mass. (d) Finite-difference time-domain simulation of one unit cell of a nanoparticle array. The color denotes the magnitude of in-plane electric field relative to an incident field at the peak of the pump pulse, |E|/|E0|. (e) Emission (blue) and absorption (red) profiles of the IR-792 molecule. Location of the pump (dashed line) and the energy ξ_abs (solid line) where absorption is effectively zero are shown. The emission maximum is at 1.46 eV. Figure reproduced with permission from Publication I (© 2018 Springer Nature).

towards the lower energies, as shown in Figure 4.2(a). The red shift of the luminescence was attributed to a thermalization process which, at weak light-matter coupling, occurs through recurrent absorption and emission of photons by the dye [25, 136]. The SLR excitations propagate along the array due to their finite momentum k, and during propagation the dye molecules absorb photons from the lattice modes and emit photons back to the modes. Each time a molecule is excited it loses some energy through vibrational and rotational relaxation before emitting the photon. Therefore, the photons emitted back to the SLR modes have been reduced in energy, which is seen as a red shift of the luminescence as a function of distance from the pump spot along the array y-axis. The red shift proceeds towards lower energies until reaching ξ_abs, where the thermalization naturally stops as the absorption rate becomes too low.

In photon BECs, thermalization rate has shown to be linearly proportional to the density of the dye molecules [93]. Group velocity of the SLR excitations is constant in the linear part of the dispersion, and therefore
the distance along the array can be converted to time. We extracted the thermalization rate for different dye concentrations and confirmed that the linear dependence also holds in our system, as shown in Figure 4.2(e).

**Lasing.** When the band edge was set lower in energy than \( \xi_{\text{abs}} \), we observed lasing at the band edge. The band edge provides feedback for lasing action, and since the absorption rate is vanishing at the energies around the band edge, the net gain is very high. As evident in Figure 4.2(b), lasing takes place at the top edge and extends throughout the array. We have studied lasing in nanoparticle arrays extensively in the recent years [231, 232, 300, 298, 308], and the phenomenon seen here fulfilled the characteristics of plasmonic lasing: non-linear increase of emission intensity as a function of pump fluence, extended spatial coherence, and linewidth narrowing.

**Bose–Einstein condensation.** Choosing the periodicity such that the band edge matches with \( \xi_{\text{abs}} \) led to thermalization and formation of a BEC at the band edge. As shown in Figure 4.2(c), red shift starts at the
top edge of the array at high energy and continues until the band-edge energy is reached. At this point, the thermalization is complete and excess photons accumulate to the band edge. As we will see shortly, the spectrum exhibits a macroscopic population at the band edge, followed by a thermal tail at higher energies according to the BE distribution. In contrast, the lasing described above had a Lorentzian spectral shape, and fitting to a BE distribution yielded a poor fit with unrealistically low temperature (25 K), as shown by Figure 2 in the Supplementary Information of Publication I.

Besides the spectral line shapes, a striking difference between the lasing and BEC cases is evident by comparing the evolution of relative intensities at the band edge and at the higher energies, shown in Figure 4.2(f-g). In the lasing case, the band edge is highly populated across the entire array, while there is essentially no population at higher energies. In the BEC case, accumulation of population to the band edge occurs via the red shift. The SLR excitations that survive the propagation and form the condensate at a distance of around 150–200 μm have undergone sufficiently many cycles of absorption and emission to reach a thermal distribution. Driven-dissipative systems, in general, are far from equilibrium, but may reach a quasi-equilibrium state through a dynamical balance of pump and dissipation [135, 360]. In Figure 4.2(g), the relative intensity at the band edge wins out that of the thermal cloud at around 150–200 μm, after which the ratio of populations in the condensate peak and thermal cloud stabilizes. Figure 4.3 presents a smooth crossover from incomplete thermalization to condensation and lasing for increasing periodicity.

### 4.1.2 Characterization of the condensate

To complement the spatially resolved luminescence experiments, we characterized the BEC by angle-resolved measurements. The results shown in Figure 4.4(a-b) confirmed that the emission originates from the SLR mode dispersion. Note that a single dispersion arm is visible, supporting our interpretation that only one propagation direction is occupied, along +y direction. As shown in Figure 4.4(c), a macroscopic population accumulates at the band edge, followed by a thermal tail close to room temperature \( T = 269 \pm 67 \) K given by a non-linear least squares fit to the BE distribution. The 2D \( k \)-space measurements in Figure 4.4(e) showed that the condensate is confined in both \( k_x \) and \( k_y \), and the threshold curve in Figure 4.4(f) depicts the non-linear increase of luminescence intensity.

Bose–Einstein condensation is expected to lead to the build-up of spatial coherence. We measured spatial coherence using a Michelson interferometer with an L-shaped mirror that inverts an image around the horizontal \( x \) axis. Therefore, interference fringes that appear when combining an inverted image with a non-inverted one, indicate spatial coherence in \( y \)-direction of the array. The measurement in Figure 4.5 showed that the
spatial coherence at the part of the array where the BE distribution was observed has increased to approximately 90 μm at the onset of condensation. We did also a separate, complementary test of spatial coherence by a standard double slit measurement. Measuring the double-slit interference pattern with different slit separations confirmed that in the condensate the spatial coherence has indeed increased beyond 90 μm. The coherence length of bare SLR modes was estimated from the dispersion linewidth as $2\pi/\Delta k = 45 \mu m$ close to the band edge, hence the coherence length at the condensate phase has at least doubled.
Figure 4.4. Momentum and energy distributions of the plasmonic BEC. (a-b) Momentum space spectra measured at different spatial locations marked by the dashed blue and red circles on the array schematic. White dashed line in (b) marks the SLR dispersion relation. The measurements show that the luminescence originates from one dispersion arm and accumulates to the band edge. (c) Measured population distributions for increasing pump rates. The distributions are collected over the region where (b) was measured. The distributions are averaged over ten measurements with standard deviation given by the error bars. (d) Simulation of the population distributions for increasing pump rates. Green solid lines in (c-d) are fits to the BE distribution. (e) 2D $k$-space measurements as a function of pump fluence. (f) Non-linear increase of intensity at the band edge. Figure reproduced with permission from Publication I (© 2018 Springer Nature).

Mapping the distance travelled along the array to time via the group velocity of the SLR modes suggested that the thermalization and condensation occurs in a picosecond timescale. To get a direct confirmation of the timescale, we performed a pump-probe experiment where the pump and the probe were spatially separated: the probe was set to the position where we observed the BEC, while the pump was kept at the top edge of the array. Sweeping over the delay between the pump and the probe pulses revealed that the dynamical response, i.e. the decay of the curve in Figure 4.6, indeed took place in a picosecond timescale.

4.1.3 Simulation of condensation

The non-equilibrium model of photon condensation [135, 136] was applied to our plasmonic system to study the condensate formation. As described in detail in Section 2.2.1, the model considers a number of discrete bosonic modes weakly coupled to emitter with two electronic states, which are surrounded by a ladder of harmonic oscillator states which represent the rotational-vibrational states of organic molecules. The rotational-vibrational states act as a thermal reservoir, providing a route to thermalization via dissipation of energy. In our system, the dye molecules are in
Results

Figure 4.5. Spatial coherence measurements for the BEC. (a) Interferogram (left) and a crosscut (right) obtained by the Michelson interferometer measurement. The real space image is flipped around its horizontal axis and overlapped with the non-inverted image. \( y = 0 \) here corresponds to the center of the BEC. The BEC exhibits interference fringes over a distance of 90 \( \mu \text{m} \). (b) Fringe contrast shows the build-up of spatial coherence as a function of pump fluence for BEC. The error bars represent the standard deviation for two measurements. (c) Double slit experiment for BEC. The width of each slit was 30 \( \mu \text{m} \) and the inter-slit distance was 90 \( \mu \text{m} \). The resulting pattern is typical for double slit interference, indicating that the luminescence is coherent at least up to the inter-slit distance, thereby confirming the result of the Michelson interferometer measurement. Figure reproduced with permission from Publication I (© 2018 Springer Nature).

Figure 4.6. Luminescence intensity observed in the pump-probe experiment. A probe pulse with attenuated fluence was directed to the center of the array in the region where the BEC was observed. The luminescence intensity as a function of the pump-probe delay was measured from the same area. We set the pump fluence to 1.1 times the BEC threshold and the probe intensity to 20% of that of the pump. The pump is high enough to induce condensation at the center of the array, meaning that the system is in the regime of nonlinear response: the inset illustrates the pump and probe fluences as well as the response of the system. Spatial and temporal overlap of the probe pulse with the condensate is expected to lead to nonlinear increase of the observed luminescence intensity. Positive delays \( \tau > 0 \) refer to the pump arriving at the sample before the probe. At delays \( 2.5 \text{ps} < \tau < 3.0 \text{ps} \), a fast picosecond decay in the intensity occurs, confirming the ultrafast dynamics of the BEC. The data points represent an average of three measurements with the error bars standing for the standard deviation. Figure reproduced with permission from Publication I (© 2018 Springer Nature).
thermal equilibrium due to frequent collisions with the solvent molecules. The pump may drive the dye molecules out of equilibrium, but further away from the pump spot all the dye molecules are in the ground state and in thermal equilibrium. The weak coupling allowed for treating the interaction term as a perturbation to the system Hamiltonian, leading to the rate equations in Eq.(2.19) that describe the occupation of the SLR modes and the number of excited molecules.

