LEVERAGING PHOTOLUMINESCENCE FROM ANISOTROPIC NANOMATERIALS
FOR ENHANCED PHOTOVOLTAIC ENERGY CONVERSION

A Dissertation
by
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ABSTRACT

Solar power, despite its abundant availability, is yet to reach its full potential as a clean and renewable energy source, primarily due to the low power conversion efficiencies and high manufacturing costs of photovoltaic (PV) modules. The path to making solar cells more affordable lies through either reducing the manufacturing cost of cells or increasing the efficiency without significantly increasing the cost. This dissertation explores strategies that improve the conversion efficiency of PV modules by leveraging anisotropic optical nanomaterials that can alter the entropy of radiation from a cell.

This work investigates two distinct approaches for integrating aligned assemblies of highly luminescent semiconductor nanorods (NRs) into PV modules: (1) a conventional luminescent solar concentrator (LSC) geometry where the medium containing NRs is placed adjacent to the PV and (2) a novel geometry where the NR medium sits directly above the PV cell. The benefits of each approach are investigated using appropriate theoretical models, while accounting for various loss mechanisms associated with realistic materials.

A main focus of this dissertation is to develop theoretical framework for modeling PV systems that do not conform to traditional detailed balance approximations of the cell emissivity. The conventional detailed balance analysis assumes an equivalence between the angle-dependent absorptivity and emissivity of a PV cell, even outside of radiative equilibrium. While this is a perfectly reasonable approximation for materials that absorb or emit isotropically, it does not necessarily hold for nanostructured materials that exhibit optical anisotropy. This distinction can be effectively harnessed to modify the angular distribution of emission from a cell through absorption and reemission from anisotropic luminophores, as shown in the subsequent sections of this dissertation.
Additionally, this work outlines experimental progress toward the development of highly anisotropic optical nanocomposites. The AC field-driven alignment of colloidal CdSe/CdS NRs is investigated as a means for producing functional materials that support the proposed implementations. In addition to quantifying the degree of field-driven ordering, this study provides significant insight into the spontaneous mesoscale aggregation of colloidal NRs into superstructures as well as its impact on the ensemble anisotropy and overall alignment.
DEDICATION

For Randinu.
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Dr. Ryan Kutayiah and Smriti Kumar assisted with detailed balance calculations in Chapter 2 and Markov chain simulations in Chapter 3. Nicholas Gripp assisted with the AC field-driven alignment of nanorods in Chapter 5. Freddy Rodríguez Ortiz assisted with fluorescence anisotropy measurements in Chapter 5. All other work conducted for the dissertation was completed by Rivi Ratnaweera independently.

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<table>
<thead>
<tr>
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<tr>
<td>$J_{sc}$</td>
<td>short-circuit current density</td>
</tr>
<tr>
<td>LSC</td>
<td>luminescent solar concentrator</td>
</tr>
<tr>
<td>NR</td>
<td>nanorod</td>
</tr>
<tr>
<td>PLQY</td>
<td>photoluminescence quantum yield</td>
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<tr>
<td>PV</td>
<td>photovoltaic</td>
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<tr>
<td>$V_{oc}$</td>
<td>open-circuit voltage</td>
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<tr>
<td>QD</td>
<td>quantum dot</td>
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1. INTRODUCTION

1.1. Motivation

The past decade has seen a dramatic upsurge in solar power usage, with the global consumption leaping from below 50 TWh in 2010 to over 300 TWh in 2016.\(^1\) However, despite its overwhelming abundance, the low power conversion efficiencies and high manufacturing costs of photovoltaic (PV) devices have prevented solar energy from reaching its full potential as a clean and renewable alternative to fossil fuels. While recent advances in the solar cell industry have enabled higher conversion efficiencies, further improvements will be required to facilitate widespread adoption of solar energy.

Strategies for improving the performance of solar cells can be broadly classified into two approaches: (1) improving material properties and (2) improving module design. Given the steady improvement in the materials quality of semiconductors in the past few decades, the focus of much contemporary PV research has shifted toward understanding and optimizing module design. Some of the more common strategies include using multi-junction or mixed band gap cells for more efficient utilization of the solar spectrum\(^2-9\) and manipulating the angular range of light entering or leaving the solar cell to reduce entropic losses. The latter can be achieved through optical schemes that either increase the flux and angular range of incoming light through concentration,\(^10-14\) or promote photon recycling by restricting the angular range of light leaving the cell.\(^15-20\) In a similar vein, the entropy of the outgoing radiation field from a solar cell can be modified through anisotropic absorption and luminescent emission from nanostructured materials, which is a key area of focus for this research.\(^21-23\) This concept serves as a foundation for much of the theoretical and experimental work presented in the following chapters.
My research aims to contribute to the ongoing efforts in improving the efficiency of PV systems by developing novel approaches that leverage linearly polarized absorption and emission from highly luminescent semiconductor nanorods (NRs). In particular, this work explores strategies for integrating aligned NR assemblies into novel PV modules, with the aim of achieving conversion efficiencies that surpass the well-known Shockley-Queisser limit. This dissertation outlines the development of theoretical framework for modeling the performance of proposed PV systems and highlights experimental progress querying and developing optically anisotropic functional nanocomposites that would support the fabrication of such devices.

1.2. Fundamentals of Photovoltaic Energy Conversion

1.2.1. Solar Cell Structure

In simplest terms, a solar cell is an electronic device that converts sunlight into electricity. Incident light is absorbed by the device to produce both a current and a voltage that combine to generate usable electric power. The underlying mechanism involves the photo-excited electrons in the PV material being raised to a higher energy state, followed by extraction of these high-energy electrons through an external circuit.\textsuperscript{10} While there are a host of materials that can potentially satisfy the requirements for PV energy conversion, in practice, nearly all solar cells use semiconductor materials in the form of a p-n junction.
A typical silicon solar cell consists of a negatively doped (n-type) layer of silicon and a positively doped (p-type) layer of silicon tightly bonded together. When two dissimilar semiconductor layers are combined, the free electrons in the n-type silicon migrate across the interface to fill the electron holes in the p-type silicon, resulting in the formation of a so-called depletion region which prevents further electron migration. When the electrical imbalance reaches an equilibrium state, a fixed electric field is established across the boundary separating the two layers. When photons with sufficient energy impinge on the solar cell and are absorbed, they generate excited electrons that can move freely through the material. The fixed electric field across the depletion region causes free electrons near the p-n junction to be swept across the interface from the n-layer to the p-layer. This unidirectional flow of electrons creates a charge imbalance between the two layers, which in turn provides the driving force for electrons to flow through the external circuit from the p-layer to the n-layer. It should be noted that this brief explanation of a functional solar cell is aimed to offer a basic understanding of the operating principles. A more comprehensive discussion on solar
cell engineering can be found in many standard textbooks which may delve deeper into the subject than what is covered in this chapter.\textsuperscript{10}

1.2.2. Solar Cell Parameters

The main electrical characteristics of a solar cell or module are summarized in the relationship between the current and voltage at the existing conditions of irradiance and temperature. This correlation can be graphically represented in terms of an I-V characteristic curve, as shown in Figure 1.2. When the solar cell is open-circuited, i.e., not connected to any load, the current will be at its minimum (zero) and the voltage across the cell is at its maximum, commonly referred to as the open-circuit voltage (\(V_{OC}\)). At the other extreme, when the cell is short-circuited, i.e., the terminals are connected together with no resistance, the voltage across the cell is at its minimum (zero) while the current reaches its maximum value, also known as the short-circuit current (\(I_{SC}\)). The power delivered by the cell at any given point on the I-V curve is the product of the output current and voltage (\(I \times V\)). There exists one particular combination of current and voltage for which the generated power reaches a maximum value. This point, commonly referred to as the maximum power point (MPP), is the ideal operating condition for a PV cell.\textsuperscript{10}
1.3. **Losses in a Solar Cell**

The power conversion efficiency of a solar cell is limited by various losses that occur during its operation. This section explores different types of losses that solar cells experience and their impact on the overall efficiency of the device.

Absorption losses occur due to incomplete absorption of incident sunlight by the solar cell. These losses depend on the material properties of the cell, in particular, the bandgap of the semiconductor material which limits the spectral range of the solar cell’s absorption. In theory, using semiconductor materials with lower bandgaps would allow the absorption of a wider range of the solar spectrum. However, this comes at the cost of increased thermalization losses (see below).

Reflection losses occur when a portion of the incident sunlight is reflected off the surface of the solar cell and not absorbed. These losses can be minimized by using an antireflective coating on the surface of the cell.

![Figure 1.2. Schematic of a typical solar cell I-V characteristic curve.](image-url)
Transmission losses occur when some of the incident sunlight transmits through the cell instead of being absorbed and generating electron-hole pairs. These losses can be reduced by increasing the thickness of the solar cell to improve absorption or by adding a mirror/reflecting surface to the bottom of the PV module to reflect transmitted light back into the solar cell. The latter approach is particularly useful for thin-film solar cells, which have significantly thinner absorbing layers compared to conventional solar cells.

Recombination losses occur when the electron-hole pairs generated by the absorption of sunlight recombine before they can be collected by the electrodes. This type of loss can be mitigated by decreasing the number of recombination centers in the cell, or by using materials with a high carrier mobility. Improving the quality of the p-n junction interface also helps minimize recombination losses.

Thermalization losses in a solar cell refer to the energy loss that occurs when excited electrons with high energies thermalize and relax to the band edge, releasing excess energy as heat. These losses can be reduced by utilizing multi-junction solar cells which allow a broader range of wavelengths to be absorbed in comparison to a single-junction cell. In a typical multi-junction configuration, semiconducting materials are stacked in a layered structure, arranged in order of decreasing bandgap, with the highest bandgap material positioned on top and the lowest bandgap material at the bottom. This arrangement enables each layer to capture distinct wavelengths of sunlight, increasing the overall conversion efficiency of the cell.
1.4. Strategies for Improving Efficiency of Solar Cells

Increasing the efficiency of PV systems can reduce the overall cost of solar energy production, independent of economic innovations such as tax incentives or more efficient manufacturing. Using PV cells with higher efficiency reduces the number of solar panels needed to generate a given amount of electric power, as well as the land area required for installation. Moreover, higher efficiencies can increase the lifetime and reliability of a PV module, reducing maintenance costs and improving the overall return on investment.

Besides improving materials quality to minimize losses in solar cells, the PV research community is continuously exploring various strategies to improve upon the existing theoretical limit for conversion efficiency—33.7% for a single-junction flat plate solar cell, assuming no losses and ideal materials. Some of these strategies focus on utilizing optical schemes to alter the flux and angular range of incoming and outgoing radiation in a cell while other methods involve physical alteration to the semiconductor surface as well as application of designed geometries to the cell surface.

One strategy for improving the efficiency of a solar cell is to use geometric solar concentrators, i.e., lens- or mirror-based concentration schemes that increase the flux and angular range of incoming sunlight. This approach can enhance the efficiency of a single-junction cell up to a theoretical maximum of 45.1%. However, in practice, implementation of this strategy is severely limited by the generation of excessive current densities that lead to overheating of the cell. Moreover, geometric concentrators require mechanical tracking of the Sun’s position, which further increases the manufacturing cost of PV modules.

Another possible strategy is the use of angle-restricting optics to constrain the angular range of emission from a solar cell. This method relies on photon recycling to
increase the chemical potential in the PV material, giving rise to increased voltages and, thereby, higher efficiencies. Angle-restriction can, in theory, increase the efficiency of a single-junction cell to 45.1% which is equivalent to the theoretical maximum efficiency of geometric concentration. However, like geometric concentrators, angle-restricting optics also require precise mechanical solar tracking.

Luminescent solar concentrators (LSCs) are an alternative to lens-based concentrators: they concentrate sunlight through absorption and reemission from luminophores embedded in a dielectric medium into waveguide modes coupled to a PV element. The main advantage of this technique is that it allows large areas of expensive PV material to be replaced by more cost-effective absorbing materials. Additionally, in contrast to the previous two strategies, the implementation of LSCs does not require solar tracking. However, it is worth noting that conventional LSCs do not offer any true benefits in conversion efficiency, as explained in Chapter 2.

Surface structuring of PV materials has also been explored as a strategy to improve the efficiency of solar cells. The use of texturing techniques increases the amount of light trapped within the semiconductor material and enhances the absorption path length of photons, leading to more efficient photon-to-electron conversion. One approach is the implementation of nanostructured materials such as nanowires or NRs which exhibit unique optical and electronic properties that can enhance light absorption and charge transport in the solar cell. Additionally, surface texturing by etching or deposition can create a graded index of refraction, which improves light trapping and reduces reflection losses. Various studies have demonstrated the effectiveness of surface texturing in enhancing the efficiency of PV cells, with reported improvements ranging from a few percent to over 20%.[25-28]
1.5. Structured Emission from Semiconductor Nanorods

Integrating nanomaterials into PV devices is an increasingly popular strategy that aims to utilize the unique optical properties of nanoparticles such as quantum dots (QDs) or semiconductor NRs to enhance cell performance through improved absorption and photon extraction. The highly tunable optical and morphological properties of nanoparticles make them excellent candidates for next-generation PV devices. Semiconductor NRs, in particular, have been widely studied as potential building blocks for optoelectronic devices due to their strong optical anisotropy, tunable band-edge emission and near-unity photoluminescence quantum yield. The one-dimensional geometry of these nanocrystals creates quantum confinement perpendicular to their long axes, which modifies the spatial distribution of photoexcited charge carriers, giving rise to linearly polarized absorption and emission of light.