The simulation included only one phenomenological parameter, the absolute value of coupling strength $|g|$ in Eq. (2.19). All other parameters were either directly obtained from the experiments (SLR dispersion relation, density of states $d(\omega)$, SLR mode lifetime $1/\kappa$, spontaneous emission lifetime $1/\Gamma_\downarrow$, pump pulse duration) or mapped to the experiments by comparing with several measurements (pump rate, number of molecules $N_m$). The measured absorption and emission spectra were placed in the variables $\Gamma^{\pm}$, which in the original theory are computational [135, 136].

The model was able to reproduce the process of the condensate formation in time domain, see Figure 4.2(d,h). In the linear part of the dispersion, the SLR group velocity is constant and thus the distance along the array $y$-axis can be converted to time. It should, however, be noted that approaching the band edge, the group velocity reduces towards zero. Therefore, the spatial measurement and the temporal simulation do not correspond one-to-one in all energies. The population distributions provided by the simulations for different pump rates matched qualitatively with the experimental ones in Figure 4.4(c,d). A fit to the BE distribution provided approximately the same temperature (265 K) as for the experimental data. The ratio between consecutive pump rates shown in Figure 4.4(d) was in agreement with the ratio of pump fluences in the experiment, see Figure 4.7. Likewise, the number of molecules in the simulation was calibrated with the experiment where thermalization rate was altered by changing the molecule concentration, shown in Figure 4.2(e).
Results

4.2 Plasmonic Bose–Einstein condensate at strong coupling regime

In the second realization of plasmonic BEC, presented in Publication II, two major changes were made to the sample and the experiment. First, dye concentration was increased from 50 to 80 mM, bringing the system into strong coupling regime [277]. Second, the sample was pumped at normal incidence over the whole array, and BEC was observed in the time-integrated luminescence collected over the array. The experimental scheme is illustrated in Figure 4.8(a).

We also changed the parameters of the lattice to the following. We used square arrays of gold nanocylinders with a diameter of 100 nm and height of 50 nm. The periodicity in the y-direction, $p_y$, was varied between 520 nm and 590 nm, and the lattice size between $40 \times 40$ and $200 \times 200 \mu m^2$. The optimal combination of lattice size and periodicity for observing the BEC was found to be $100 \times 100 \mu m^2$ and $p_y = 570$ nm. We set longer periodicity in the x-direction, $p_x = p_y + 50$ nm, to separate the dispersion cones of y and x-polarized light, simplifying data interpretation. In the following, we focus on the x-polarized dispersion cone. The SLR modes are denoted as TM or TE depending on the propagation direction with respect to the polarization, as explained in Section 2.1.3 and defined in Figure 4.8(b-e).

The arrays fabricated on a glass slide were attached to another glass with silicon seals. The chamber between the glasses was filled with IR-792 dye solution. Adding the dye solution led to shifting of the SLR dispersion bands downward in energy and to avoided crossing between the TE mode and the molecule absorption which is at 1.53 eV. These are typical signatures of strong light-matter coupling [15, 284]. A fit of the reflection maxima to the coupled modes model yielded Rabi splitting of 164 meV and exciton content of 23% at $k = 0$ (band edge). Hereafter, we refer to the strongly coupled plasmon-exciton-polariton hybrids as polaritons. The spatial coherence length of the polaritons was estimated from the dispersion linewidth close to the band edge as $2\pi/\Delta k = 24 \mu m$. Notice that close to $k = 0$ the upper dispersion branch of the TE mode is dark in the transmission and reflection measurements in Figure 4.8(c-d), but, as we will shortly see in Figure 4.11(f), the upper branch becomes visible when the samples are being pumped. Second notable thing about the dispersions is that, in contrast to Publication I, here the band gap is very narrow due to the small cylindrical nanoparticles. Nevertheless, as shown by the results below, it is still enough to gather macroscopic population at the band edge, and stop the population from relaxing into the lower dispersion branch.

The samples were excited by a pulsed laser (1 kHz repetition rate, 800 nm center wavelength) with a horizontally ($x$ direction of the array) polarized pump spot that covered the whole array. The pulse duration was varied between 50 fs and 750 fs by tuning the stretcher-compressor of the amplifier.
The pump was directed onto the sample at normal incidence through the microscope objective. We studied real space and $k$-space intensity distributions as a function of pump fluence. Importantly, we resolved the luminescence spectrum also spatially, as was done in Publication I, which revealed several interesting features about the formation of the BEC.

4.2.1 Three regimes as a function of pump fluence

In our previous works on lasing [231, 308, 298, 300, 232] and condensation [10] in plasmonic nanoparticle arrays at weak coupling, the luminescence intensity as a function of pump fluence has shown a single threshold. In Publication II, the measurements displayed a peculiar double threshold, show in Figure 4.9(a), when the 100x100 μm² lattice was pumped with short 50 fs pulses. The first threshold was identified as a polariton lasing threshold and the second one as a polariton BEC threshold. A linear
plateau between the two thresholds was attributed to a stimulated thermalization process that competes with the band-edge lasing triggered at the first threshold. We will next characterize the different regimes and discuss their differences.

**Lasing.** Increasing pump fluence beyond the first threshold, the sample showed lasing. The real space intensity distribution in Figure 4.9(b) is quite uniform over the array, with some fine structure, vertical lines, in the y-direction of the array. The spatially resolved luminescence spectrum in Figure 4.9(c) revealed that lasing originates from the band-edge energy and extends throughout the lattice. The k-space intensity distributions in Figure 4.11(a-c) showed that the lasing is confined in k_y and spread to large angles in k_x (TM mode).

**Thermalization process.** Above the first threshold, both the real space image, Figure 4.9(d), and the spatially resolved spectrum, Figure 4.9(e), appeared very different from those at the lasing regime. The luminescence exhibits red shift in the ±y directions, starting from the top and bottom edges of the array, towards the center. Close to the top and bottom edges of the array, the luminescence becomes visible at around 1.46 eV, and the red shift leads down to the band-edge energy (∼1.4 eV) in the center of the array. The line spectra in the inset of Figure 4.9(a) and more detailed in Figure 4.10(a-d) show that the population at the higher energies is increased with respect to the lasing peak: the thermalization process competes with the band-edge lasing. The thermalization was shown to be a stimulated process, discussed below in Section 4.2.2. The k-space measurements in Figure 4.11(d-f) showed that the thermalization occurs along the TE mode, which was consistent with our interpretation of polaritons thermalizing while propagating along ±y.

The wavy pattern in the real space image, Figure 4.9(d), and in the spatially resolved spectrum, Figure 4.9(e), arise from interference between counter-propagating modes. We found a direct connection between the real space wavelength of the interference, λ_RS(E), and the momentum k_y(E) at each energy E, given by Δk_y(E) = 2|k_y(E)| = 2π/λ_RS(E). More information can be found in Supplementary Note 1 of Publication II.

**Bose–Einstein condensation.** Upon further increase of the pump fluence, a second threshold appeared. In this pump regime, the population accumulates to the band edge forming a BEC. The line spectrum in the inset of Figure 4.9(a) shows a peak at the band edge and a thermal tail which follows the Maxwell–Boltzmann distribution close to room temperature (T =313±2 K). The thermal tail extends over several k_BT in energy and more than an order of magnitude in intensity. Based on the spectrometer counts we calculated the number of photons emitted by the condensate; with 10⁹ photons per pulse the condensate was 5 orders of magnitude more luminous than the first plasmonic BEC in Publication I, due to pumping and collecting the luminescence over the whole sample.
Results

Figure 4.9. Three regimes as a function of pump fluence in real space. (a) Total mode occupation per pulse as a function of pump fluence. Three regimes are identified: the first threshold corresponds to lasing and the second one to BEC; in between there is the regime of (incomplete) thermalization. The insets show the line spectra at the corresponding regimes, obtained by integrating over the y-axis of the array (between the white lines) in (c,e,g). Real space images of the sample luminescence in the (b) lasing, (d) thermalization, and (f) BEC regimes. (c,e,g) Spatially resolved spectra for the corresponding pump fluences. The real space images were collected for single pump pulses whereas the corresponding spectra were integrated over (c, e) 500 and (g) 70 pulses. Figure reprinted with permission from Publication II (© CC BY 4.0).

Figure 4.10. Pump fluence dependence of population distributions for 50 fs and 500 fs pulses. Top row shows the results for 50 fs excitation pulse duration and bottom row for 500 fs pulse. (a,e) Population distributions as a function of pump fluence. The colors in the plot correspond to the threshold curve shown in (b,f). (c,g) FWHMs and (d,h) the locations of the maxima of the spectra in (a,e). Figure reprinted with permission from Publication II (© CC BY 4.0).
Results

Note that at the band edge more than one states have become macroscopically occupied, which we attributed to the lifting of the degeneracy of ground state modes in a finite system. While in thermal equilibrium condensates a single lowest-energy state is macroscopically populated, in driven-dissipative systems condensation to multiple modes is possible [129, 130]. We also note that since the sample luminescence was time-integrated, we could not rule out the possibility that it is in fact a single-mode condensate that is temporally evolving between different states during the sub-picosecond pulse.

We observed a blue shift of the polariton energy dispersion of approximately 0.02 eV: the band edge shifted from 1.38 eV in the samples without pumping to 1.40 eV in the BEC phase. Based on the blue shift and the estimated polariton density, we obtained an interaction strength of \( \sim 0.2 \, \text{μeV} \mu\text{m}^2 \). The blue shift can be attributed to the decrease of the coupling strength due to saturation of the molecules [126, 109, 108]. In Publication V, we identified such a saturation effect as the source of effective interactions in strongly coupled organic systems (Section 4.5). Despite the decrease, the coupling strength in the BEC phase was still estimated to be 40% of the coupling without pumping, indicating that the samples remain at the strong coupling regime (hence, polariton BEC).

In addition to real space spectra and population distributions, the lasing and condensation regimes were shown to differ in \( k \)-space confinement and spatial coherence properties. While the lasing was found to be confined only in \( k_y \), the BEC showed confinement in both \( k_x \) and \( k_y \), as depicted by Figure 4.11(a,g). Correspondingly, the spatial coherence measurement in Figure 4.12 revealed that while lasing exhibits increased spatial coherence in \( y \), the condensate is 2D spatially coherent. The coherence in both the lasing and the condensation regime extended over the whole 100 \( \times \) 100\( \mu \text{m}^2 \) array, thus the coherence was increased to at least four times to that of the polaritons without pumping (24 \( \mu \text{m} \)). Due to the large coherence compared to the array size, we could not study the decay of the spatial correlations. In Publication III, the decay of spatial correlations was studied in detail in arrays that were extended in the \( x \) dimension to 500 \( \mu \text{m} \).

4.2.2 Stimulated thermalization process

The intermediate pump fluence regime between the lasing and condensation thresholds was attributed to a stimulated thermalization process. The real space image and the spatially resolved spectrum in Figure 4.9(d-e) showed low-intensity ("dark") regions at the edges of the array: the luminescence intensity and the red shift become visible at a distance of about 25 \( \mu \text{m} \) from the top and bottom edges of the array. The dark regions were connected to a pulse build-up time, which in gain-switched lasers is the time between the peaks of the population inversion and the output.
lasing pulse, as defined in the rate equation simulation in Figure 4.13(g). In our case, we see the pulse build-up as a spatial signature: the pump pulse excites the molecules, which emit to the polariton modes at high energy and high momentum $k$. During propagation the modes gain more population and the peak of the propagating "pulses" appear after a certain distance travelled along the array. This distance is visible in the real space measurements at the edges of the array as the dark zones, and they correspond to the temporal pulse build-up.

The effect is illustrated in Figure 4.13(h) where we have summed up output pulses (a Gaussian profile here approximates the shape of the lasing output pulse in Figure 4.13(g)) at each point of the array $y$-axis, mimicking the thermalizing polaritons that begin to propagate in $\pm y$. Summing up the pulse profiles results in an envelope (red dashed line) where the edges have about 50% less intensity than the central part of the array, because there is no propagation starting from the outside of the array. We confirmed our interpretation by measuring the width of the dark edge regions in several different lattice sizes. Figure 4.13(a,c,e) present the real space images at the intermediate pump fluence regime for three different lattice
Results

Figure 4.12. Spatial coherence as a function of pump fluence. Spatial coherence of the nanoparticle array was measured using Michelson interferometer with a mirror that inverts the image along one direction. The real space image is split into two, and the inverted image is overlapped with the non-inverted image at the camera. The contrast of the resulting interference fringes (measured at a single delay position $\tau = 0$) was obtained by Fourier analysis. The contrast is directly proportional to the first-order correlation function $g^{(1)}$. (a) Fringe contrast as a function of pump fluence. The blue (red) solid line shows the contrast for real space image inverted along $x$ ($y$) axis of the nanoparticle array, therefore representing the spatial coherence in $y$ ($x$) direction. The light blue and yellow solid lines present reference measurements obtained by applying the Fourier analysis to non-inverted images. (b-c) Interferograms obtained at two pump fluences, inverted around the horizontal dashed line. (d-e) Interferograms inverted around the vertical dashed line. Note that the vertical "stripes" visible in (b,d) are caused by lasing that occurs independently in domains of single or several columns of nanoparticles. These stripes are differentiated from the interference fringes by the Fourier analysis. Figure reprinted with permission from Publication II (© CC BY 4.0).

sizes. The larger arrays in Figure 4.13(c,e) show the dark zones at the top and bottom edges of the array. In Figure 4.13(a), the array size is so small that the pulses become visible at the opposite sides of the array. The width of the zone (the scale bar) seemed to be independent of the lattice size. The observations were confirmed by the real space spectra, shown in Figure 4.13(b,d,f), where for all array sizes the red shift appears at a certain distance from the edges of the array. The width of the dark zones was indeed found to be independent of the lattice size and inversely proportional to the pump fluence, as characteristic for temporal pulse buildup [12]. The measured distances for different lattice sizes as a function of pump fluence are presented in Figure 4.13(i), where the inset shows the corresponding rate equation simulation result.

Observing the BEC with thermal distribution in the time-integrated luminescence is likely enabled by the stimulated nature of the thermalization, which speeds up the condensate formation. In Publication I, we determined the thermalization rate for samples that were pumped from the edge, and so the propagation and thermalization took place in a region of the array where there are only ground state molecules available for absorption and re-emission. From Figure 4.2(e), we can interpolate that
Figure 4.13. Observation of pulse build-up. (a,c,e) Real space images and (b,d,f) real space spectra at thermalization pump fluence regime ($2.2 \text{ mJcm}^{-2}$) for lattice sizes (a-b) $40 \times 40 \mu\text{m}^2$, (c-d) $60 \times 60 \mu\text{m}^2$, (e-f) $150 \times 150 \mu\text{m}^2$. (g) 4-level rate equation simulation of stimulated emission. The pulse build-up time is the time between the peaks of the population inversion $N^*$ and the output pulse (vertical dashed lines). (h) Envelope (red dashed line) that results as a sum of spatial intensity profiles that are set to each point along the $y$-direction of the array. The yellow (blue) pulses correspond to left (right)-propagating pulses. The insets on the right side of the real space images (a,c,e) present the envelopes next to the arrays. (i) Distance from the edge of the array to a location where the red shift appears as a function of pump fluence for different lattice sizes. The scale bars in (a,c,e) are 25 μm. The legend lists the edge length of the square arrays in μm. The diagonal dashed line is the inverse of the pump fluence ($50/P$), and the horizontal dashed line marks the saturation value ($\approx 18 \mu\text{m}$) at higher pump fluences. The inset shows the simulated pulse build-up time (converted to distance by multiplying with the SLR mode group velocity) as a function of pump fluence. Figure reprinted with permission from Publication II (© CC BY 4.0).

the thermalization rate would be around 0.08 eV/ps for 80 mM concentration, whereas here the rate we observed is more than twice higher, approximately 0.20 eV/ps. Although the systems studied in Publication I and Publication II are not identical, this suggests that the larger number of photons and stimulated processes speed up the thermalization.

Due to the strong coupling, it is plausible that instead of absorption and re-emission of photons, thermalization involves a coherent energy exchange between the molecules and the SLR modes. The effect of coherent thermalization mechanism was studied by a simple quantum model including a few cavity modes strongly coupled to a two-level system which is coupled to a vibrational mode. The model is described by the Hamiltonian in Eq. (2.7) in the master equation Eq. (2.10) without the pump term. As
an initial condition for the simulation, the two-level system was set to be at the excited state. The results presented in Figure 4.14(a-f) demonstrate that while in a fully coherent system the population continues to oscillate between different states indefinitely, adding just the vibrational mode dissipation leads to thermalization into the lowest-energy cavity mode. Figure 4.14(g-i) show that even in a highly dissipative system the population can end up in a lower energy cavity mode before decaying. This model is undoubtedly too simple to capture the physics of our experiment, but it underpinned the role of vibrational dissipation as the driver of the thermalization also in a strongly coupled system. In Publication V, we took a step towards a more complete description by introducing a multimode model for strongly coupled light-matter systems with several vibrational modes.