The optical anisotropy of individual NRs can be extended to the macroscopic scale by assembling large populations of NRs into ordered superstructures. For instance, previous studies have highlighted the potential of aligned anisotropic emitters for application in LSCs, although the limiting efficiency of such devices is not well understood. The advantage of integrating aligned NRs into a PV module lies in modifying the entropy of radiative emission from the device. This effect increases the chemical potential of the cell which in turn improves the overall conversion efficiency of the device, as elaborated in Chapter 2.
1.6. Overview of Dissertation

The main focus of this dissertation is to investigate the role of optically anisotropic nanomaterials in improving the performance of solar cells through absorption and reemission of sunlight. As such, the following chapters outline theoretical and experimental efforts aimed at understanding the optical anisotropy of aligned NR assemblies as it pertains to their integration into high-efficiency PV modules. Chapter 2 investigates a strategy for integrating aligned dipole emitters into a conventional LSC and demonstrates the theoretical benefits of concentrating sunlight through anisotropic luminophores, in particular, when coupled with optics that restrict the angular range of emission from the PV cell. Chapter 3 introduces a statistical approach based on ergodic Markov chains for modeling absorption, photoluminescence, and scattering in nanophotonic systems. This method is thought to add further sophistication to the traditional detailed balance approach employed in Chapter 2, allowing the analysis of more complex PV systems. Building upon this approach, Chapter 4 explores a novel device architecture for a NR LSC in which the NR layer acts as a filter that serves to modify the angular entropy of the cell emission. The limiting conversion efficiency of this device is calculated using the Markov chain model developed in Chapter 3. Finally, Chapter 5 investigates an experimental method for aligning colloidal NR dispersions using AC electric fields as a means to producing nanocomposite materials with strong optical anisotropy. The degree of NR alignment is determined by measuring the field-driven change in absorbance and the ensemble fluorescence anisotropy of NR dispersions.
**2. DETAILED BALANCE ANALYSIS OF LUMINESCENT SOLAR CONCENTRATOR WITH VERTICALLY ALIGNED NANORODS**

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**2.1. Fundamentals of Detailed Balance Theory**

Standard thermodynamics dictates that for a system to be at radiative equilibrium, the incoming and outgoing photon fluxes must equal one another. This principle, commonly referred to as “detailed balance”, can be used to calculate the limiting efficiency of a single-junction solar cell as shown by Shockley and Queisser in 1961. In brief, the analysis considers the balance of incoming radiation with the outgoing radiation and the total current extracted from the cell. Assuming that all photons with energy greater than the PV band gap \(E_g\) are fully absorbed, and that all electron-hole pairs that do not radiatively recombine are collected through the external circuit, the current extracted from the cell is proportionate to the difference between the incoming and outgoing radiation fluxes.

The total current generated per unit absorbing area, \(J_{\text{tot}}\), is given by

\[
J_{\text{tot}} = q(N_{\text{abs}} + N_{\text{amb}} - N_{\text{emit}}) \tag{2.1}
\]

where \(q\) is the elementary charge, \(N_{\text{abs}}\) is the number of incident photons (per unit time and area) absorbed by the solar cell, \(N_{\text{amb}}\) is the number of photons absorbed due to thermal radiation from the ambient environment, and \(N_{\text{emit}}\) is the number of photons emitted from the cell due to radiative recombination. The absorption and emission fluxes can be expressed as

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\[ N_{\text{abs}} = \int_{E_g}^{\infty} \int_{\varphi=0}^{2\pi} \int_{\theta=0}^{\theta_{\text{Sun}}} a(\theta, \varphi, E) S(E) d\theta d\varphi dE, \quad (2.2) \]

\[ N_{\text{amb}} = \frac{2}{\hbar^3 c^2} \int_{E_g}^{\infty} \int_{\varphi=0}^{2\pi} \int_{\theta=0}^{\theta_{\text{Sun}}} a(\theta, \varphi, E) \frac{E^2}{e^{\left(\frac{E}{k_B T_{\text{cell}}}\right)} - 1} \cos \theta \sin \theta d\theta d\varphi dE, \quad (2.3) \]

\[ N_{\text{emit}} = \frac{2}{\hbar^3 c^2} \int_{E_g}^{\infty} \int_{\varphi=0}^{2\pi} \int_{\theta=0}^{\theta_{\text{emit}}} e(\theta, \varphi, E) \frac{E^2}{e^{\left(\frac{E - qV_{\text{app}}}{k_B T_{\text{cell}}}\right)} - 1} \cos \theta \sin \theta d\theta d\varphi dE. \quad (2.4) \]

In Equation 2.2, \( S(E) \) is the spectral flux of incident sunlight integrated over the solid angles of light received from the Sun, \( 0 \leq \theta \leq \theta_{\text{Sun}} = 0.267^\circ \), and \( a(\theta, \varphi, E) \) is the angle- and energy-dependent absorptivity quantifying the fraction of photons absorbed by the cell where \( \theta \) and \( \varphi \) are the zenith and azimuthal angles, respectively. In Equations 2.3 and 2.4, \( N_{\text{amb}} \) and \( N_{\text{emit}} \) are defined in terms of the generalized Planck distribution for a blackbody over the energy range \( E_g \leq E \leq \infty \). The angular range of light leaving the device can be described as \( 0 \leq \theta \leq \theta_{\text{emit}} \), with \( \theta_{\text{emit}} \) denoting the maximum zenith angle at which emission occurs (\( \theta_{\text{emit}} = 90^\circ \) for a flat-plate cell).\(^{41}\) The operating temperature of the cell, \( T_{\text{cell}} \), is assumed to be 300 K. Constants \( \hbar, c, q, \) and \( k_B \) denote Planck’s constant, speed of light, elementary charge, and Boltzmann constant, respectively. In Equation 2.4, \( V_{\text{app}} \) is the applied voltage, which is related to the chemical potential of the cell through \( \mu = qV_{\text{app}} \).

Kirchhoff’s law of thermal radiation states that at thermal equilibrium, the wavelength- and angle-specific power radiated by an object must be equal to the power that it absorbs.\(^{42}\) As such, in the context of detailed balance, the emissivity of the cell, \( e(\theta, \varphi, E) \), is necessarily equal to the absorptivity, \( a(\theta, \varphi, E) \), at a given wavelength and angle.\(^{43,44}\) However, since this condition only applies at the same wavelength or energy, using materials that conform to Kirchhoff’s law does not require that the angle-dependence of broadband absorption match that of luminescent emission, if the two processes occur at different
energies. This subtle distinction is crucial for understanding the benefits provided by nanorods (NRs) which exhibit dipolar absorptivity and emissivity in the energy range of luminescent emission and isotropic absorptivity and emissivity at higher energies.\textsuperscript{36,37}

Equations 2.1–2.4 can be used to generate the current-voltage characteristics of the cell by solving for $J_{\text{tot}}$ as a function of $V_{\text{app}}$. The short-circuit current density, $J_{\text{SC}}$, can be calculated by setting $V_{\text{app}} = 0$ in Equation 2.1 which gives $J_{\text{SC}} = qN_{\text{abs}}$. The open circuit voltage, $V_{\text{OC}}$, can be calculated by setting $J_{\text{tot}} = 0$ and solving for $V_{\text{app}}$ using Equations 2.1–2.4. The analytical solution for $V_{\text{OC}}$, assuming $E - qV_{\text{app}} \gg k_B T_{\text{cell}}$, is

\[
V_{\text{OC}} = \frac{k_B T_{\text{cell}}}{q} \ln \left( \frac{J_{\text{SC}}}{J_0} + 1 \right)
\]  

(2.5)

where $J_0$ is the reverse saturation current density.\textsuperscript{16,19,40,41} The output power from the cell per unit absorbing surface area, $P$, is the product of the current density, $J_{\text{tot}}$, and the applied voltage, $V_{\text{app}}$. The maximum power density, $P_{\text{max}}$, determines the maximum efficiency, $\eta$, when divided by the total optical power incident on the cell, $P_{\text{in}}$, according to

\[
\eta = \frac{P_{\text{max}}}{P_{\text{in}}} \times 100\%.
\]  

(2.6)

2.2. Detailed Balance Perspective of Light Management Strategies

2.2.1. Lens-Based Concentration and Angle Restriction

Several researchers have explored strategies for improving the theoretical efficiency of solar cells by manipulating certain parameters in the detailed balance model.\textsuperscript{10,15-20,40,41} In particular, optimizing the angular ranges of incoming and outgoing light, or so-called “light management”,\textsuperscript{19,28} has been shown to provide benefits that are independent of a particular semiconductor material system. For instance, two closely related strategies that can
significantly improve efficiency are lens-based concentration optics\textsuperscript{10-14} and angle-restriction optics.\textsuperscript{11,15-20}

In a typical cell geometry, light is received from the small angular range spanning the solar disk (0 ≤ θ ≤ θ\textsubscript{Sun} = 0.267°). For a flat-plate cell operating at \(V\textsubscript{OC}\), the light is emitted isotropically into a wider angular range defined by 0 ≤ θ ≤ \(θ\textsubscript{emit} = 90°\). According to Equations 2.1–2.4, the cell \(V\textsubscript{OC}\) can be increased by increasing \(N\textsubscript{abs}\), which leads to an increased value of \(N\textsubscript{emit}\) (Equation 2.1), and therefore, an increased cell potential (Equation 2.4). This can be practically achieved by placing a concentrating optic (lens) in front of the cell to increase the angular range and total flux of incident light. The theoretical limit for concentration (equivalent to ~46,000 Suns) is reached when \(θ\textsubscript{Sun}\) is effectively expanded to equal \(θ\textsubscript{emit} = 90°\).\textsuperscript{17,41,46} In addition to the voltage benefits outlined above, the enhanced \(N\textsubscript{abs}\) also increases the \(J\textsubscript{tot}\) from the cell and can increase the overall conversion efficiency to a theoretical maximum of 45.1% for a band gap energy of 1.12 eV. However, the practical limit for solar concentration lies at approximately a few hundred Suns where the excessive current densities lead to deleterious heating of the cell, increased series resistance, and overall loss of efficiency.\textsuperscript{10,11} Moreover, most optical concentration schemes require precise tracking of the Sun’s position throughout the day, adding to the manufacturing cost of PV modules.\textsuperscript{14}

An alternative approach to increasing the chemical potential of a solar cell is by limiting the angular range of light leaving the cell using angle-restriction optics. Reducing \(θ\textsubscript{emit}\) in Equation 2.4 forces \(V\textsubscript{app}\) to increase in order to maintain the flux balance between incoming and outgoing light (Equation 2.1). In contrast to lens-based concentrator optics, this strategy preserves the angular range of light received from the Sun, while constraining
the angular range of light emitted from the cell using mirrors or directionally selective filters.\textsuperscript{16-19,47} In a typical geometry, an angle-restriction optic selectively reflects photons emitted along more oblique angles (larger $\theta$) while transmitting photons emitted at more normal angles (smaller $\theta$), leading to photon recycling within the cell.\textsuperscript{11,16,48} At steady state, the increased number of trapped photons enhances the $V_{OC}$ of the cell while leaving $J_{SC}$ unchanged. Theoretically, perfect restriction optics, where $\theta_{emit} = \theta_{Sun} = 0.267^\circ$, can provide the same maximum efficiency as perfect concentration ($\theta_{Sun} = 90^\circ$), without producing excessive current densities that cause deleterious heating. However, this strategy requires PV materials with extremely high radiative efficiencies, and still requires precision tracking to maintain alignment between the Sun and the optical path to the cell.\textsuperscript{47,48} The enhanced $V_{OC}$ provided by both concentrators and angle-restriction optics can be attributed to a net decrease in angular entropy of photons emitted from the cell relative to a conventional flat-plate geometry.\textsuperscript{17,19,49,50}

\textbf{2.2.2. Luminescent Concentration}

A common misconception among the photovoltaics (PV) community is that traditional LSCs can provide improved conversion efficiencies relative to a single-junction flat-plate solar cell, when in fact, the efficiency benefits achieved through optical concentration or angle restriction cannot be realized, even theoretically, using conventional LSCs. This can be understood in terms of detailed balance by analyzing how $J_{SC}$ and $V_{OC}$ of the cell are affected by light trapping in an LSC. Assuming that refractive index contrast provides light trapping in a conventional LSC, while $J_{SC}$ is increased, the device efficiency is unchanged due to the equivalent scaling of the radiative dark current, $J_0$, in Equation 2.5.\textsuperscript{51} Thus, only when a PV material is defective, so that the dark current has significant
contributions from other nonradiative recombination pathways, can increasing $J_{SC}$ raise $V_{OC}$ and hence improve conversion efficiency. However, even under these conditions, the maximum efficiency that can be achieved is still 33.7% as opposed to the limit of 45.1% provided by lens-based concentrators or angle-restriction optics. In other words, unlike lens-based concentrators or angle-restriction optics, conventional LSCs do not modify the angular entropy of reemitted photons. Moreover, the common claim that LSCs are useful for concentrating diffuse radiation (e.g., sunlight on a cloudy day) is irrelevant if the LSC is coupled to a high-efficiency PV with little non-radiative loss. That being said, LSCs can still provide benefits in ultrahigh-efficiency concentrator PV applications by replacing large areas of expensive PV absorber material with low-cost luminophores.