![Figure 4.14](image.png)

**Figure 4.14.** Results of the quantum model. The model includes 6 photon modes coupled to a single two-level system with one vibrational state. The left column is without any losses, the middle column is with vibrational dissipation, and the right column is with all loss channels activated. Top and middle row presents the occupation of the photon modes as a function of time. Bottom row shows the occupation of the excited electronic state (blue line) and the vibrational mode (orange line). Figure reprinted with permission from Publication II (© CC BY 4.0).

### 4.2.3 Critical pulse duration for condensation

In the results discussed above, the samples were excited by 50 fs pulses. To probe the temporal dynamics of the system, we altered the excitation pulse duration. Remarkably, it turned out that the double threshold with distinct regimes of lasing, stimulated thermalization, and BEC, only appears with
short excitation pulses. For 500 fs excitation pulses, we observed only a single threshold and no signs of thermalization or condensation even for higher pump fluences, see Figure 4.10(e-f). As presented in Figure 4.15, the real space images and spectra remain almost unchanged throughout the studied pump fluences. The real space intensity distribution and spectra resemble the lasing regime for the case of 50 fs excitation pulse. $k$-space measurements (can be found in Figure 7 of the Supplementary Information of Publication II), further confirmed that the lasing is spread along the TM mode and there is no 2D confinement.

We probed the response of the system for pulse durations between 50 and 750 fs and found that the critical pulse duration for the occurrence of the BEC was around 250 fs. For 100 fs and 250 fs pulses we observed the double threshold and a thermal distribution above the second threshold, with fits of the tail to the MB distribution at $316 \pm 2 \text{ K}$ and $331 \pm 4 \text{ K}$ temperatures, respectively. For a 350 fs pulse we did not observe a complete thermal distribution. The results for different pulse durations are summarized in Figure 4.16.

To fully explain the observations would require a way of directly accessing the temporal evolution of the system. Based on our results, we could only hypothesize that if the excitation pulse is too long, the peak population inversion does not reach a high enough value for the thermalization process to win out the band-edge lasing. Interestingly, the critical pulse duration for observing thermalization and condensation matches with the time that it takes for the polaritons to propagate from the edge to the center of the $100 \times 100 \mu\text{m}^2$ array. Therefore, an alternative (or complementary) explanation to the observed dependency on pulse duration is that a longer pulse disturbs the thermalization process, as molecules are put to the excited state – not only in the beginning, but also – during the propagation.

Observing the BEC required that the thermalization time and the propagation time are matched so that polaritons have red shifted all the way to the band-edge energy during propagation from the edges to the center of the array. In the future, it would be interesting to study condensation in different-sized arrays: it should be possible to observe the BEC in variable array sizes if the dye concentration (affecting the thermalization time) is tuned accordingly. Note that the array periodicity is yet another degree of freedom as it determines the band-edge energy. Finally, it should be emphasized that modifying the experiment from pumping with an angle in Publication I to pumping at normal incidence in Publication II was crucial for observing the BEC in the time-integrated luminescence collected over the whole array. This is due to the timescales involved: when pumping from the side of the objective at an angle of about $45^\circ$, the pulse would hit the opposite edges of a $100 \times 100 \mu\text{m}^2$ array at a $230 \text{ fs}$ delay. This is significant compared to the timescales of the excitation, propagation, and thermalization.
Results

Figure 4.15. Real space images and spectra for 500 fs excitation pulse. (a) Total mode occupation per pulse as a function of pump fluence. The insets show that the energy spectra at different pump fluences above the threshold. (b,d,f) Real space images of the sample luminescence at pump fluences denoted above the images. (c,e,g) Spatially resolved spectra for the corresponding pump fluences. Figure reprinted with permission from Publication II (© CC BY 4.0).

Figure 4.16. Critical pulse duration for the observation of BEC. (a) Population distributions closest to the BE distribution for different pulse durations. (b) Threshold curves for different pulse durations. The double threshold occurs only for pulses < 350 fs. (c) Summary of the results for different pulse durations. While lasing is observed for all pulse durations, BEC is observed only for pulses < 350 fs. Figure reprinted with permission from Publication II (© CC BY 4.0).
4.3 Spatial and temporal coherence in plasmonic Bose–Einstein condensates

Although the occurrence of true long-range order in 2D condensates is prevented by thermal fluctuations [147, 148, 149], several scenarios to establish quasi-long-range order have been predicted. In equilibrium systems, quasi-long-range order could persist through the BKT transition [150, 151], which allows for algebraic (power-law) decay of both spatial and temporal correlations with equal exponents $< 0.25$ [361]. In driven-dissipative systems, the spatial correlation exponent might be twice the temporal exponent [155, 362]. In non-equilibrium systems, the occurrence of the BKT transition has been under debate [134, 363, 155]; quasi-long-range correlations could be revived by the dynamical phase ordering of KPZ [152]. The KPZ equation predicts decay of correlations as a stretched exponential with universal scaling exponents [134, 364, 142]. A crossover from the equilibrium-like BKT mechanism and the KPZ dynamics has been predicted based on the level of anisotropy of the system [141, 134].

One of the key factors constraining the experimental studies of these regimes and their crossover in non-equilibrium systems has been the small system size [142, 134]. In Publication III, we proposed strongly coupled plasmonic BECs as a platform for studying long-range correlations, with both system size and spatial correlation decay exceeding those of the previously reported photon and polariton condensates [309]. We presented the first characterization of spatial and temporal coherence in plasmonic BECs, revealing non-exponential decay of both.

We used similar samples as in Publication II, but to study spatial correlations at long distances we extended the array size in $x$ direction to 500 μm. The $y$ dimension of the array was kept at 100 μm, which is optimal for observing the BEC with dye concentration of 80 mM and periodicity $p_y$ of 570 nm [277]. The samples were excited by 50 fs pulses (1 kHz, 800 nm), which led to the characteristic double-threshold behaviour and formation of a BEC at the second threshold. The threshold curve and luminescence spectra upon increasing pump fluence are presented in Figure 4.25(a,c). First-order spatial and temporal correlations were measured by the Michelson interferometer setup described in Section 3.2.5 and illustrated in Figure 4.17. The interferometer includes a retroreflector which inverts the real space image centrosymmetrically, i.e., in both $x$ and $y$ directions of the array. Delay between the two arms of the interferometer is determined by the longitudinal position of a mirror on a motorized linear stage. The inverted image is overlapped with a non-inverted one, and the combined image (interferogram) shows interference fringes when the sample luminescence is coherent. The fringe contrast is directly proportional to the first-order correlation function $g^{(1)}$, which is obtained using the methods described in Section 3.2.5.
Figure 4.17. Schematic of the spatial and temporal coherence experiment. Michelson interferometer is used to study first-order spatial and temporal correlations of the plasmonic BEC. One arm of the interferometer is equipped with a retroreflector and the other arm with a delay stage mirror. The real space image of the sample luminescence is collected with a microscope objective (10x, NA 0.3) and divided to the two arms of the interferometer by a cube beam splitter. The image inverted by the retroreflector is re-combined with the original image and focused on to a camera by a lens (L) with 450 mm focal length.

4.3.1 Spatial coherence

Figure 4.18(a-f) show interferograms and $g^{(1)}$ maps for three different regimes: below, at, and above the BEC threshold. The line plots in Figure 4.18(g-i) show $g^{(1)}(x)$ averaged over the y-axis of the array, to give a qualitative picture of the correlation decay in the x direction. Below the BEC threshold, spatial coherence emerges at the center of the array and decays quickly towards the edges. At the threshold, the coherence covers the whole array but a decay is still clearly visible. Above the threshold, spatial coherence extends throughout the entire array and shows very little decay. It is non-trivial that the spatial coherence extends to such large distances in $x$, even though the thermalization during propagation occurs along $y$. Figure 4.19 and Figure 4.20 show the complete evolution of interferograms and $g^{(1)}$ maps as a function of pump. The maps of the phase $\phi$ of the interference fringes are shown in Figure 4.21. The phase reflects the long-range ordering of spatial correlations and can be used to confirm that the contrast of the interference fringes has been extracted reliably.

To characterize the decay of spatial correlations quantitatively, we looked at the $g^{(1)}$ as a function of radial separation of points around the autocorrelation point (center of the array). The measured $g^{(1)}(\Delta r)$ were fit to Gaussian, exponential, stretched exponential, and power-law functions:

\[ g^{(1)}(\Delta r) = ae^{-d(\Delta r/d)^\beta}, \quad \text{(4.1)} \]

\[ g^{(1)}(\Delta r) = a\Delta r^{-b}, \quad \text{(4.2)} \]

where $\beta = 2$ gives a Gaussian and $\beta = 1$ an exponential function, $b$ is the
power-law exponent, and $0 < a \leq 1$ is a free scaling parameter. We fixed the fit range such that we excluded the short-range correlations between the autocorrelation point (center of the array, $\Delta r = 0$) and the spatial coherence length of the polaritons in the uncondensed system (below the first threshold, 22 μm, see Figure 4.22).

Results of the fits are presented in Figure 4.23. Figure 4.23(a-c) show the $g^{(1)}(\Delta r)$ for the three pump fluences highlighted by filled circles in Figure 4.23(d), with the best-fitting function plotted as a solid black line. At pump fluences until the BEC threshold, the data was best fit to a Gaussian function. Above the threshold, the data was best described by a power-law function with a very small exponent of 0.07. The stretched exponential function fitted approximately equally well with an exponent of around 0.1. The correlation decay by Gaussian and exponential fits are shown in Figure 4.23(d) together with the threshold curve. The filled circles with color correspond to the data and fits shown in Figure 4.23(a-c). Notably, the correlation decay given by an exponential function extends beyond 3000 μm, which is more than two orders of magnitude larger than the spatial coherence length of the polaritons or six times the long axis of the system. The exponents given by stretched exponential and power-law fits are shown in Figure 4.23(e-f) and the root-mean-square error (RMSE) of the fits in Figure 4.23(g). Fits of the BEC case to all four functions can be found in the Supplemental Material of Publication III.

In Publication II, we showed that the thermalization is a stimulated process. Here, we studied the spatial coherence of the thermal cloud separately by using band-pass filters, and found out that some coherence is present in the emission, suggesting that the thermalization is a coherent process, see Figure 4.24. However, we noted that the obtained values of $g^{(1)}$ are small, and that the filters do let some emission through also at the band-edge energy (Figure 4.25), which may contribute to the coherence.
Results

Figure 4.19. Interferograms as a function of pump fluence. (a-i) Interferograms for increasing pump fluence.

Figure 4.20. Spatial correlation maps as a function of pump fluence. (a-i) Spatial correlation maps for increasing pump fluence.

Figure 4.21. Maps of the phase of the interference fringes as a function of pump fluence. (a-i) Phase $\phi$ obtained by the analysis of interference fringes for increasing pump fluence.
Figure 4.22. Spatial and temporal coherence of the polaritons below the first threshold. Measured (a) spatial and (b) temporal coherence at the lowest pump fluence that gave a detectable signal (~ 0.3 mJcm$^{-2}$). In (a) a fit to an exponential function gives a decay length of 22 μm. In (b) a fit to a Gaussian function yields half-width at 1/e decay of 104 fs. These values are used as the short-range correlation scales that are excluded from the fits in Figure 4.23 and Figure 4.26.

Figure 4.23. Spatial coherence decay. Measured values of $g^{(1)}(\Delta r)$ at three pump fluences corresponding to Figure 4.18: (a) below, (b) at, and (c) above the BEC threshold. The error bars show the standard deviation of three measurements. The best-fitting functions are presented by black solid lines. (d) Threshold curve (black circles) and correlation decay from Gaussian (blue circles) and exponential fits (red squares). The fluences that correspond to (a-c) are marked with filled symbols; the blue circles refer to the Gaussian fits and the green triangle to the power-law fit. For the exponential function the reported length is the decay constant $d$ in Eq. (4.1) and for the Gaussian function the half width (HW) at 1/e decay which is comparable to the exponential decay. Exponents given by fits to (e) stretched exponential and (f) power-law function. (g) RMSE of the fits.
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**Figure 4.24.** Interferograms and spatial correlation maps for the thermal cloud. Interferograms at three pump fluences (a) below (0.83 mJcm$^{-2}$), (b) at (1.66 mJcm$^{-2}$), and (c) above (3.31 mJcm$^{-2}$) the BEC threshold. (d-f) Maps of $g^{(1)}$ for the corresponding pump fluences. (g-i) Average $g^{(1)}(x)$ taken over the $y$-axis in (d-f). The error bars stand for the standard deviation of three measurements. Due to low number of counts, the thermal cloud data was analyzed without subtracting the background counts. Subtracting the background would lead to large negative values in the normalization procedure causing problems in the data analysis. Consequently, the absolute values of $g^{(1)}$ here are not correctly normalized between [0, 1]. To separate the thermal cloud from the sample luminescence, we used two band-pass filters centered at 850 nm (1.458 eV) with bandwidth of 40 nm, which efficiently block the photoluminescence from the lowest energy modes. The corresponding luminescence spectra and threshold curve are presented in Figure 4.25(b,d).

**Figure 4.25.** Luminescence spectra as a function of pump fluence. Luminescence spectrum for (a) the whole spectrum and (b) the thermal cloud as a function of pump fluence from low (blue) to high (red). The pump fluence values are color-coded respective to (c) and (d), which show the threshold curves for the whole spectrum and the thermal cloud, respectively. The dashed line in (a,b) shows a Maxwell-Boltzmann distribution at $T = 300$ K. Note that the thermal tail population increases linearly after the first threshold, but the growth saturates at the second threshold. This is a manifestation of the Bose–Einstein condensation: at the second threshold, the photons accumulate non-linearly to the lowest energy state.
4.3.2 Temporal coherence

Temporal coherence was measured with the same experimental setup as the spatial coherence. The analysis was done more straightforwardly by fitting the spatial interference fringes in normalized interferograms directly to a sinusoidal function. Figure 4.26(d) shows the measured temporal coherence for delays ranging from -1.25 ps to 1.25 ps at fixed steps, for pump fluences according to the color-coded threshold curve shown as the inset. We took the average of $g^{(1)}(\tau)$ between negative and positive time delays to obtain the $g^{(1)}(|\tau|)$ curves shown in Figure 4.26(a-c). We then fitted the data to Gaussian, exponential, stretched exponential, and power-law functions, and the best-fitting functions are shown in Figure 4.26(a-c). The fits were done using equal range for each pump fluence: we excluded the short-range correlations between the autocorrelation point $\tau = 0$ and the temporal coherence of the polaritons in the uncondensed system (below the first threshold, $\tau \approx 104$ fs, see Figure 4.22). Below the BEC threshold, temporal correlations decay exponentially. At the onset of condensation and above the threshold, the correlations show a clearly non-exponential decay, which is best described by power law with a large exponent of 0.7 – 0.8; the stretched exponential fits again approximately equally well with an exponent of ~0.2. The exponents obtained from stretched exponential and power-law fits above the BEC transition are shown in Figure 4.26(e-f). Figure 4.26(g) shows the RMSE of the fits.

When extracting the temporal coherence from very small spatial regions, we observed side peaks that arise from interference between the counter-propagating polaritons along ±y of the lattice, see Fig. 4.27(b) for an example. For the data used in the analysis of temporal correlation decay, we averaged the $g^{(1)}(\tau)$ obtained from all the locations along the y-axis so that the interference peaks did not compromise the non-linear least squares fitting. Details of the analysis can be found in the Supplemental Material of Publication III.

4.3.3 Comparison to previously reported studies

The measurements showed that the decay of both spatial and temporal correlations above the BEC threshold are non-exponential. The measured correlations fitted best to a power-law function with a small exponent for spatial coherence, $b_s \approx 0.07$ and a large exponent for temporal coherence, $b_t \approx 0.8$. This clearly deviates from the equilibrium BKT transition which entails power-law exponents < 0.25 for both spatial and temporal correlations. In non-equilibrium case the exponents might vary by a factor of two, but in the opposite direction i.e. spatial exponent would be larger than the temporal one [155, 362]. Other studies have suggested that larger exponents may be found in driven-dissipative systems [363, 155], and in
Figure 4.26. Temporal coherence decay. Measured values of $g^{(1)}(|\tau|)$ at three pump fluences corresponding to Figure 4.18: (a) below, (b) at, and (c) above the BEC threshold. The data shown in (a-c) is obtained by averaging the data points in negative and positive side of $\tau = 0$ in (d). The error bars show the standard deviation of the two values. The best-fitting functions are presented by black solid lines. (d) Measured $g^{(1)}(\tau)$ as a function of pump fluence. The pump fluences are color-coded according to the threshold curve shown as inset. The threshold curve is repeated from Figure 4.23(d) and Figure 4.18(a). Exponents given by the fits to (e) stretched exponential and (f) power-law function. (g) RMSE of the fits.

Figure 4.27. Spatial locations for temporal correlation analysis. (a) The white rectangles illustrate the spatial locations from which the temporal correlations were extracted around $x = 0$. The rectangles were 24×12 μm$^2$. (b) Fringe contrast extracted from one rectangle, exemplifying side peaks related to interference of counter-propagating polaritons.
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fact have been reported by earlier experiments in microcavity polariton condensates [156]. However, our findings did not directly align with any of the previously reported measurements or theoretical studies.