2.3. **Analysis of Luminescent Solar Concentrator with Aligned Nanorods**

An alternative approach to achieving light trapping in a solar cell is through modifying the angle-dependent emission intensity. This can be practically implemented by placing emitters with anisotropic radiation patterns (e.g., NRs) optically in-series between the cell and the Sun, as depicted in Figure 2.1b. This approach can be used in conjunction with the angular restriction strategy outlined above, although its benefits are independent of the angular range of light leaving the cell. That is, even if the solar cell emits radiation into the same angular range as a conventional flat-plate solar cell ($\theta_{emit} = 90^\circ$), structuring the intensity profile of emission can promote light trapping within the device, leading to enhanced cell voltages.
Figure 2.1. Schematic representations of (a) a dipole emitting semiconductor NR and (b) the proposed LSC structure incorporating vertically aligned NR dipole radiators within a dielectric medium that is optically in-series with a PV cell (not to scale). The angle-dependence of the surface emission from the device follows a $\sin^2 \theta$ function characteristic of dipole emitters.

The specific materials of interest for this application are highly luminescent semiconductor NRs that exhibit anisotropic dipolar emission. The differences in quantum confinement of electronic states along the short and long axes of NRs promote linearly polarized band-edge luminescence (Figure 2.1a), while maintaining broadband, angle-independent absorption at higher energies.\(^5\)\(^2\) Several researchers have proposed the use of aligned NRs—or other luminophores with linearly polarized emission—to enhance the performance of LSCs by preferentially reemitting radiation into waveguide modes that couple to a PV cell to increase $J_{SC}$.\(^2\)\(^3\)\(^,\)\(^3\)\(^1\) However, as outlined in the discussion that follows, the primary benefit of this approach can be attributed to the modification of the angular distribution of radiation that is emitted into free space, which improves $V_{OC}$, even when $J_{SC}$ is held constant and nonradiative loss is negligible.\(^2\)\(^1\)-\(^2\)\(^3\)

The angle-dependence of absorptivity and luminescent emission in semiconductor NRs exhibits a pronounced energy dependence: photons from all incident angles with energy above the band gap will be absorbed with some efficiency, but internal relaxation of excited carriers results in luminescence that is Stokes shifted and highly polarized.\(^3\)\(^6\)-\(^3\)\(^7\) This
distinction is crucial for understanding the function of the proposed device in that it allows for contrasting angular entropies of absorption and emission without violating Kirchhoff’s law of radiation. While the spectral behavior of the optical anisotropy is strongly dependent on the composition and morphology of the nanostructure, state-of-the-art Cd-based chalcogenide NRs exhibit highly polarized absorption and emission near the band edge, and consistently lower optical anisotropy at higher energies.\textsuperscript{36,37} The linearly polarized emission from semiconductor NRs shows extremely high photoluminescence quantum yield (PLQY), approaching unity in certain cases.\textsuperscript{35} Further, the wavelength of emission and the magnitude of the Stokes shift can be tuned based on the semiconductor material as well as structural and design motifs, as demonstrated in core-shell heterostructured NRs.\textsuperscript{36,37} In comparison to conventional semiconductors that down-convert all absorbed radiation into band edge reemission, NRs additionally constrain the angular intensity profile of reemission.

This study considers an idealized LSC-type structure similar to the schematic depiction in Figure 2.1b. The luminescent medium consists of vertically aligned NRs embedded in a transparent dielectric medium that is optically coupled to a PV element. The entire device—barring the top surface of the NR medium—is surrounded by perfect specular reflectors. A concentrating or angle-restricting optic can also be placed on the exposed top surface to further improve cell performance. The following basic assumptions are made in order to simplify the detailed balance analysis of the proposed system. (1) All photons entering the device are absorbed and reemitted by the NRs before absorption by the PV element and that all photons emitted from the PV element that exit the device are first absorbed and reemitted by the NRs. (2) The Stokes-shifted emission from the NRs have the same energy as the PV band edge, $E_g$. (3) The NR layer is sufficiently thick that it absorbs
all incident sunlight with energy greater than the NR band gap, \( E_{g}^{NR} \). (4) Radiative emission is the only energy loss pathway. (5) The concentration of NRs in the medium is sufficiently dilute that multiple reemission and reabsorption events can be neglected, as in most high-performing LSCs demonstrated to date.\(^{21,22}\)

Building from the analysis of a single-junction flat-plate solar cell (Equations 2.2–2.4), the expression for \( N_{\text{emit}} \) can be modified to account for the angle- and energy-dependent emissivity, \( e(\theta, \varphi, E) \), and absorptivity, \( a(\theta, \varphi, E) \), of the device, as well as the Stokes shift, \( \Delta E_{S} = E_{g}^{NR} - E_{g} \), of the emitted radiation from the NRs. Vertically aligned NRs alter the angle-dependent relative intensity of radiation with a weighting factor, \( I(\theta, E) \), that can take on any value between 0 and 1. The modified expression for \( N_{\text{emit}} \) accounting for these additional factors is

\[
N_{\text{emit}}(\theta_{\text{emit}}, E, V_{\text{app}}, E_{g}^{NR}, T_{\text{cell}}) = \frac{2}{h^3 c^2} \int_{E_{g}}^{E_{g}^{NR}} \int_{\varphi=0}^{2\pi} \int_{\theta=0}^{\theta_{\text{emit}}} I(\theta, E) e(\theta, \varphi, E) \frac{E^2}{e\left(\frac{E-qV_{\text{app}}}{k_{B}T_{\text{cell}}}\right)} - 1 \cos \theta \sin \theta \cos \varphi \sin \theta \, d\varphi \, d\theta \, dE
\]

(2.7)

The functional form of the weighting factor, \( I(\theta, E) \), depends on the type of luminophore used: \( I(\theta, E) = 1 \) for a conventional isotropic luminophore and \( I(\theta, E) = \sin^2 \theta \) for an ideal dipole emitter. For NRs, the modified emission flux scales the fraction of \( N_{\text{emit}} \) in the energy range \( E_{g} \leq E \leq E_{g}^{NR} \) by a factor of \( \sin^2 \theta \) for any given angle. This relative decrease in emission intensity into certain angles requires \( V_{\text{app}} \) to be increased in order to maintain flux balance with the Sun, leading to an increase in conversion efficiency. The full energy dependence of \( e(\theta, \varphi, E) \) and \( a(\theta, \varphi, E) \) of the composite structure accounts...
for the effect of both dipolar band edge emission and absorption. Thus, \( e(\theta, \varphi, E) = a(\theta, \varphi, E) \) would hold as required by Kirchhoff’s Law with no need to use the additional term \( I(\theta, E) \). However, the term is included here to emphasize that the emission pattern is not an intrinsic property of the bulk semiconductor that comprises the PV element, but it is imposed by the NRs in the LSC.

Figure 2.2 (a) The detailed-balance efficiency as a function of band gap energy for the geometries (A, B, C and D) if there is no Stokes shift. The result is equivalent to the detailed balance efficiency of conventional flat plat cells. (b) The effect of a Stokes shift for NR luminophores (solid traces) and isotropic luminophores (dashed traces) at the optimal band gap energy for the cases considered. (c) Schematic representation of the radiative emission from (A) an LSC with a conventional luminophore emitting isotropically, (b) a conventional LSC with emission that is restricted by an optical structure that allows light to leave the surface only within a narrow angular range (blue),
while all other light is blocked from leaving (red), (c) an LSC with aligned NRs oriented normal to the top surface, (d) combined angle-restriction and dipole emission, where the angular range and relative intensity of light escaping the cell has been constrained (green).

**Table 2.1.** Calculated $V_{OC}$, $J_{SC}$ and $E_g$ values corresponding to the maximum efficiency cell for each of the cases A, B, C, and D described in Figure 2.2c as well as the dependence on a typical Stokes shift of 70 meV in these geometries. The restricted geometries (B, D) use a direct solar spectrum (AM 1.5D) as angle restriction requires that the cell only absorbs direct sunlight. The non-restricted geometries (A, C) use an AM 1.5G spectrum including diffuse sunlight.

<table>
<thead>
<tr>
<th>Case</th>
<th>Stokes shift (meV)</th>
<th>Efficiency (%)</th>
<th>$E_g$ (eV)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotropic (A)</td>
<td>-</td>
<td>33.7</td>
<td>1.34</td>
<td>1.08</td>
<td>35.0</td>
</tr>
<tr>
<td>Isotropic (A)</td>
<td>70</td>
<td>31.1</td>
<td>1.34</td>
<td>1.08</td>
<td>32.5</td>
</tr>
<tr>
<td>Restricted (B)</td>
<td>-</td>
<td>45.1</td>
<td>1.12</td>
<td>1.15</td>
<td>39.4</td>
</tr>
<tr>
<td>Restricted (B)</td>
<td>70</td>
<td>41.4</td>
<td>1.12</td>
<td>1.15</td>
<td>36.2</td>
</tr>
<tr>
<td>Dipole (C)</td>
<td>70</td>
<td>31.7</td>
<td>1.34</td>
<td>1.10</td>
<td>32.5</td>
</tr>
<tr>
<td>Dipole-restricted (D)</td>
<td>70</td>
<td>44.0</td>
<td>1.12</td>
<td>1.22</td>
<td>36.2</td>
</tr>
</tbody>
</table>

Detailed balance calculations were performed for LSCs with isotropic or dipole emitters, both with and without perfect angle-restriction. Figure 2.2 and Table 2.1 summarize the detailed balance efficiencies corresponding to the cases depicted in Figure 2.2c as a function of PV band gap and Stokes shift energy, $\Delta E_S$. Additionally, the optimal band gap performance of flat plate ($E_g = 1.34$ eV) and angular-restricted ($E_g = 1.12$ eV) cases were analyzed as a function of $\Delta E_S$ to compare the performance of dipole-emitting NRs (solid trace) with isotropic luminophores (dashed trace), as shown in Figure 2.2b. For both luminophores, the maximum in conversion efficiency correlates with the smallest possible Stokes shift. This is expected because the Stokes shift decreases the bandwidth of solar radiation that can be absorbed by the NRs, leading to lowered $J_{SC}$ values, as seen in Table 2.1. However, for a given magnitude of $\Delta E_S$, vertically aligned NRs always outperform isotropic emitters, and this benefit is even more pronounced when coupled with angle restriction optics as shown in Figure 2.2b. For the angle-restricted case, it is assumed that
the Sun is at normal incidence above the device, as facilitated by a solar tracker. It should be noted that these calculations estimate a best-case scenario for the efficiency improvements provided by NRs due to the assumptions of complete absorption of above-band gap radiation \((E > E_{g}^{\text{NR}})\) and reemission as a perfect dipole radiator. This ideal behavior is approximated by the luminescence observed in recent studies of Cd chalcogenide-based semiconductor NRs.\(^{36,37}\)

This implementation of an LSC with aligned NRs deviates from that of a conventional LSC in that it does not rely on refractive index contrast to increase \(J_{\text{SC}}\). In this context, the only function of the refractive index contrast is to ensure that the NRs are optically in-series with the PV cell. The dipolar emission from the NRs and the high refractive index of the waveguide combine to ensure that nearly all of the emitted radiation from the luminophores is trapped within the waveguide instead of directly escaping into free space. It has been shown that dipole emitters asymptotically approach unity trapping efficiency as the refractive index approaches values of \(n > 2\).\(^{23}\) Thus, the results of the calculations based on Equation 2.7 are independent of the choice of refractive index, as long as the assumption that all light enters or leaves the device mediated by absorption and reemission by the luminophores holds. Further, as a consequence of Snell’s law, the angle-dependence of the emission intensity from the LSC is unaffected by the refractive index contrast between the NR medium and free space. Conventional LSCs are thought to benefit from a large Stokes shift which minimizes the losses from luminophore reabsorption and reemission. However, since the absorption and reemission from luminophores is crucial to the function of this device, it does not benefit from having a larger Stokes shift. In fact, as outlined above, a larger Stokes shift would lead to a reduction in conversion efficiency. In
the limit of unity PLQY, the efficiency benefits of aligned NRs arise purely due to entropic effects related to the angular distribution of emission into free space.

It is generally accepted that $E_g/q$ defines the upper limit for $V_{OC}$ under non-concentrated light. The expression for $N_{emit}$ in Equation 2.4 is valid when classical Boltzmann statistics are upheld, i.e., when $E_g - qV_{app} \gg k_B T_{cell}$. However, under concentrated light or during angle restriction (cases B and D in Figure 2.2c), when $E_g \approx qV_{app}$, the Bose–Einstein function approaches a singularity, and the ideal diode approximation fails. Under these conditions, the energy-dependent part of the emission flux (Equation 2.4) may be adapted as

$$E^2 \exp \left( \frac{V_{app} - E}{k_B T_{cell}} \right).$$  \hspace{1cm} (2.8)

This approximation assumes that electrons in the conduction band reach thermal equilibrium before they relax through band edge recombination and corrects for the singularity when $E = qV_{app}$. Although not explicitly stated, the calculations account for this adjustment to Equation 2.4 wherever necessary.

The idealized detailed balance analysis of the proposed LSC assumes two distinct energy regimes for NR absorption and emission: a dipolar region from $E_g$ to $E_g^{NR}$ and an isotropic region from $E_g^{NR}$ onward to higher energies. Real NRs, however, deviate from this ideal behavior in that their angle-dependent absorptivity and emissivity in the aforementioned energy regimes are neither purely dipolar nor purely isotropic. To demonstrate this experimentally, the solution-phase fluorescence anisotropy of CdSe/CdS dot-in-rod heterostructures is measured as shown in Figure 2.3b. Optical anisotropy is typically characterized through fluorescence anisotropy measurements, and theoretical
studies as well as growing experimental evidence have shown that both absorption and emission anisotropies of nanoparticles are highly tailorable based on geometry and composition.\textsuperscript{57} It should be noted, however, that the specific band gap energy of the sample analyzed here is different from the ideal band gap energies incorporated into the detailed balance calculations outlined above. The anisotropy spectrum in Figure 2.3b shows the variation in ensemble solution-phase fluorescence anisotropy as a function of excitation energy/wavelength. Consistent with previous studies of CdSe/CdS NRs,\textsuperscript{36,37} two distinct regimes of anisotropy are observed. The NRs exhibit high fluorescence anisotropy near the band edge while the anisotropy is consistently lower at higher excitation energies (> 2.1 eV). This optical behavior corroborates the assumption of two separate energy regimes for anisotropy in the detailed balance analysis. However, the exact degree of anisotropy in the two regimes somewhat deviates from the theoretical values corresponding to pure dipole emitters (0.4) and pure isotropic emitters (0), respectively.\textsuperscript{58,59}
Figure 2.3. (a) Transmission electron micrograph of dot-in-rod CdSe/CdS NRs; inset: optical image of NR suspension in toluene under UV excitation. (b) Fluorescence anisotropy of the NRs. The dashed line indicates the step-function anisotropy of the dipole and isotropic regimes assumed in the nonideal model.