Notably, the correlations fitted roughly equally well to a stretched exponential function, with $\beta_s \approx 0.1$ and $\beta_t \approx 0.2$ above the BEC threshold. The stretched exponential relates to the universal scaling given by the non-linear KPZ equation. In non-equilibrium systems, it has been shown theoretically that a crossover from between KPZ dynamics to equilibrium-like BKT phase is possible and determined by the degree of anisotropy in the system [141, 134]. In isotropic systems, the KPZ mechanism leads to stretched exponential decay of long-range correlations with $\beta_s = 2\chi = 0.78$ for spatial and $\beta_t = 2\chi/(2 - \chi) = 0.48$ for temporal correlations [141]. Here $\chi$ is the roughness exponent that takes the universal value of 0.39 in two dimensions [365, 366, 367]. In strongly anisotropic systems, the KPZ equation leads to an algebraic decay of spatial correlations with a power-law exponent of $b_s = 2\chi$. Also the temporal correlations would decay as power law but with an exponent that is 1/2 of the spatial exponent, $b_t = \chi$. Our results indicated $\beta_s \approx 0.1$ and $\beta_t \approx 0.2$ above the BEC threshold, which did not match directly to the reported theoretical values.

Note that our system is not isotropic. The nanoparticles act as small dipoles (or multipoles), which leads to directional radiation. This together with the x-y periodicity of the array makes the SLR modes anisotropic in the plane, in contrast to modes in typical planar cavities. The x-y symmetry can be further broken by the pump polarization, as discussed above. Estimating the degree of anisotropy in comparison with the theoretical predictions is not straightforward since our system is not analogous to those considered in Refs. [141, 134], nevertheless the KPZ scaling is expected to be rather universal.

For observing KPZ scaling experimentally, it has been suggested to increase the system size or reduce the quality factor (i.e. decrease polariton lifetime) [368, 134, 142, 141]. Thus, the combination of large and scalable system and ultrafast dynamics makes plasmonic lattices amenable for studying the non-equilibrium BKT transition or KPZ dynamics. Beyond fundamental studies of correlations, the spatial correlation decay is on the millimeter-scale, which is 1–2 orders of magnitude larger than in other polariton or photon condensates before. The extent of spatial coherence could be utilized in the future, for instance, in on-chip applications for sensing or optical communications.
4.4 Polarization and phase textures in plasmonic Bose–Einstein condensates

Polarization textures of light have been studied in polariton condensates at cryogenic temperatures [117, 118, 119, 120, 121, 369], often involving complex structural engineering [370, 371, 372]. In Publication IV we studied polarization and phase of the strongly coupled plasmonic BECs, introducing a novel way of producing polarization textures [373]. The plasmonic BEC displayed a non-trivial spatial phase profile, which together with non-uniform intensity distribution lead to the formation of domain walls for the polarization state. We reconstructed the phase of the BEC by a phase retrieval algorithm, thus avoiding interferometric measurements, and explained the observed patterns by an intuitive theoretical model.

We studied similar $100 \times 100 \ \mu m^2$ arrays as in Publication II, but with symmetric periodicities. Whereas in Publication II and Publication III we used horizontally ($x$) polarized pump, in this work we pumped the system with circularly polarized light (50 fs, 1 kHz, 800 nm) which led to non-uniform condensate density in both $x$ and $y$ directions. To characterize the polarization states of the condensate, we filtered the polarization in the detection side. The schematic of the experiment is shown in Figure 4.28(a). Figure 4.28(b) shows the dispersion relation and an SEM image of the array, and Figure 4.28(c) the double-threshold curve. The results presented next were obtained at a pump fluence above the BEC threshold. Examples of real space intensity distributions are shown in Figure 4.28(d-e) without a polarization filter and with a horizontal polarizer, respectively.

4.4.1 Real space polarization patterns

Figure 4.29 presents real space images of the condensate filtered using six different polarizers: horizontal, vertical, right circular, left circular, diagonal, and antidiagonal polarization. The horizontal and vertical bright stripes across the center of the array in Figure 4.29(a-b) arise straightforwardly from the symmetry of the array. Also the diagonally and antidiagonally polarized patterns in Figure 4.29(e-f) can be made equal by a rotation of $90^\circ$. In contrast, the right and left circular polarizations in Figure 4.29(c-d) show complementary intensity patterns. Right circularly polarized light is emitted from the center (and the corners) of the array, whereas emission from the center of each edge is left circularly polarized. Remind that right and left circular polarizations are superpositions of horizontal ($x$) and vertical ($y$) polarizations: $|\uparrow\rangle + ie^{i\phi_{R/L}}|\downarrow\rangle/\sqrt{2}$, where the phase differs by $\pi$: $\phi_R = \pi$, $\phi_L = 0$. Thus, the real space images of circularly polarized emission, Figure 4.29(c-d), indicated that there could be a phase shift of $\pi$ between the edges and the center.

When pumping with a diagonally polarized beam, we observed different
Figure 4.28. Strongly coupled plasmonic BEC excited by a circularly polarized pump. (a) Schematic of the sample and the experiment. (b) Dispersion of the SLR modes. An SEM image is shown as the inset, where the scale bar is 1 μm. (c) Threshold curve shows the typical double-threshold behaviour, where the first threshold corresponds to lasing and the second one to BEC. Real space images of the condensate (d) without a polarization filter and (e) for horizontal polarization. Figure reprinted with permission from Publication IV (© 2021 American Chemical Society).

patterns (the results can be found in the Supplementary Information of Publication IV). This was attributed to the pump polarization dependence of the stimulated thermalization, and indicates that the patterns could be switched optically.

4.4.2 k-space measurements and phase retrieval

Figure 4.30 displays 2D $k$-space images corresponding to the real space intensity patterns in Figure 4.29. The $xy$-symmetry of the lattice is showcased by the horizontally and vertically polarized $k$-space patterns in Figure 4.30(a-b): they can be made the same by a rotation of 90°. The same accounts for the diagonally and antidiagonally polarized patterns in Figure 4.30(e-f), in accordance with the real space patterns. The circularly polarized cases in Figure 4.30(c-d), again, cannot be made equal by a rotation.

Phase of polariton condensates and lasers is typically obtained with interferometric techniques that require a reference beam with a known
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Figure 4.29. Real space polarization patterns. Sample luminescence filtered with polarizers to show (a) horizontal, (b) vertical, (c) right circular, (d) left circular, (e) diagonal, and (f) antidiagonal polarization components. (g-l) Electric field intensities provided by a phenomenological model for polarizations respectively to (a-f). Figure reprinted with permission from Publication IV (© 2021 American Chemical Society).

phase profile. We employed for the first time a phase retrieval method to obtain the phase of the condensate based on real space and $k$-space measurements. The phase retrieval algorithm by Gerchberg-Saxton [374] has been previously utilized e.g. in molecular orbital tomography [375, 376]. The algorithm iterates between object domain (real space image) and Fourier domain ($k$-space image) and reconstructs the real space phase distribution.

The results for the six different polarization components are shown in Figure 4.30(g-l). The reconstructed phase profiles are consistent with the expected phase variation: for example, Figure 4.29(c) showed that at the center of the array the condensate is right circularly polarized, $(|\uparrow\rangle - i|\rightarrow\rangle)/\sqrt{2}$. Now, as indicated by the phase map of horizontally polarized light in Fig. 4.30(g), moving from the center towards the edges in the $x$-direction adds a $\pi$ phase shift to the $|\rightarrow\rangle$ component, producing $(|\uparrow\rangle + i|\rightarrow\rangle)/\sqrt{2}$, i.e. left circular polarization. Remind that a phase shift of $\pi$ is given by a multiplication factor $e^{i\pi} = -1$ to the polarization vector component. In the vertical direction Fig. 4.30(h), a corresponding move in the $y$-direction adds a $\pi$ phase shift to the $|\uparrow\rangle$ component, leading again to left circular polarization $(-|\uparrow\rangle - i|\rightarrow\rangle)/\sqrt{2} = -(|\uparrow\rangle + i|\rightarrow\rangle)/\sqrt{2}$, but with an overall phase shift of $\pi$ with respect to the vertical edges. This is consistent with the phase map of the left circularly polarization in Fig. 4.30(j), where the adjacent edges have a phase difference of $\pi$. 

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4.4.3 Phenomenological model and Stokes vector fields

The observations were reproduced by a phenomenological model which takes into account both the amplitude and the phase variation. Schematic of the model is presented in Figure 4.31. The model is applied as a 2D grid of Jones vectors that represent the polarization of the emitted light as $(E_H, E_V) = (A_H e^{i\phi_H}, A_V e^{i\phi_V})$ for horizontally (H) and vertically (V) polarized components of the electric field $E$ with amplitude $A$ and phase $\phi$. We may assume that in nanoparticle arrays the dipole radiation becomes gradually weaker from the center of the array towards edges, as there is no source of scattering outside the array. In the simplest approximation, the decrease of amplitude is linear and of a factor of two, symmetrically in both $x$ and $y$ (black and blue lines in Figure 4.31(a)). The experimentally observed patterns implied a phase change of $\pi$ between the edges and the center of the array. Here we applied a linearly changing phase: $\phi_H$ is set to go from 0 to $\pi$ and back along $x$ (purple line in Figure 4.31(a)), and $\phi_V$ from $\pi/2$ to $3\pi/2$ and back when crossing the array in of $y$ (red line). The relative phase difference of $\pi/2$ between $\phi_H$ and $\phi_V$ was determined by the observation that right circular polarization appears at the centre of the array.

Stokes vectors are a compact representation of the polarization field, which can be considered as a pseudospin texture. The Stokes vector components are defined as

$$S_1 = \frac{I_H - I_V}{I_H + I_V}, \quad S_2 = \frac{I_R - I_L}{I_R + I_L}, \quad S_3 = \frac{I_D - I_A}{I_D + I_A},$$

(4.3)
where $I$ are the intensities of horizontal (H), vertical (V), right circular (R), left circular (L), diagonal (D), and antidiagonal (A) polarization. Stokes vector fields obtained from the measurements and from the theoretical model (with and without the phase shift) are presented in Figure 4.31(b-d). Clearly, the non-uniform phase is required to reproduce the experimentally observed texture. Finally, as shown in Figure 4.31(e-f), we investigated winding of the Stokes vectors across adjacent domains of the texture, such as along the red and blue arrows marked in Figure 4.31(d). A closed loop around the center of the sample yields a total winding number of zero.

This was the first demonstration of polarization textures in plasmonic lattice condensates. Here, the array structure was a simple symmetric square lattice. We have already studied lasing in more complex geometries such as the honeycomb lattice [232]. As an interesting future prospect, topologically non-trivial polarization textures could be achieved by engineering the lattice geometry and the pump polarization.

Figure 4.31. Model of Jones vector grid and comparison of Stokes vectors. (a) Illustration of the phenomenological model of Jones vectors on a spatial grid. The arrow length and direction denote the amplitude and phase, respectively. Red arrows stand for vertical and blue arrows for horizontal polarization. The amplitude and phase are taken to vary linearly such that the amplitude increases by a factor of 2, and phase undergoes a linear shift from 0 to $\pi$ from the array edge to the center. Stokes vectors calculated from (b) experimental real space data and from the model (c) with constant phase and (d) with phase varying according to the profiles in (a). The Stokes vectors represent the different polarization states: horizontal (H), vertical (V), right circular (R), left circular (L), diagonal (D), and antidiagonal (A). The color scale represents the length of the Stokes vector along the circular polarization axis, going from -1 (left circular) to +1 (right circular polarization). Winding of the Stokes vectors along the (e) red and (f) blue arrows in (d), viewed parallel to the array plane and towards negative values of $x$. Figure reprinted with permission from Publication IV (© 2021 American Chemical Society).
4.5 Multimode organic polariton lasing

The non-equilibrium model of photon condensation by Kirton and Keeling [135, 136] was successfully applied in Publication I to reproduce the experimental observation of the first plasmonic BEC. As discussed in Section 2.2.1, the model assumes weak coupling between the cavity modes and molecules, and the vibrational modes are treated as a dissipative reservoir. These assumptions preclude the application of the model to polariton systems which build upon strong light-matter coupling.

In Publication V, we introduced a model for strongly coupled organic systems hosting multiple photon modes [109]. We utilized Gell-Mann matrices as the basis for molecules that consist of two electronic states coupled to $N_v$ vibrational modes. The second-order cumulant equations in Eq. (2.24) provide the photon mode occupation and the population inversion of the molecules. We studied polariton lasing as a function of pump rate and detuning between the photon modes and the exciton energy. The results were computed under continuous pump, reaching a steady state. We also computed the photoluminescence spectrum to reveal the polariton mode energies and studied their pump dependency.

4.5.1 Lasing phase diagrams

The model was benchmarked with results by a previous model based on mean-field theory [138]. The phase diagrams of total photon mode occupation for weak and strong coupling are presented in Figure 4.32(a-b). While the mean-field theory provides only the boundary inside which there is macroscopic occupation of the lasing mode (white solid line), the second-order cumulants reveal the details of the mode occupation. The boundary for lasing given by the two models matched almost one-to-one, except for some minor deviation; for example, in the strong coupling case there is some difference at large negative detunings in the bottom left corner of Figure 4.32(b). In this parameter regime the multimode model permits lasing at $k > 0$ modes, as depicted by Figure 4.32(d). It should be emphasized that the lasing phase boundary given by the two models agreed so well because we had $N_m >> N_{ph}$; in case of smaller $N_m$, we found that fluctuations shift the transition to higher pump rates in the multimode model (the results can be found in the Supplemental Material of Publication V).

Figure 4.32(c-d) show which lasing $k$ mode has attained the highest occupation. In the weak coupling case, when the lowest-energy photon mode $\omega_0$ is set around the $(n - 0)$ molecular transitions ($\omega_0 = \epsilon - n\omega_v$ for $n = 0, 1, 2, ...$), lasing occurs mainly in the $k = 0$ mode. An interesting regime was found between the $(1 - 0)$ and $(2 - 0)$ transitions, where the $k = 0$ mode lasing competes with higher $k > 0$ modes. Let us have a closer look at the
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Figure 4.32. Lasing phase diagrams at weak and strong coupling regimes. Total photon occupation $n_{\text{tot}} = \sum_K W_K n^K$ as a function of photon detuning $\omega_0$ and pump $\Gamma_\uparrow$ for (a) weak coupling and (b) strong coupling. Lasing mode index $k$ as a function of photon detuning $\omega_0$ and pump $\Gamma_\uparrow$ for (c) weak coupling and (d) strong coupling. Figure reprinted with permission from Publication V (© 2020 American Physical Society).

Threshold curves at weak and strong coupling for detuning $\omega_0 = \varepsilon - 1.5 \omega_v = 0.7$ eV are presented in Figure 4.33(a-b). At weak coupling, lasing first takes place at $k = 4$ mode which is resonant with the $(1-0)$ transition. Upon increasing the pump rate, lasing switches to $k = 0$. The switching can be understood by different thresholds and slope efficiencies (the gradient of photon occupation as a function of pump) of the modes. The mode with highest gain will win out other modes that are above the lasing threshold. Around a narrow regime of pump rates, the gain is almost equal for more than one mode, and therefore lasing at multiple modes is possible. Such a case is exemplified in Figure 4.33(c) by the blue solid line, where the steady-state solution shows two lasing peaks at 0.7 eV and 0.8 eV.

At strong coupling, switching between modes occurs in a more complex way. Figure 4.33(b) shows how lasing first starts at the $k = 4$ mode overlapping with the $(1-0)$ transition but, instead of switching to $k = 0$, is pushed to higher-energy modes upon increasing the pump. This can be explained by the combination of two effects that occur when pump is increased: first, the increased pumping causes blue shift of the polariton dispersion due to saturation effects (see Section 4.5.2 and Figure 4.34). Second, the gain spectrum as a whole shifts towards higher energies upon increasing the pump rate, as the higher energy vibrational side bands become inverted.

Another distinct feature of the strong coupling, visible in the top right corner of Figure 4.32(d), is a part of the phase diagram where high $k$ lasing occurs for very high pump rates, shown as yellow color in the graph. The high $k$ lasing can be understood as an effect of total inversion of the
two-level system, which leads to net gain for far-detuned modes away from the vibronic structure.

4.5.2 Photoluminescence spectrum

We calculated photoluminescence spectrum with Eq. (2.25) to find polariton energies, and studied how the spectrum changes as a function of pump rate. Bright peaks in Figure 4.34(a-b) correspond to polariton mode energies, widths of the peaks to mode lifetimes, and intensities to occupations. The spectra are computed for the parameters of the strong coupling case discussed above. Avoided crossing between the lower and upper polariton branches is visible from low to high pumping, indicating that strong coupling persists throughout the studied pump rates. However, the split gets decreased upon increasing the pump due to the saturability of the two-level systems. This causes a blue shift of the lower polariton branch, which is especially notable around $k = 0$.

Figure 4.34(c) shows how the blue shift of the $k = 0$ mode goes hand-in-hand with the inversion of the two-level system. This means that the blue shift can be fully attributed to the saturation of the emitters, in accordance with a recent phenomenological saturation model of polariton interaction [108]. Note that even though the blue shift here does not arise from direct polariton-polariton or polariton-reservoir interactions, the saturation is a source of effective interactions: an excited molecule cannot be excited twice, leading effectively to repulsive interactions.
Figure 4.34. Photoluminescence spectrum and blue shift of the lower polariton branch. Photoluminescence spectra for increasing pump rates: (a) $\Gamma_\uparrow = 0.1 \Gamma_\downarrow$ and (b) $\Gamma_\uparrow = \Gamma_\downarrow$. (c) Energy of the $k = 0$ mode in the lower polariton branch (purple solid line) and the inversion of the molecule (yellow dashed line) as a function of pump rate. Figure reprinted with permission from Publication V (© 2020 American Physical Society).
In this dissertation, the properties of plasmonic Bose–Einstein condensates (BECs) have been investigated, and a new theory model for strongly coupled organic systems has been presented. The system where the first plasmonic BECs have been achieved consists of gold nanoparticle arrays immersed in a solution of organic fluorescent molecules IR-792. Periodic arrays of nanoparticles, i.e. plasmonic lattices, give rise to surface lattice resonances (SLRs) that form as a consequence of strong coupling between localized single particle resonances in individual nanoparticles and the diffracted orders of light in the lattice. The excitations of SLRs are bosonic quasiparticles that are mostly light but also partly matter due to the coupling with electrons in metal. The SLRs can be strongly coupled to organic molecules, which creates another type of quasiparticle called plasmon-exciton-polariton.