The nonideal dipole behavior of NRs can be modeled by treating the emission as a linear combination of pure isotropic emission and pure dipole emission. To this end, the dipole weighting factor, \( I(\theta, E) \), in Equation 2.7 is modified according to

\[
I(\theta, E) = \beta \sin^2 \theta + (1 - \beta)
\]

(2.9)

where the dipole and isotropic contributions are given by \( \beta \) and \( 1 - \beta \), respectively. The parameter \( \beta \) is related to the single-particle polarization \( P \) or ensemble anisotropy \( r \) according to Equations 2.10 and 2.11.
\[ P = \frac{\beta}{2 - \beta} \quad (2.10) \]

\[ r = \frac{2\beta^2}{20\beta^2 - 60\beta + 45} \quad (2.11) \]

Single-particle studies have found CdSe/CdS seeded NRs to have a band-edge polarization of \( P \approx 0.8 \), where a value of \( P = 1 \) corresponds to a perfect dipole emitter.\(^{36,38}\) According to Equations 2.10 and 2.11, this value correlates to a \( \beta \) value of 0.89 and therefore, an ensemble anisotropy of \( r = 0.21 \), showing excellent agreement with the anisotropy values measured in this study (Figure 2.3b). The average anisotropy of NRs in the above-band-edge region is estimated to be \( r = 0.12 \), which corresponds to a \( \beta \) value of 0.78. Accounting for this non-ideality, the results for the dipole and dipole-restricted cases can be revised according to Table 2.2.

**Table 2.2.** Limiting efficiency, \( V_{OC} \) and \( J_{SC} \) values for an LSC with non-ideal dipole emitters.

<table>
<thead>
<tr>
<th>Case</th>
<th>Stokes shift (meV)</th>
<th>Efficiency (%)</th>
<th>( E_g ) (eV)</th>
<th>( V_{OC} ) (V)</th>
<th>( J_{SC} ) (mA/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipole (C)</td>
<td>70</td>
<td>31.6</td>
<td>1.34</td>
<td>1.09</td>
<td>32.5</td>
</tr>
<tr>
<td>Dipole-restricted (D)</td>
<td>70</td>
<td>43.5</td>
<td>1.12</td>
<td>1.20</td>
<td>36.2</td>
</tr>
</tbody>
</table>

Deviation from ideal dipole behavior increases the angular entropy of NR emission. This leads to a reduction of light-trapping, as evidenced by the decrease in \( V_{OC} \) relative to the ideal dipole cases (Table 2.1). These revised \( V_{OC} \) values, however, are still larger in comparison to those of corresponding isotropic cases (1.08 V and 1.15 V, respectively). \( J_{SC} \) remains unaffected by the nonideal dipole behavior as the absorption flux \( (N_{abs}) \) is unchanged. Overall, these results suggest that real semiconductor NRs can be expected to enhance the conversion efficiency in LSCs.
While these calculations provide attractive targets for LSC designs implementing aligned semiconductor NR luminophores, the theoretical efficiency values calculated thus far assume no nonradiative loss mechanisms. Real semiconducting materials exhibit seemingly unavoidable, more complex loss pathways including Auger recombination, free carrier absorption, and Shockley–Read–Hall recombination, along with losses associated with the module such as parasitic absorption from optical components or scattering from NRs in the waveguide medium. Even using NRs that exhibit unity quantum fluorescence yield (QFY), these additional loss pathways reduce the emitted flux from a device or the anisotropy of emission. Ultrahigh efficiency devices, as analyzed here, require semiconductor materials that have extremely high radiative efficiencies. Recent single crystalline GaAs cells made by Alta Devices exhibit unprecedented external radiative efficiencies approaching 35% and have demonstrated power conversion efficiency values of 28.8%, within a few absolute percent of the maximum flat-plate detailed balance limit of 33.7%. Although the $J_{SC}$ in these record cells was lower compared to that of the previous 28.8%-efficiency GaAs cells, the cell $V_{OC}$ was nearly 100 mV larger, confirming that high efficiency cells are excellent light emitters. State-of-the-art, defect-free, single crystal GaAs cells have effectively eliminated most nonradiative loss pathways besides Auger recombination and are thus the focus of a more realistic materials-based model for the strategy outlined in Figure 2.1. Adapting the procedure from Kosten et al., the Auger losses in a GaAs cell can be readily accounted for using the detailed balance model by adding an Auger recombination term that represents nonradiative energy loss (Equation 2.12).

$$
(1 - R)N_{abs} = (1 + R)N_{abs}(\theta_{emit}, E, V_{app}, E_{g}^{NR}, \Delta, T_{cell}) + WCn_i^3 e^{\left(\frac{3qV_{app}}{2k_B T_{cell}}\right)}
$$

(2.12)
where \( W \) is the cell thickness, \( C \) is the Auger coefficient of \( 7 \times 10^{-30} \text{ cm}^6\text{s}^{-1} \), and \( n_i \) is the intrinsic carrier concentration in GaAs.\(^{48,63,64}\) Additional optical losses and other nonidealities—e.g., imperfect mirrors, scattering, or non-unity QFY of luminophores—are accounted for by considering an average optical efficiency for the coupling scheme such that \( R \) times the radiative emission from the cell gives the nonradiative loss due to coupling optics.\(^4\) This loss is separate from the voltage-dependent losses to Auger recombination and will additionally decrease the amount of sunlight that reaches the PV element. The thickness of the GaAs slab is set to 3 \( \mu \text{m} \), ensuring complete absorption within the ray optics limit, although the angle-dependent emissivity and absorptivity of the GaAs slab is explicitly accounted for in these calculations.\(^{17,65}\) The geometry of the modeled PV element is assumed to be planar, with no surface texturing. It should be noted that perfect vertical alignment of each individual dipole radiator in the ensemble represents a difficult engineering challenge, though there have been significant recent strides in this area.\(^{23,66-69}\) Therefore, to account for this imperfection, the calculations outlined above were repeated assuming a small amount of rotation and canting of individual rods (shown in Figure 2.1b), by setting \( I(\theta, E) \) to the average value of \( \sin^2 \theta \) over the angles spanned by direct sunlight. The efficiency values calculated using this more realistic emissivity function were found to be identical—within numerical accuracy—to the values reported in Figure 2.4.
Figure 2.4. Efficiency plot versus the angular range of emitted light for a 3-μm planar GaAs cell integrated in a NR-based LSC (green) or conventional LSC (orange) accounting for Auger losses in the GaAs. (a) A Stokes shift of 10, 50, and 100 mV is compared to a device with no Stokes shift (black dashed). (b) Analysis of LSCs with a 50-meV Stokes shift, Auger losses, and additional optical losses of 2% and 10%. The black traces correspond to a device with no Stokes shift, and the dashed traces correspond to a device with no optical losses. The equivalent lens-based solar concentration factor is provided on the top axes.

Figure 2.4 plots the detailed balance efficiency of GaAs cells coupled to LSCs with and without Auger losses (Figure 2.4a), while also accounting for the combined effects of angle restriction, Stokes shift, and the angular emission profile provided by dipole radiators (green traces) versus isotropic emitters (orange traces). In Figure 2.4b, the effect of other in-
series optical losses for LSCs with a 50 meV Stokes shift is compared with devices with no Stokes shift (black traces). The efficiency is plotted against the angular range of light emission to highlight several features resulting from the interaction of these effects. Losses due to Auger recombination significantly limit the maximum theoretical efficiency of any device to a value of 35.9% (dashed black trace, no Stokes shift), well below the detailed balance limit of 45.1% when emission is limited to the same angular range as direct sunlight, $\theta_{\text{emit}} = \theta_{\text{Sun}} = 0.267^\circ$. While a Stokes shift systematically lowers efficiency further, in comparison with isotropic emission, NRs provide an improved efficiency for any amount of angle restriction that has not reached the Auger-limited value.

Importantly, there is also a decrease in the required amount of angular restriction at which the maximum efficiency is reached, by $\sim 18^\circ$ for an LSC with a 100-meV Stokes shift. By relaxing the requirements for the angular range over which light can exit or enter the LSC, aligned NRs allow less extreme angle restriction to realize the same efficiency. The required precision for a solar tracker is often reported as a solar concentration factor, which is also indicated in Figure 2.4. Thus, for the case of an LSC with a 100 meV Stokes shift, a tracking device with a tolerance of up to $\sim 18^\circ$ ($\sim 6 \times$) can provide the same maximum conversion efficiency value of 31.5% as a lens-based concentrator or angle restriction optic that must track the Sun within $3^\circ$ ($\sim 300 \times$) to maintain the same maximum efficiency. Therefore, this benefit of NRs could potentially enable less-demanding trackers to be used in conjunction with ultrahigh efficiency converter designs, and significantly decrease the level of lens-based concentration required to achieve the highest theoretical conversion efficiency limited by the Stokes shift. Further, while in-series optical losses and scattering also systematically decrease device efficiency, Figure 2.4b shows that NR-based
luminophores in a structure with 2% optical loss can still outperform an ideal conventional LSC (orange-dashed trace) for a range of concentration factors between 3 × and 50 ×. This trend highlights the advantage of using vertically aligned NRs, even if this comes at a slight decrease in QFY or optical efficiency due to the more sophisticated design.

2.4. Conclusion

This study demonstrates that the performance of an LSC can be improved by modifying the angle-dependent emission pattern of radiation leaving the device, specifically, by using semiconductor NRs which can be prepared with extremely high QFY and strong linearly polarized emission. When placed optically in-series with a PV element, vertically aligned NRs provide a dipolar radiation pattern. Accounting for this emission pattern using the detailed balance method shows several advantages for this strategy in comparison with conventional LSCs that emit isotropically. Moreover, this study investigates nonradiative Auger losses in high-efficiency planar GaAs cells integrated within a NR LSC, also accounting for other factors impacting the optical efficiency. Results indicate that efficiency improvements can be anticipated in realistic device implementations while simultaneously relaxing the requirement for solar tracking, provided that other engineering challenges associated with nanocrystal-based LSCs, such as manufacturing costs and material toxicity, can be overcome.70-72 This strategy may be further extended to incorporate nanocrystals with higher order multipoles, or other arbitrary radiations patterns, to even more effectively structure the optical emission from LSCs and thereby enhance light trapping.
3. MARKOV CHAINS FOR MODELING OPTICAL PROCESSES IN COMPLEX NANOPHOTONIC SYSTEMS*

3.1. Introduction

Recent progress in the study of nanophotonics, encompassing research topics such as metamaterials, plasmonics, and quantum-confined matter has established that the optical interaction between light and matter is broadly tailorable across the electromagnetic spectrum via precise control of sub-wavelength-scale optical structures.73-77 Developments in radiation theory, aided by sophisticated computational methods, have informed experimental studies in nanophotonics, for example, as encapsulated in the inverse design approach78 and references therein. Complex features of the optical response of nanoscale structures including scattering, absorption, emission, and nonlinear behavior are increasingly well understood.32,79-88 However, a significant outstanding challenge is the behavior of macroscopic systems comprising large assemblies of sub-wavelength nanophotonic elements. In such systems, complex interactions between individual elements at the nano- and mesoscale give rise to the macroscopic optical response. The challenge is compounded when these systems are optically pumped and driven away from equilibrium, so that commonly employed simplifying assumptions, such as Kirchhoff’s law for equating absorptivity and emissivity, are not a priori guaranteed to be applicable.89,90 Further, standard analytical or computational strategies, such as finite element methods, may be difficult or

* Part of this chapter, including all figures and tables, is reprinted with permission from “Markov chains for modeling complex luminescence, absorption, and scattering in nanophotonic systems” by A. Ryan Kutayiah, Smriti Kumar, Rivi J. Ratnaweera, Kenny Easwaran, and Matthew Sheldon, 2021. Optics Express, 29 (3), 4249–4269, Copyright 2021 by Optical Society of America.
intractable to extend beyond nanoscale volumes or without simplifying boundary conditions.\textsuperscript{91}

The work described in this chapter focuses on demonstrating how a computational strategy based on statistical analysis using Markov chains provides a powerful tool for modeling complex interactions between assemblies of nanophotonic elements. These interactions are mathematically described as pathways of radiative and non-radiative energy exchange within the optical system and between itself and the environment, including absorption, photoluminescence, scattering, and various losses. This approach offers deep insight into the steady state distribution of light and energy through the system as well as other important optical properties such as the angle-dependent emission/scattering from the assembly as a whole, even when the system is driven out of equilibrium. The ability to model optical processes in non-equilibrium systems, in particular, makes this method especially useful for analyzing the performance of photovoltaic (PV) systems, as demonstrated in Chapter 4.

Markov chains have been previously employed in modeling light-matter interactions. For example, several studies have used absorbing Markov chains to determine the distribution of photons when they occupy their final absorbing states.\textsuperscript{92-96} However, this work utilizes ergodic Markov chains to focus instead on the steady-state distribution of photons in nanophotonic systems and how it gives rise to the macroscopic optical response.