In Publication I, we introduced the first BEC in a plasmonic system in a 100×300 μm² (in x × y) array of nanorods overlaid with a thin layer of 50 mM dye solution. With this concentration, the coupling between SLRs and molecules remains weak, thus the quasiparticles that formed the condensate were excitations of the SLR modes (mostly photonic). In the lack of readily available technologies for directly imaging the dynamics in this timescale, we developed a new way to indirectly access the temporal evolution. We pumped the samples from one edge and measured the luminescence as a function of distance along the array, and transformed the travelled distance into time by using the group velocity of the SLR modes. We characterized the BEC via spatially and angle-resolved luminescence measurements, spatial coherence, and pump-probe spectroscopy. The plasmonic condensate was formed at room temperature in a picosecond timescale. The experimental results were reproduced by a model of non-equilibrium photon condensation applied to our plasmonic system.

In Publication II, we achieved the first plasmonic BEC at strong coupling regime. Compared to Publication I, we made two major changes in the experiment: first, we ramped up the molecule concentration from 50 mM to 80 mM to establish strong coupling between the SLRs and the dye
molecules. Second, we pumped the samples with a spot that covers the whole array, and observed the BEC in a time-integrated measurement. The samples were 100×100 μm² square arrays with asymmetric periodicities, made of cylindrical nanoparticles. We showed that the thermalization occurs through a stimulated process and that a BEC with prominent thermal distribution appears only with excitation pulses that are shorter than 250 fs. Similar, sub-picosecond, stimulated scattering times have been reported in organic polariton microcavities, however the condensates have not shown thermal distribution [377, 378]. The strongly coupled condensate was 100000 times more luminous than the first plasmonic condensate. Due to the room temperature operation and high luminosity, the strongly coupled plasmonic condensate provides a promising platform for fundamental studies of condensates of light and also in the future for possible applications, for instance, in sensing, imaging, and information processing.

In Publication III, we studied spatial and temporal coherence in strongly coupled plasmonic BECs. We used arrays that were similar to those in Publication II but elongated in the x dimension (500×100 μm²) in order to study the decay of spatial correlations at longer distances. We found that above the BEC threshold, the correlations exhibit decay in the millimeter scale. We fitted the measured spatial correlations to Gaussian, exponential, stretched exponential, and power-law functions. Below the BEC threshold, the correlations were found to decay as a Gaussian. Above the BEC threshold, we evidenced a decay that best fit to a power-law function with a very small exponent of 0.07; a stretched exponential function fit almost equally well with an exponent of 0.1. We also measured the temporal correlations and fit the results to the different functions. Below the BEC threshold, the temporal correlations showed an exponential decay, while above the threshold the data was best fit to a power-law function with a high exponent of 0.7–0.8. Again, the stretched exponential function yielded almost equally good fit with an exponent of around 0.2. The obtained exponents did not directly align with any of the previously reported experiments or predicted theoretical values. The plasmonic BECs provide a system amenable for studying non-equilibrium BKT transition or KPZ dynamics due to the large and scalable system size and short lifetime of the modes [368, 134, 142, 141]. The BEC studied in Publication III is half a millimeter long, making it reportedly the largest condensate of light to date.

In Publication IV, we demonstrated polarization textures in strongly coupled plasmonic BECs. The arrays were similar to those in Publication II, 100×100 μm², but with symmetric periodicities. We pumped the samples with a circularly polarized light, leading to non-uniform intensity distributions in both vertical and horizontal directions of the lattice. We then analyzed the polarization components present in the condensate by
filtering different polarizations in the detection side. The phase of the condensate was obtained by a phase retrieval algorithm, applied for the first time to any type of condensate to our knowledge. The phase retrieval reconstructs the real space phase distributions based on real space and $k$-space measurements. The results revealed a non-trivial phase shift of $\pi$ between the center and the edges of the lattice. The polarization textures could be explained by a phenomenological model taking into account the intensity and phase variations. The textures in the square array were topologically trivial, but creating topologically non-trivial polarization textures is a feasible future prospect given the freedom to engineer the lattice geometry and/or the pump polarization. Beyond fundamental studies, polarization textures are utilized in beam engineering, lasing and holography [379, 380, 381, 382, 383].

In Publication V, we presented a new theoretical model for strongly coupled organic systems. The model took a step forward from the non-equilibrium model of photon condensation, which assumed weak light-matter coupling [135, 136, 10]. The new model was benchmarked with a previous model based on mean-field theory [138]. We found some peculiar regimes of detuning and pumping, where multiple modes can show lasing simultaneously. Multimode lasing will be studied in the future more thoroughly and also with a pulsed pump, which is typical for organic systems. The model was also used to demonstrate that the origin of blue shift in organic polariton systems can be attributed to saturation effects. For the theoretical descriptions, there is still work to do to catch up with the recent experimental observations. One subject is that the current approaches are not able to fully describe the thermalization processes in strongly coupled systems. Considering plasmonic lattices, a complete description will also need to take into account the spatial degrees of freedom.

In Publication I and Publication II, we observed crossovers from lasing to BEC as functions of periodicity and pump fluence, respectively. Lasing and BEC are macroscopic quantum coherent phenomena which both show extended spatial and temporal coherence and are observed as highly directed and intense luminescence at a single wavelength (the ground energy state of the system). A closer look at their spectra, however, reveals a difference. A BEC at finite temperature exhibits a “thermal tail” of energy states above the ground state occupied according to the theory by Bose and Einstein [24]. In order to have the higher energies occupied in this way, the particle population must undergo a thermalization process, in which the energies of the particles are gradually reduced until the ground state of the system is met. At a critical particle density, a phase transition into a BEC occurs, and the whole ensemble of particles behaves as if it was one large particle. In contrast, in lasing it is enough to have one mode highly occupied through stimulated emission.

Another distinct feature between a laser and a BEC is the second-order
correlation function, $g^{(2)}(\tau)$, which tells about the probability to observe one or many photons coming from the source at the same time. The value of $g^{(2)}(\tau = 0)$ would be 2 for thermal light and 1 for laser light, so this can be used to further identify BEC and lasing. Whereas in a canonical ensemble, particle number is fixed but energy can fluctuate around an average value determined by the temperature of a thermal reservoir, in grand-canonical statistics both the energy and particles can be exchanged with a large reservoir. Photon BECs formed in grand-canonical ensemble have shown large number fluctuations on the order of the particle number [90]. Our system is possibly under the grand-canonical conditions due to the high number of molecules. Measuring the second-order correlations is experimentally challenging due to the ultrafast dynamics of our system. However, as demonstrated in the group, the sub-picosecond dynamics in plasmonic lasing and BEC have become accessible [10, 277, 308]. Therefore, it is realistic to expect that also the second-order correlation measurements will be possible in the near future. This will provide invaluable information about the differences of the lasing and BEC regimes observed in the present experiments.

An important direction for future research is to investigate the role of interactions further. The involvement of interactions in microcavity polariton systems is known to lead to the formation of quantized vortices and suppressed scattering related to superfluidity, among other exotic phenomena [127]. Interactions may be evidenced through the modification of the polariton dispersion relation (such as the blue shift observed in Publication II), which in luminous condensates is easy to access by the angle-resolved measurements. At present, the blue shift observed in Publication II is believed to arise from effective interactions, which, as modelled in Publication V, can be caused by the saturation of molecules. For experimentally probing the interactions, it is useful that we can control the ratio of exciton and photon content by changing the dye concentration and tuning the band-edge energy with respect to the exciton energy. The origin of the non-trivial phase structure observed in Publication IV is yet to be identified; interactions can potentially be responsible for such effects.

While the research results presented in this dissertation have primarily contributed to the fundamental understanding of plasmonic lasers and BECs, the phenomena may eventually find also practical applications. Various polariton devices have already been proposed [164], including polariton light-emitting diodes [165, 166, 167, 168], amplifiers [169], spin switches [170], and polariton transistors [171, 172]. Also electrical injection has been demonstrated for plasmonic [384, 385, 304] and polariton lasers [187, 188, 189, 190, 191]. Due to the ability to combine light with electrons in metal, plasmonics has potential for fast and compact on-chip solutions for e.g. sensing and optical communications.
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