Mathematically, Markov chains share some similarities with the more commonly used computational approach of Monte Carlo ray tracing. A key distinction, however, is that Monte Carlo methods approximate a distribution by sampling many instances from it, while the Markov chain approach allows direct determination of the steady-state distribution.
Although Monte Carlo ray tracing is the more popular approach, it can be computationally taxing, which limits its scalability to larger and more complex systems. In contrast, Markov chains have been shown to be computationally more efficient when applied to the same problems, making them a powerful tool for modeling complex interactions between assemblies of nanophotonic elements.

This work highlights the conceptual appeal of using Markov chains to model nanophotonic assemblies. The strategy is based on identifying the probabilities that connect the pathways of energy exchange between the nanoscale elements, e.g., the angle-dependent emission or absorption profile of individual emitters. These descriptions of the optical behavior of individual elements in the ensemble can be obtained using other methods such as Mie theory or extended Mie theory, finite element modeling, or finite-difference time-domain simulations. Once the probabilities of transitioning between individual elements are identified, the steady-state behavior of the system can be obtained simply by solving a single eigenvalue problem as outlined below.

3.2. Methods

3.2.1. General Markov Chain Theory

Using terms defined below, a discrete time, time-homogeneous Markov chain is an appropriate modeling device for a “memoryless” system in which the transitions at any moment depend only on the current state of the system, and not on the system’s previous states or duration of operation. Under certain simple conditions, the probability distribution of the system converges to a unique stationary distribution that can be used to determine the steady state of the system it represents.
Mathematically, a Markov chain can be described as a stochastic process, or in other words, a collection of random variables $X = \{ Z_t : t \in T \}$ defined on a common probability space, taking on values in a common state space $S$, and indexed by a set $T$, often representing time. In this particular application, the set $T$ is considered as a discrete set of “time steps” representing the number of elapsed transitions between states. It should be noted, however, that in this context, there is no direct correspondence of the number of time steps to a precise measurement of physical time in an experiment. The point of the model is not to determine the precise time at which a given event occurs, but rather, to evaluate the steady state distribution of photons in the system. The development here assumes that the lifetimes of different states are approximately equal, and that transition times are negligible in comparison to the state lifetimes. However, the model can be modified to accommodate known divergences from these assumptions. For the sake of clarity, the subsequent sections refer to a “time step” simply as a “step” to avoid any associations with physical time.

Since the set of states is finite, the probability distribution for a random variable $X_t$ is determined by the probabilities of the individual states, $P(Z_t = i)$. For convenience, let us denote $P(Z_t = i)$ by $d_i^{(t)}$ and the combined vector of probabilities for all states as $\vec{d}^{(t)} = \langle d_i^{(t)} : i \in S \rangle$.

If the variables are all independent of each other, then the joint distribution $P\left( (Z_0 = i_0) \cap (Z_1 = i_1) \cap (Z_2 = i_2) \cap \ldots \right)$ is simply the product of the distributions of individual variables $d_{i_0}^{(0)} d_{i_1}^{(1)} d_{i_2}^{(2)} \ldots$. In general, a stochastic process may have arbitrary dependencies among the variables, so that computing this joint distribution would require information about the conditional probabilities of each variable on every combination of the previous ones. However, if the variables obey the Markov property, then these conditional
probabilities are determined by the value of the previous variable, and are independent of the values of all preceding variables. That is,
\[ P(Z_t = j | Z_{t-1} = i, Z_{t-2} = i_{t-2}, \ldots, Z_0 = i_0) = P(Z_t = j | Z_{t-1} = i). \] (3.1)

Furthermore, if the process is time-homogeneous, then this conditional probability is independent of \( t \), and the probability of the system transitioning from state \( i \) to state \( j \) can be defined as:
\[ p_{ji} = P(Z_t = j | Z_{t-1} = i). \] (3.2)

By the law of total probability,
\[ P(Z_1 = j) = \sum_{i \in S} P((Z_1 = j) \cap (Z_{t-1} = i)) \]  
\[ = \sum_{i \in S} P(Z_1 = j | Z_{t-1} = i)P(Z_{t-1} = i) \] (3.3)

or,
\[ d_j^{(t)} = \sum_{i \in S} p_{ji} d_i^{(t-1)}. \] (3.4)

This relationship can be expressed in matrix form as
\[ \vec{d}^{(t)} = P\vec{d}^{(t-1)} \] (3.5)

where the column vector, \( \vec{d}^{(t)} \), represents the state of the system at a given instance and the so-called transition matrix, \( P \), represents the probabilities of transitioning from a state \( i \) to state \( j \), with \( p_{ji} \) located in the \( j^{th} \) row and \( i^{th} \) column. Since the columns of \( P \) represent the probabilities of all possible values of \( Z_t \) given a specific value of \( Z_{t-1} \), they must necessarily sum to 1. This property qualifies the transition matrix, \( P \), as a stochastic matrix.

A state \( i \) is said to be transient if there is another state \( j \) such that a system in state \( i \) has a finite probability of eventually reaching state \( j \), but a system in state \( j \) has a 0 probability of eventually reaching state \( i \). With probability 1, there is some step after which
the system is never in a transient state again. A state $i$ is said to be absorbing if, with probability 1, a system in state $i$ remains in state $i$ at all future steps. A Markov chain is said to be absorbing if all non-transient states are absorbing. Previous studies\textsuperscript{92-96} have analyzed systems by using an absorbing Markov chain, and finding the probability of the system ending up in each absorbing state.

A Markov chain is said to be reducible if there are states $i$ and $j$ such that, if one of the variables ever takes value $i$, then no later variable ever takes the value $j$, and irreducible otherwise. Necessarily, an irreducible Markov chain has no transient states. It is said to be periodic if there is some integer $n > 1$ such that $Z_t = Z_{t'}$ only if $|t - t'|$ is a multiple of $n$, and aperiodic otherwise. A Markov chain that is irreducible and aperiodic is said to be ergodic. This analysis focuses on the long-run behavior of ergodic Markov chains.

Each vector $\vec{d}^{(t)}$ represents the probability distribution of the system at a given step. If there is a distribution $\vec{d}^{(s)}$ with

$$P\vec{d}^{(s)} = \vec{d}^{(s)},$$

(3.7)

then it is said to be a stationary distribution of the system. For an ergodic Markov chain, there is always a unique stationary distribution\textsuperscript{100,101}, and furthermore, for any initial distribution $\vec{d}^{(0)}$,

$$\lim_{t \to \infty} P^t \vec{d}^{(0)} = \vec{d}^{(s)}.$$  

(3.8)

Thus, for such a Markov chain, the stationary distribution represents the steady-state behavior of the system, and can be determined by solving Equation 3.7. It is interesting to note that this is equivalent to solving for the eigenvector of matrix $P$ that corresponds to an eigenvalue of 1.
3.2.2. Markov Chain Model for Analyzing Nanophotonic Systems

This section demonstrates how the theoretical framework of the Markov chain approach discussed above can be applied to model optical processes in nanophotonic systems. In this simplified representation, the system comprises a medium and an environment that interact with each other via photon exchange. In this context, the medium is a solid matrix of uniform refractive index, $n_m$, that hosts a uniformly distributed ensemble of fluorophores. The environment surrounding the system has a refractive index of $n_e$, and irradiates the medium with a constant photon flux defined by a fixed angular profile.

The emission from either the environment or the luminescent medium is assumed to be azimuthally symmetric. Thus, the angle of emission is represented by the zenith angle, $\theta$, and the emission into any given angle is proportional to some function, $f(\theta)$. This work considers two different types of fluorophores labeled “isotropic” or “dipolar” with reference to their angle-dependent absorptivity and emissivity. An isotropic fluorophore absorbs and emits radiation with equal probability along any direction, i.e., the absorption cross-section, $\sigma$, has no angle-dependence while the angular distribution of emission can be represented as $f(\theta) = 1$. In contrast, a dipolar fluorophore features anisotropic absorption and emission, and is defined by $\sigma \propto \sin^2 \theta$ and $f(\theta) = \sin^2 \theta$. Common types of dipolar fluorophores encountered in nanophotonic systems are semiconductor nanorods (NRs) or dot-in-rod nanostructures that preferentially absorb and emit light polarized along their long axis. The model assumes that all of the dipolar fluorophores emit radiation with the dipoles oriented parallel to each other and normal to the top surface of the medium, similar to the arrangement of NRs in the integrated LSC module discussed in Chapter 2.
Light emitted from either type of fluorophore is considered to be monochromatic while the light leaving the environment could be monochromatic (e.g., laser excitation) or follow a specific spectral profile (e.g., solar irradiance) depending on the nature of the system. The host material of the medium is non-absorbing, and the real part of the fluorophore refractive index is matched to that of the host medium. Additionally, it is assumed that the fluorophores are positioned far enough apart so that near-field effects and resonant energy transfer can be neglected in the probabilistic description for energy transfer. Finally, the medium is considered to have a finite thickness, $L$, along the $z$-direction while extending infinitely along $x$- and $y$- directions.

The following discussion describes the state space, $S$, random variables, $Z_t$, with distributions, $\vec{d}^{(t)}$, and transition matrix, $P$, as they relate to the system. The Markov chain tracks the movement of an individual photon through the system according to a set of probabilities defined by materials properties and system dimensions. For a system with multiple photons, the stationary distribution of each photon will be the same, and the observed distribution of photons in the steady state will be proportional to this distribution.

The state space, $S$, is constructed by stratifying the medium into $M$ parallel slabs or layers of equal thickness. For a medium of total thickness, $L$, a single layer has thickness $\Delta z = L/M$. Each layer is treated as a state representing a possible location for the photon at a given step, i.e., $Z_t$ represents the “position” of a photon at step $t$. It should be noted that the position of a photon is tracked only along the $z$-axis since the state space, $S$, for $Z_t$ is created by discretizing the system along the $z$-direction. The assumption here is that the systems modeled are large enough and homogeneous enough along the horizontal dimensions that they can be treated as infinite.
The probability \( d_i^{(t)} = P(Z_t = i) \) represents the probability that a photon experienced its most recent absorption event at layer \( i \) at step \( t \), that is, the probability that a photon is “located” at this layer. In describing systems with multiple photons, \( d_i^{(t)} \) will sometimes be referred to as the population of layer \( i \).

**Figure 3.1.** (a) Illustration showing the stratification of the system into layers along with how distances between the layers are computed. The purple arrow indicates the transition probability density from layer \( i \) to layer \( j \) at an angle \( \theta \): \( dp^{(e)}(\theta)p^{(s)}(\theta, i, j)p^{(a)}(\theta) \). The transition probability \( p_{ji} \) is obtained by integrating the transition probability density over \( \theta \) from 0 to \( \pi/2 \). (b) A transition diagram for the system. The rectangles represent the states, and the arrows represent the transition probabilities.

A transition probability \( p_{ji} \) of the system is identified as the probability that a photon from layer \( i \) at step \( t - 1 \) moves to layer \( j \) at step \( t \). To move from layer \( i \) to layer \( j \), a photon must be (1) emitted from layer \( i \), (2) transmitted through all intervening layers, and (3) absorbed at layer \( j \). In this simplified model, the probabilities of these three events depend only on the zenith angle at which the photon is emitted. Thus, the total probability of transitioning from \( i \) to \( j \) can be expressed as a product of these three probabilities at each zenith angle, integrated over the full range of possible angles. Denoting the emission
probability density as \( dp^{(e)}(\theta) \), the transmission probability as \( p^{(l)}(\theta, i, j) \), and the absorption probability as \( p^{(a)}(\theta) \), the transition probability \( p_{ji} \) can be written as

\[
p_{ji} = \int_{0}^{\pi/2} dp^{(e)}(\theta) p^{(l)}(\theta, i, j) p^{(a)}(\theta). \tag{3.9}
\]

From a strictly physical perspective, the operation of the model involves, photons being sent into the medium at a constant rate, moving according to well-defined transition probabilities from layer to layer within the medium, and eventually escaping. While this escape of photons could potentially be treated as an absorbing state\(^{92-96}\), this particular model employs an alternative approach to maintain the ergodicity of the Markov chain. To this end, a related fictitious system is constructed with the same transition probabilities among the states in the medium, but with an extra dummy state. Photons entering the medium transition from the dummy state to the medium, while photons escaping the medium transition from the medium to this dummy state. This means that the photons that enter the medium are essentially the same photons that have just escaped. Since the total number of photons is conserved and there is no periodicity, this fictitious system qualifies as an ergodic Markov process, and therefore, possesses a unique, identifiable steady state distribution.

It is worth noticing that the behavior of the two systems deviate from each other outside of steady-state conditions. In the fictitious system, the number of photons entering the system at step \( t \) is necessarily equal to the number of photons that escaped at step \( t - 1 \), whereas in the physical system, the number of photons entering the system at any given step is a constant. However, the steady-state distribution of the two systems must be identical since both systems are defined by the same exact transition probabilities among the states within the medium. Thus, the analysis focuses on finding the steady state of this fictitious ergodic Markov process, which is also the steady state of the physical system. In the
discussion that follows, the dummy state is referred to as the “environment”. The complete
set of states is given by \( S = \{0, 1, \ldots, M\} \) where layer 0 represents the environment and the
remaining layers 1 through M comprise the medium (Figure 3.1).

The steady state distribution, \( \vec{d}^{(s)} \), is an eigenvector, and thus can be scaled by any
non-zero constant and still remain an eigenvector of the transition matrix, \( P \). To be
consistent with the physical picture, all steady-state distributions are normalized such that
the population of the environment layer is a constant. From a physical perspective, this is
analogous to all modeled systems experiencing the same incident light intensity. Thus, the
normalized steady-state distribution is given by

\[
\vec{d}^{(s)} \rightarrow \left(1, \frac{d_1^{(s)}}{d_0^{(s)}}, \ldots, \frac{d_M^{(s)}}{d_0^{(s)}}\right).
\tag{3.10}
\]

The emission probability density, \( dp^{(e)}(\theta) \), for a medium layer is defined as the
probability that a photon is emitted at an angle whose zenith is infinitesimally close to \( \theta \). If
\( f(\theta) \) is proportional to the probability of emission in solid angle \( d\Omega = \sin \theta \, d\theta \, d\phi \), then
integrating over azimuth angle \( \phi \) yields

\[
dp^{(e)}(\theta) = 2\pi \nu f(\theta) \sin \theta \, d\theta
\tag{3.11}
\]

where is a normalization constant that ensures a total probability of 1. That is,

\[
\nu = \frac{1}{\int_0^{\pi} 2\pi f(\theta) \sin \theta \, d\theta}.
\tag{3.12}
\]

For isotropic fluorophores, \( f(\theta) = 1 \) and \( \nu = 1/4\pi \). For dipolar fluorophores, \( f(\theta) = \sin^2 \theta \)
and \( \nu = 3/8\pi \).

Assuming that a photon traveling at a zenith angle of \( \theta \) reaches a layer, the probability
of the photon being absorbed by the layer can be determined based on the well-known Beer-
Lambert law.\textsuperscript{104,105} The absorptivity, \( \alpha \), of a medium layer is defined in terms of the
fluorophore concentration, $\rho$, and the intrinsic absorption cross-section of a fluorophore, $\sigma$, as $\alpha(\theta) = \rho \sigma(\theta)$. Recalling that $\Delta z$ is the thickness of a single layer, the path length through the entire layer can be expressed as $\Delta z/\cos \theta$. Then, the probability of transmitting through the layer is $\exp(-\alpha(\theta)\Delta z/\cos \theta)$, and the probability of being absorbed by the layer is given by

$$p^{(a)}(\theta) = 1 - \exp(-\alpha(\theta)\Delta z/|\cos \theta|).$$

(3.13)

The probability of a photon that is emitted from one layer $i$ at an angle $\theta$ transmitting to another layer $j$ is equivalent to the probability of it not being absorbed along the path from layer $i$ to layer $j$. The length of the complete path the photon travels before reaching layer $j$ depends on where precisely in layer $i$ the photon originated from. Here, the model assumes that all emissions occur at the central plane of a layer, which is a reasonable approximation in the limit where the layer-thickness is infinitesimal.

The path of a photon moving from layer $i$ to layer $j$ could be direct or could involve reflections at the medium-environment interface. The refractive index contrast between the medium and the environment determines the escape cone for any radiation emitted from the medium, i.e., photons emitted at angles outside of the escape cone are susceptible to total internal reflection. The angular range of the escape cone is defined by the critical angle, $\theta_c$, which can be determined using Snell’s law of refraction. In some cases, there is an ideal mirror placed directly beneath the luminescent medium, which provides an additional reflection pathway that can specularly reflect photons with no constraint on the incident angle.

These reflections can, in principle, change the angle of travel from $\theta$ to $\pi - \theta$ and vice versa. However, the intrinsic symmetry of the system ensures that $dp^{(e)}(\theta) = $
\[ dp^{(c)}(\pi - \theta) \) and \( p^{(a)}(\theta) = p^{(a)}(\pi - \theta) \). Thus, the calculations that follow treat \( \theta \) as a number between 0 and \( \pi/2 \), with the understanding that it could represent the angle from the vertical in either direction, so that it is unaffected by reflections.

Since direct and reflected pathways are two mutually exclusive ways for a photon emitted at angle \( \theta \) from layer \( i \) to reach layer \( j \), the total transmission probability is the sum of the direct and reflected transmission probabilities

\[
p^{(t)}(\theta, i, j) = p^{(t)}_D(\theta, i, j) + p^{(t)}_R(\theta, i, j).
\] (3.14)

While it is the sum of the two components that factors into determining the transition probability from layer \( i \) to layer \( j \) (Equation 3.9), the contribution from reflected transmission is negligible in systems where the medium is thick and highly absorbing. Figure 3.2 presents a graphical and conceptual illustration of the paths associated with direct and reflected transmission probabilities for a transition from layer \( i \) to layer \( j \).

Under the assumption that emission occurs at the center of layer \( i \), the length of the direct path from layer \( i \) to layer \( j \) is \((j - i - 1/2)\Delta z/\cos \theta\) if \( i < j \) or \((i - j - 1/2)\Delta z/\cos \theta\) if \( i > j \) (see Figure 3.1a). Thus, the direct transmission probability from layer \( i \) to layer \( j \) along an angle \( \theta \) is given by

\[
p^{(t)}_D(\theta, i, j) = \exp(-\alpha(\theta)(|i - j| - 1/2)\Delta z/\cos \theta).
\] (3.15)

Since \( \theta \) is now assumed to be between 0 and \( \pi/2 \), there is no need to consider the absolute value of \( \cos \theta \).
Figure 3.2. (a) Illustration showing transitions from layer $i$ to $j$ by a direct path (solid arrow) and by reflections (dashed arrows). (b) A probability tree representing the different paths a photon, first emitted into the lower hemisphere, can take depending on the angle at which it is emitted in that hemisphere.

Calculating $p^{(1)}_R(\theta, i, j)$ involves several considerations, depending on whether a mirror is present at the bottom of the medium, and whether $\theta$ is within the escape cone for medium-environment interfaces. For angles within the escape cone, $\theta < \theta_c$, there is only one possible reflected path, which occurs only if there is a mirror at the bottom of the medium, and the photon initially travels downward from layer $i$ and is reflected back up to layer $j$. For angles outside the escape cone, the light can initially travel either upwards or downwards, and can reflect any number of times, regardless of whether a mirror is in place.
Thus, for $\theta < \theta_c$, the probability of transmission by reflection, $p_R^{(i)}$ is either 0 (if there is no mirror at the bottom surface) or can be calculated using the path length of the downwards reflection (in the presence of a mirror). This path passes through $M - i + 1/2$ layers as it moves downwards (from layer $i$ to the mirror), and then $M - j$ layers after reflection (from the mirror to the bottom of layer $j$). In this case, the only reflection that contributes to $p_R^{(i)}$ is a single reflection of a downwards path:

$$p_R^{\downarrow}(\theta, i, j) = \exp(-\alpha(\theta)(2M - i - j + 1/2)\Delta z/\cos \theta). \quad (3.16)$$

For $\theta \geq \theta_c$, a photon can travel from layer $i$ to layer $j$ via any number of reflections originating from an initial upwards or downwards emission. It is convenient to express $p_R^{(i)}$ as the sum of four separate terms: $p_R^{\downarrow O}$, representing transmission probability along any path that starts by moving downwards and has an odd number of reflections; $p_R^{\downarrow E}$, representing transmission probability along any path that starts by moving downwards and has an even number of reflections; $p_R^{\uparrow O}$, representing transmission probability along any path that starts by moving upwards and has an odd number of reflections; and $p_R^{\uparrow E}$, representing transmission probability along any path that starts by moving upwards and has an even number of reflections.

For each of these terms, the shortest path involves either one or two reflections, while the longer paths differ in length by increments of $2M \Delta z/\cos \theta$, corresponding to two successive reflections across the entire thickness of the medium. Thus, the transmission probability along each path can be expressed as $\exp(-2\alpha(\theta)M \Delta z/\cos \theta)$ times the probability along the same path with two fewer reflections. These transmission probabilities combine to make up a geometric series, whose sum can be calculated by multiplying the first
term by $1/(1 - \exp(-2\alpha(\theta)M\Delta z/cos\theta))$. The first term in the series can be determined by calculating the transmission probability of the shortest path length beginning with an emission in the relevant direction (up or down). For example, the shortest path for a photon that is emitted downward and has an odd number of reflections was given in Equation 3.16. Following the mathematical framework developed above, the probabilities for multi-reflection transmission can be expressed according to Equations 3.17–3.20 given below.

$$p_{R}^{\downarrow O}(\theta, i, j) = \frac{\exp(-\alpha(\theta)(2M - i - j + 1/2)\Delta z/cos\theta)}{1 - \exp(-2\alpha(\theta)M\Delta z/cos\theta)}$$ (3.17)

$$p_{R}^{\downarrow E}(\theta, i, j) = \frac{\exp(-\alpha(\theta)(2M - i + j - 1/2)\Delta z/cos\theta)}{1 - \exp(-2\alpha(\theta)M\Delta z/cos\theta)}$$ (3.18)

$$p_{R}^{\uparrow O}(\theta, i, j) = \frac{\exp(-\alpha(\theta)(i + j - 3/2)\Delta z/cos\theta)}{1 - \exp(-2\alpha(\theta)M\Delta z/cos\theta)}$$ (3.19)

$$p_{R}^{\uparrow E}(\theta, i, j) = \frac{\exp(-\alpha(\theta)(2M + i - j - 1/2)\Delta z/cos\theta)}{1 - \exp(-2\alpha(\theta)M\Delta z/cos\theta)}$$ (3.20)

To summarize, for $\theta < \theta_c$, the reflected transmission only applies if there is a mirror at the bottom, and the relevant probability expression is given by Equation 3.16. For all other angles ($\theta \geq \theta_c$), the probability of reflected transmission can be expressed as a sum of the individual expressions given in Equations 3.17–3.20. The overall transmission probability can be calculated by combining the relevant reflected transmission probabilities with the direct transmission probability (Equation 3.15) according to Equation 3.14.

Thus far, the analysis of a general transition from a layer $i$ to layer $j$ was developed assuming that $i \neq j$. However, a transition from a given layer to itself ($i = j$) requires special treatment as it does not conform to the general probability rules derived above. When $i = j$, the probability of absorption on a direct path is different from the probability of absorption on reflected paths. On a direct path, a photon emitted from the center of the layer only has
half of a layer thickness in which it can be absorbed, whereas on the reflected paths, the photon can be absorbed anywhere along the full thickness of the layer. This distinction prevents the multiplication of the sum of transmission probabilities along all paths by a single absorption probability, as in the case of a general transition where $i \neq j$. The probability of self-absorption on the direct path, $p_S^{(a)}$, can be calculated according to the Beer-Lambert law for a path length of $\Delta z/2 \cos \theta$ as shown in Equation 3.21 below.

$$p_S^{(a)} = 2 \left( 1 - \exp(-\alpha(\theta)\Delta z/2 \cos \theta) \right)$$

It is worth noting that the absorption probability expression for a path length of $\Delta z/2 \cos \theta$ has been doubled to account for both the upward and downward paths at an angle of $\theta$. Thus, the transition matrix element $p_{ii}$ is given by

$$p_{ii} = \int_0^{\pi/2} d\theta (e^{(c)}(\theta) \left( p_S^{(a)}(\theta) + p_R^{(t)}(\theta, i, i) p^{(a)}(\theta) \right)).$$

In all systems considered in this study, photons are assumed to enter the medium from a source above layer 1, with some characteristic angular distribution. Thus the transition probability from the “environment” to the medium can be defined as

$$p_{j0} = \int_0^{\theta_c} dp_{\text{env}}^{(e)}(\theta) p^{(t)}(\theta, 0, j) p^{(a)}(\theta).$$

Although the integration goes up to the critical angle, the emission density may be zero for some range of angles less than the critical angle. Specifically, if light from the environment impinges on the medium at an angle $\theta_e$, then $dp_{\text{env}}^{(e)}$ is zero in the range $\theta_m < \theta < \theta_c$ where $\theta_m = \sin^{-1}\left( \frac{n_e}{n_m} \sin \theta_c \right)$. The amount of light, or the emission density, $dp_{\text{env}}^{(e)}$, from the environment will differ in the different systems considered, and will thus be described in each of the relevant sections. Out of the remaining terms, $p^{(a)}(\theta)$ is the same as described
earlier while \( p^{(i)}(\theta, 0, j) \) is different from the general term \( p^{(i)}(\theta, i, j) \). The disparity lies in the definition of path length for transitions that originate from the environment. In the context of this model, the environment layer is treated as a surface rather than a layer with finite thickness, and as such, the path for a transition originating from the environment is thought to begin at the environment-medium interface. This results in modified expressions for transmission probability that include path lengths that are integer multiples of \( \Delta z/\cos \theta \). Furthermore, light from the environment always moves in the downward direction (unless reflected at the bottom mirror). Thus, the transmission probability from the environment to layer \( j \) along the direct path is given by

\[
p^{(i)}_D(\theta, 0, j) = \exp(-\alpha(\theta)j\Delta z/\cos \theta).
\] (3.24)

For \( \theta \) within the escape cone, assuming no mirror at the bottom of the medium, the direct term is the only contributor to the total transmission probability, that is, \( p^{(i)}(\theta, 0, j) = p^{(i)}_D(\theta, 0, j) \). For \( \theta \) within the escape cone in cases with a mirror at the bottom, \( p^{(i)}(\theta, 0, j) = p^{(i)}_D(\theta, 0, j) + p^{(i)}_R(\theta, 0, j) \), where

\[
p^{(i)}_R(\theta, 0, j) = \exp(-\alpha(\theta)(2M - j)\Delta z/\cos \theta).
\] (3.25)

Since light from exterior can only enter the medium at angles within the escape cone, it is unnecessary to consider transmission probabilities for angles outside of the escape cone.

Photons that escape from the medium are said to transition to the “environment” layer. While medium-to-medium transitions can occur along any angle from 0 to \( \pi/2 \), medium-to-environment transitions can only occur at angles within the escape cone. Thus, the probability of such transitions can be defined as

\[
p_0^{(e)} = \int_0^{\theta_c} d\theta \exp^{(e)}(\theta) p^{(i)}(\theta, i, 0).
\] (3.26)
Since the photons that reach the medium-environment interface within the escape cone are assumed to escape, there is no need to define an absorption probability. In fact, this is equivalent to assuming an absorption probability of 1.

When there is no mirror at the bottom, there are two direct paths from layer \( i \) to the environment: an upward and a downward path. Thus, the transmission probability can be expressed as \( p^{(i)}(\theta, i, 0) = p^\uparrow(\theta, i, 0) + p^\downarrow(\theta, i, 0) \), where \( p^\uparrow(\theta, i, 0) = \exp(-\alpha(\theta)(i+1/2)\Delta z / \cos \theta) \) and \( p^\downarrow(\theta, i, 0) = \exp(-\alpha(\theta)(M-i+1/2)\Delta z / \cos \theta) \). When there is a mirror, there is a direct path upwards from layer \( i \) to the environment and a downward path with one reflection. In this case, \( p^{(i)}(\theta, i, 0) = p^\uparrow(\theta, i, 0) + p^R_\downarrow(\theta, i, 0) \), where \( p^\uparrow(\theta, i, 0) \) is the same as above, and \( p^R_\downarrow(\theta, i, 0) = \exp(-\alpha(\theta)(2M-i+1/2)\Delta z / \cos \theta) \).

The final type of transition to be considered in this model are transitions from the environment to itself:

\[
p_{00} = \int_0^{\theta_c} d\theta p^{(e)}_{\text{env}}(\theta) p^{(i)}(\theta, 0, 0).
\]

(3.27)

As above, only angles within the escape cone are considered, and there is no need for an absorption term. Furthermore, \( d\theta p^{(e)}_{\text{env}}(\theta) \) depends on the nature of the system and may be zero for some angles. The term \( p^{(i)}(\theta, 0, 0) \) can be defined as either \( \exp(-\alpha(\theta)2M\Delta z / \cos \theta) \) or \( \exp(-\alpha(\theta)M\Delta z / \cos \theta) \), depending on whether or not there is a mirror at the bottom, respectively.

Thus far, it has been assumed that each photon that is absorbed by a medium layer is re-emitted by that same layer. That is, there are no non-radiative losses, and the quantum yield of the fluorophores, \( \eta_Q \), is unity. However, in systems where such losses exist, these can be modeled as yet another type of transition from a medium layer to the dummy
“environment” layer. Previous literature has treated these losses as transitions to an absorbing “radiative limbo” state distinct from other environmental transitions. For the purposes of this model, it is sufficient to treat these losses using the same dummy state that collects photons that escape from the medium. The following discussions outline how the model is adapted to accommodate non-radiative losses that arise due to non-unity quantum yield of the fluorophores.

The initial transition matrix $P$ which is generated assuming unity quantum efficiency is modified through a simple scaling procedure to account for these non-radiative losses. The modified transition matrix, $P'$, is obtained by scaling the transition probabilities related to medium emission by a factor equal to the quantum yield and adding the remaining probability to the medium-to-environment transitions. The probabilities for transitions from the environment are unchanged.

$$p'_{ji} = \eta_Q p_{ji} \quad \text{for } i, j \neq 0$$

$$p'_{0i} = \eta_Q p_{ji} + (1 - \eta_Q) \quad \text{for } i \neq 0$$

$$p'_{j0} = p_{j0}$$

The transformation described by Equations 3.28–3.30 preserves the stochastic nature of the transition matrix, and the total number of photons in the fictitious system will be conserved. Additionally, the steady state of the fictitious system will still correspond to that of the physical system in which the sum of all losses (radiative and non-radiative) is equal to the number of photons entering the system.
3.3. Results and Discussion

3.3.1. Deviations from the Beer-Lambert Law

The well-known Beer-Lambert law allows one to analyze how a non-fluorescent and non-scattering body absorbs and transmits radiation. A standard experimental geometry usually consists of a collimated light source incident on a sample with known thickness, so the path length of the light as well as the incident and transmitted intensity can be quantified. From this, one can determine the absorption coefficient of a sample, or if the absorption coefficient is known, one can predict the transmitted intensity.

However, when the sample is strongly fluorescent and/or scatters light at the same wavelength as it absorbs or emits, it is not straightforward to analyze the optical response. Photons can be absorbed, re-emitted, and/or scattered multiple times before exiting the material, and the overall behavior is not well described by the Beer-Lambert law. By explicitly accounting for these more complex interactions, the Markov chain model can predict (1) the transmitted intensity, (2) the angle-dependent emission and scattering profile into the environment, and (3) the light intensity, i.e., photon population, as a function of position in the medium.

To analyze these deviations from Beer-Lambert’s law this section considers a slab of the luminescent semiconducting material, gallium arsenide (GaAs). In this system, the medium is sandwiched between two environment layers, i.e., there is no mirror at the bottom (Figure 3.3a), and monochromatic light from the environment impinges upon the medium at normal incidence, i.e., $\theta_e = 0$. Because light from the environment is received only at a single angle, the probability density is given by the Dirac delta function, $d_p_{env}(\theta) = \delta(\theta)$. Thus, the expressions derived in Section 3.2 for transitions originating at the environment
can be simplified accordingly. In this scenario, light from the environment only travels at an angle $\theta = 0$, and there is no mirror at the bottom, so the transmission probabilities can be simply expressed as

$$p_{j0} = \exp(-\alpha(0) j \Delta z)p^{(a)}(0),$$

(3.31)

and

$$p_{00} = \exp(-\alpha(0) M \Delta z).$$

(3.32)

The model treats GaAs as an isotropic absorber/emitter, and uses the absorption coefficient ($\alpha = 14247 \text{ cm}^{-1}$) and refractive index ($n_m = 3.63$) of GaAs at a wavelength (870.7 nm) corresponding to its bandgap energy at room temperature.$^{106}$ The GaAs slab is $10^{-3} \text{ cm}$ (10 microns) thick, and as such, absorbs 99.99994% of light impinging upon it at normal incidence (assuming the light is monochromatic). Figure 3.3b plots the steady-state population as a function of depth for different cases that analyze how its behavior depends on changes in quantum yield $\eta_Q$ with the incident light intensity held constant. High-quality GaAs samples have been reported to have quantum yields in excess of 90%, and in some cases, near unity.$^{107,108}$
Figure 3.3. (a) A schematic representation of the system: the medium is shown in light blue, the environment is shown in light orange, the incoming light impinging at normal incidence is shown in dark orange, and the angular range of emission from the medium is shown in dark blue. (b) Steady-state photon population as a function of depth for various photoluminescence quantum yields in a 10 µm-thick slab of GaAs illuminated at its bandgap energy.

The case of \( \eta_Q = 0 \) corresponds to when the Beer-Lambert law is strictly valid (no emission, only absorption). Here, the constant negative slope indicates an exponential decay in light intensity, consistent with typical Beer-Lambert behavior.

Deviations from the Beer-Lambert law occur when luminescent emission is enabled, i.e., \( \eta_Q \neq 0 \). As the quantum yield increases, the steady state population of each layer increases monotonically. However, for any given value of \( \eta_Q \), the population of the medium always decreases with increasing depth. This trend can be attributed to the greater exposure of the upper region of the medium to the incident radiation, which leads to higher photon populations toward the top region. The decrease of population with depth is less pronounced for higher \( \eta_Q \), but even with \( \eta_Q = 1 \), the steady state distribution is not uniform. Most significantly, the Markov model enables accurate determination of the deviation from strict exponential decay for any \( \eta_Q > 0 \), as illustrated in Figure 3.3b. Upon close inspection, one
observes subtle tilde-shaped features in the plots depicted in Figure 3.3b, especially in the $0.5 \leq \eta_Q \leq 0.99$ regime. These features are attributed to the total internal reflection of luminescent emission at the medium-environment interfaces. The internally reflected light has a higher probability of being absorbed by the layers closest to the two interfaces, leading to an increase in population near the top and bottom regions of the medium.

### 3.3.2. Kirchhoff’s Law and Violations of Angular Detailed Balance

This section examines Kirchhoff’s law of radiation, as it pertains to the various luminescent systems studied in this work. Kirchhoff’s law of radiation states that for a given energy or wavelength, the emissivity of a medium at any angle is equal to its absorptivity at the same angle, when the system is in thermal equilibrium. This is a stricter condition than a “steady state” which merely requires that the total flow of photons from the medium to the environment matches the total flow of photons from the environment to the medium. Kirchhoff’s law requires that at equilibrium, there is also a detailed balance along any given angle, i.e., the flow of photons from the medium to the environment at a certain angle must be equal to the flow of photons from the environment to the medium at that same angle. Although this detailed balance holds in equilibrium systems, and is very well approximated in non-equilibrium steady-state systems with isotropic fluorophores, it is clearly violated in non-equilibrium steady-state systems with aligned dipolar fluorophores, as demonstrated in the following discussion.

The analysis considers two types of environmental radiation that interacts with a medium. The first is an isotropic radiation field characteristic of thermal equilibrium, e.g., the interior radiation field of a blackbody cavity. Under these conditions, light is incident on the medium with a Lambertian angular profile\textsuperscript{109}, with
\[ dp^{(e)}_{\text{env}}(\theta) = \frac{2}{\sin^2 \theta_c} \cos \theta \sin \theta \, d\theta \]  

(3.33)

for angles \( \theta < \theta_c \). The second radiation source considered is light received from the solar disk, i.e., sunlight incident at normal angle to surface of the medium. In this case, the emission probability density is \( dp^{(e)}_{\text{env}}(\theta) = \nu \cos \theta \sin \theta \, d\theta \) for \( \theta \leq 0.267^\circ \) and \( dp^{(e)}_{\text{env}}(\theta) = 0 \) for \( \theta > 0.267^\circ \), where \( \nu \) is a normalization constant equal to \( n_m^2/(\pi n_e^2 \sin^2 0.267^\circ) \). Since the medium emits at all angles, but absorbs only at angles corresponding to the solar disk, its steady state is not an equilibrium.

The analysis also considers two versions of the medium, one with isotropic fluorophores and the other with dipolar fluorophores. The absorption, transmission, and emission probabilities for these are defined in Section 3.2.2. For the isotropic case, let us consider a slab of GaAs with parameters (thickness, refractive index, absorption coefficient and emission/absorption wavelength of light) as described in Section 3.3.1. For the dipolar case, let us consider cadmium selenide/cadmium sulfide (CdSe/CdS) dot-in-rod nanocrystals that are dispersed in a chloroform solution, and aligned such that their long axes are normal to the surface of the medium. The concentration of the CdSe/CdS dot-in-rod fluorophores is \( 10^{-6} \) M, the extinction coefficient of the fluorophores is \( 5 \times 10^6 \) cm\(^{-1}\) M\(^{-1}\), the wavelength of emission/absorption is taken as 615 nm, the refractive index of the medium is assumed to be equal to that of chloroform at 615 nm, i.e., 1.445, and the thickness of the medium is set to 2 cm.

In each of the four cases (combinations of Lambertian or solar incident radiation with isotropic or dipolar fluorophores) a mirror is placed at the bottom of the medium, and the refractive index of the environment is \( n_e = 1 \).
To probe the angular distribution of photons entering and leaving the system, the range of possible zenith angles, \(0 \leq \theta \leq \theta_c\), is partitioned into a number \((b_{\text{max}})\) of bins, each of size \(\Delta \theta = \theta_c/b_{\text{max}}\). These angle bins are indexed by an integer value \(b\) ranging from 1 to \(b_{\text{max}}\) such that an arbitrary bin, \(b\), contains angles from \((b-1)\Delta \theta\) to \(b\Delta \theta\). It is worth noting that for the equilibrium case, light entering the medium, upon refraction, spans the range \(\theta < \theta_c\). However, in the non-equilibrium case, the angular range of light entering the medium is narrower in comparison: \(\theta \leq \sin^{-1}\left(\left[n_e/n_m\right]\sin(0.267^\circ)\right)\). The analysis utilizes the same range of angle bins for both cases, although in the latter, the absorption corresponding to the bins in the range \(\sin^{-1}\left(\left[n_e/n_m\right]\sin(0.267^\circ)\right) < \theta \leq \theta_c\) is zero.

The emission from the medium into each individual angle bin can be calculated by identifying the relevant transition probabilities at angles within each bin. This involves partitioning the transition probabilities \(p_{0i}\) and \(p_{j0}\) so that the probability functions are integrated separately over the angular range of each bin. For \(i > 0\), \(p_{0i}(b)\) is the probability of a photon in layer \(i\) to leave the medium at an angle in bin \(b\):

\[
p_{0i}(b) = \int_{(b-1)\Delta \theta}^{b\Delta \theta} dp^{(e)}(\theta) p^{(l)}(\theta, i, 0),
\]

as in Equation 3.26. Similarly, for \(j > 0\), \(p_{j0}(b)\) is the probability of a photon from the environment to be absorbed at layer \(j\) at an angle in bin \(b\):

\[
p_{j0}(b) = \int_{(b-1)\Delta \theta}^{b\Delta \theta} dp^{(e)}(\theta) p^{(l)}(\theta, 0, j) p^{(a)}(\theta),
\]

as in Equation 3.23. The probability of light from the environment entering the medium, being reflected off the mirror at the bottom, and reemerging out of the medium without being absorbed is given by \(p_{00}(b)\). That is:
\[ p_{00}(b) = \int_{(b-1)\Delta \theta}^{b\Delta \theta} d\theta p^{e}(\theta)p^{s}(\theta,0,0), \]  

as in Equation 3.27.

Once these detailed probabilities are obtained, the total absorption and emission of the medium within each of these bins can be analyzed by summing over the contributions from all of the medium layers. In the steady state, the angle-dependent absorption of the medium at angles in bin \( b \) is

\[ a(b) = \sum_{j=0}^{M} d_{0}^{(s)} p_{j0}(b), \]  

and the angle-dependent emission of the medium at angles in \( b \) is

\[ e(b) = \sum_{i=0}^{M} d_{i}^{(s)} p_{i0}(b). \]

Because this is the steady state, it is clear that \( \sum_{b=1}^{b_{\text{max}}} a(b) = \sum_{b=1}^{b_{\text{max}}} e(b) \). However, the detailed balance predicted by Kirchhoff’s law in equilibrium would require that \( a(b) = e(b) \) for each bin \( b \).
Figure 3.4. Kirchhoff’s law analysis for the equilibrium case: (a) and (c) illustrate the two types of media considered, one that emits isotropically (a) and another that emits like a dipole (c). For both (a) and (c), the shaded orange region represents the angular range of incident light \(0 \leq \theta \leq \pi/2\) whereas the shaded dark blue region represents the angular range of light exiting the medium \(0 \leq \theta \leq \pi/2\). (b) is a polar plot of the light entering (green trace) the medium and light leaving the medium (black trace) in the steady state for the isotropic emitting medium. (d) is the same as (b) but for the dipole emitting case.

Equations 3.37 and 3.38 are plotted for the isotropic fluorophores and the dipole fluorophores in Figures 3.4b and 3.4d, respectively, for the case of an isotropic incident radiation field, i.e., the equilibrium state. One sees that the angle-dependent absorption and the angle-dependent emission are coincident which implies that Kirchhoff’s law is upheld.
Kirchhoff’s law analysis for the nonequilibrium case: (a) and (c) illustrate the two types of media considered, one that emits isotropically (a) and another that emits like a dipole (c). For both (a) and (c), the shaded orange region represents the angular range of incident light \(0 \leq \theta \leq \theta_m = \sin^{-1}\left(\frac{n_e}{n_m}\sin(0.267^\circ)\right)\) whereas the shaded dark blue region represents the angular range of light exiting the medium \(0 \leq \theta \leq \pi/2\). (b) and (d) are polar plots of the angular distribution of light leaving the medium in the steady state for systems with isotropic and dipole emitters, respectively. Incident light in both cases (not represented in the plots) spans the solar angle \(0 \leq \theta \leq 0.267^\circ\). One readily observes that the isotropic emitters emit with a Lambertian radiation pattern unlike the dipolar emitters.

In contrast, the non-equilibrium case shows that the angular distributions of the incoming and outgoing light do not match, i.e., \(a(b) \neq e(b)\). This can be seen in Figure 3.5 where the incoming light spans \(0 \leq \theta \leq 0.267^\circ\) (not pictured). Light exiting the medium for the isotropic case is shown in Figure 3.5b while the exiting light for the aligned dipolar fluorophores is shown in Figure 3.5d. It is commonly assumed that most bulk materials fluoresce in a Lambertian manner, similar to equilibrium radiation fields. It is evident that
this happens when the system is composed of isotropic fluorophores, but not when it is composed of aligned dipolar ones, at least with the medium thickness considered here. Interestingly, the anisotropy of the emission in the dipolar case is driven more by the lack of reabsorption along certain angles, rather than by the excess emission along other angles.

### 3.4. Conclusion

This Chapter demonstrates the use of an ergodic Markov model to study the steady state behavior of several optical systems. This approach relies on determining an eigenvector of the so-called transition matrix which contains a set of probabilities that define the movement of photons through the system. It has been shown through specific examples that this method yields expected results for systems that allow for an analytical solution (Beer-Lambert law or Kirchhoff’s law). This model also provides a description of steady states for which analytical solutions may not exist. The particular version of the model developed in this work assumes translational symmetry along horizontal dimensions, and only tracks the movement of photons along the z-direction. However, with further sophistication, this method can be extended to track additional variables leading to more accurate results. Transition probabilities can also be modified to consider additional features of radiation, such as near-field interactions, wavelength dependence, and deviation from perfect isotropic or sine-squared emission from the fluorophores. The versatility of this method allows it to model non-equilibrium steady-state systems without assuming equivalence of angle-dependent absorptivity and emissivity. This property, in particular, makes this approach especially useful in modeling the performance of more complex PV systems, as elaborated in Chapter 4 below.
4. LUMINESCENT SOLAR FUNNEL WITH VERTICALLY ALIGNED NANORODS

4.1. Introduction

Building upon the analysis outlined above, this chapter demonstrates how the Markov chain model can be extended to calculate detailed balance efficiencies of complex photovoltaic (PV) systems. In particular, this work highlights a novel design for a “luminescent solar funnel” that enhances the efficiency of a flat plate solar cell through redistribution of radiative energy by dipole-emitting luminophores such as semiconductor nanorods (NRs).

As mentioned above (Chapter 3), the standard “Shockley-Queisser” method for determining solar cell efficiencies assumes an equivalence between the absorptivity and the emissivity of a cell at any given angle, even when the system is not in thermal equilibrium, i.e., at any point on the I-V curve. This approximation, while perfectly reasonable for systems with purely isotropic absorption and emission, does not necessarily hold for optically anisotropic materials. The Markov chain approach overcomes this limitation by accommodating distinct radiation profiles for absorption and emission for non-equilibrium systems.

This chapter demonstrates the application of the Markov chain method in calculating limiting efficiencies of PV systems, by investigating a novel design for a luminescent PV module that is fundamentally different from traditional LSC geometries. The proposed device features a layer of vertically aligned dipole-emitting luminophores placed directly above a state-of-the-art solar cell (Figure 4.1a). The linearly-polarized absorption and emission from the NR layer enables recycling of emitted photons, while still allowing unobstructed collection of incident sunlight. The subsequent sections provide an in-depth
analysis of the module design, and elaborate on the underlying principles and mathematical foundation of the modified Markov model, which now features a PV medium as well as an external pathway that simulates current extraction from the cell.

4.2. Methods

This section outlines the methodology employed in adapting the previously developed Markov chain approach to model the performance of PV systems. In contrast to the systems analyzed in Chapter 3, this new system consists of two separate media: (1) a luminophore medium and (2) a PV medium, each with their own characteristic optical properties such as absorptivity and refractive index. Similar to the analysis presented in Chapter 3, both media are stratified into a large number of infinitesimally thin layers, and the transitions between different layers are modeled using the same principles as before.

![Figure 4.1](image)

**Figure 4.1.** (a) Schematic representation of the novel luminescent PV module. (b) The corresponding Markov chain transition diagram.

In this new system, the outgoing transitions from the environment layer represent the incident solar flux. The steady-state photon distribution in each case is normalized to ensure that the population of the environment, i.e., the outgoing flux from the environment, equals
the above-bandgap solar flux. The model assumes that the luminophore medium is bandgap-matched to the PV slab.

The following discussion outlines the emission, transmission, and absorption probabilities that determine the overall transition probabilities between different states in the system. The optical behavior of the system is defined by a set of parameters: number of luminophore medium layers \(N_L\), number of PV layers \(N_P\), luminophore absorption coefficient \(\alpha_L = A_0 \sin^2 \theta\), PV absorption coefficient \(\alpha_P\), layer thickness \((dz)\), refractive index of luminophore medium \((n_L)\), refractive index of PV medium \((n_P)\), and luminophore/PV bandgap \(E_g\). For the purposes of this study, it is assumed that \(n_E \leq n_L \leq n_P\), although the model can potentially accommodate other cases that do not adhere to this relationship.

The total probability for a general transition from an arbitrary layer \(i\) to an arbitrary layer \(j\) can be expressed as a product of emission, transmission, and absorption probabilities at each zenith angle, integrated over the full range of possible angles. As outlined in Section 3.2.2, the transition probability \(p_{ji}\) can be expressed as

\[
p_{ji} = \int_0^{\theta_{\text{lim}}} dp^{(e)}(\theta)p^{(t)}(\theta, i, j)p^{(a)}(\theta).
\]  

(4.1)

where \(dp^{(e)}(\theta)\), \(p^{(t)}(\theta, i, j)\), \(p^{(a)}(\theta)\) denote the emission probability density, the transmission probability, and the absorption probability, respectively. The upper bound of the zenith angle, \(\theta_{\text{lim}}\), represents the maximum zenith angle at which a photon could be emitted from layer \(i\) and be absorbed at layer \(j\). Certain special cases exist where the transition probability deviates from this general formula, and they will be discussed in detail later on.
The emission probability density for the environment layer, $d_p^{(e)}(\theta)$, is defined according to

$$d_p^{(e)}(\theta) = 2\pi \nu f(\theta) \sin \theta \cos \theta \, d\theta$$

(4.2)

where $f(\theta) = 1$ (isotropic emission) and the normalization constant $\nu = 2 / \sin^2 \theta_{\text{Sun}}$. The half-angle for incident sunlight, $\theta_{\text{Sun}}$, is equal to 0.267° when considering direct sunlight and equal to 90° when considering diffuse sunlight. The emission probability density for the luminophore medium, $d_p^{(e)}(\theta)$, can be defined according to

$$d_p^{(e)}(\theta) = 2\pi \nu f(\theta) \sin \theta \, d\theta$$

(4.3)

where $f(\theta) = \sin^2 \theta$ (dipolar emission) and the normalization constant $\nu = 3/8\pi$. Similarly, the emission probability density for the PV layer, $d_p^{(e)}(\theta)$, can be described by

$$d_p^{(e)}(\theta) = 2\pi \nu f(\theta) \sin \theta \, d\theta$$

(4.4)

where $f(\theta) = 1$ (isotropic emission) and the normalization constant $\nu = 1/4\pi$.

The probability for absorption at a medium or PV layer can be expressed as

$$p^{(a)}(\theta) = 1 - \exp(-\alpha(\theta)\Delta z/|\cos \theta|)$$

(4.5)

where $\alpha(\theta)$ is the characteristic angle-dependent absorption coefficient and $\Delta z$ is the thickness of a single infinitesimal layer. For the luminescent layer with vertically aligned NRs, $\alpha_L(\theta) = \alpha_0 \sin^2 \theta$ where the constant $\alpha_0$ is proportional to the magnitude of the overall absorptivity. The absorption coefficient for the PV medium, $\alpha_p$, has no angle-dependence as the PV is assumed to absorb and emit isotropically. No absorption coefficient is defined for the environment layer which absorbs any incident photons traveling along any angle with a 100% probability.
The probability of self-absorption for direct transitions, $p_S^{(a)}$, can be calculated by considering a path length of $\Delta z/2 \cos \theta$ according to

$$p_S^{(a)} = 2 \left( 1 - \exp(-\alpha(\theta)\Delta z/2 \cos \theta) \right). \quad (4.6)$$

The absorption probability expression for a path length of $\Delta z/2 \cos \theta$ has been doubled to account for both the upward and downward paths at an angle of $\theta$.

The refractive index contrast between different media within the system has a significant influence on the trajectory of each transition. For clarity, the direction of an emitted photon is defined by the zenith angle ($\theta$) of its travel path within its medium of origin. If a photon is refracted at either the luminophore/environment interface or the PV/luminophore interface, the subsequent angle of travel is determined based on the original zenith angle according to Equations 4.7–4.10.

$$f_{\text{ref}}^{E \rightarrow L}(\theta) = \sin^{-1} \left( \frac{n_E}{n_L} \sin \theta \right) \quad (4.7)$$

$$f_{\text{ref}}^{E \rightarrow P}(\theta) = \sin^{-1} \left( \frac{n_E}{n_P} \sin \theta \right) \quad (4.8)$$

$$f_{\text{ref}}^{L \rightarrow P}(\theta) = \sin^{-1} \left( \frac{n_L}{n_P} \sin \theta \right) \quad (4.9)$$

$$f_{\text{ref}}^{P \rightarrow L}(\theta) = \sin^{-1} \left( \frac{n_P}{n_L} \sin \theta \right) \quad (4.10)$$

Therefore, for transitions where emission and absorption occur within different media, the zenith angle ($\theta$) in Equations 4.5 and 4.6 should be replaced by $f_{\text{ref}}^{M_1 \rightarrow M_2}(\theta)$, where $M_1$ and $M_2$ represent the emitted and absorbed media, respectively. The refractive index of the environment is assumed to be 1.

The overall probabilities for $i$ to $j$ transitions ($p_{ji}$) can be categorized into three classes based on the nature of their travel paths: (1) direct transitions, (2) single reflections off the
bottom mirror, and (3) multiple reflections via total internal reflection. For clarity, the probabilities corresponding to the three classes are defined in separate matrices whose sum represents the overall transition matrix according to

$$p_{ji} = p_{ji}^{(D)} + p_{ji}^{(R1)} + p_{ji}^{(TIR)}.$$  \hfill (4.11)

The transmission probabilities for direct transitions between the three media, $p_{D}^{(t)}(\theta, i, j)$, can be expressed according to Beer’s law, as shown below. Since the system features multiple layers with distinct absorption coefficients, the attenuation of light through the different media must be treated separately. Equations 4.12–4.19 describe the transmission probability for a direct transition from an arbitrary layer $i$ to an arbitrary layer $j$, where E, L, and P represent the environment, the luminophore medium, and the PV cell, respectively.

$$p_{E \rightarrow L(D)}^{(t)}(\theta, j) = \exp \left[ -\alpha_L \left( f_{\text{ref}}^{E \rightarrow L}(\theta) \right) (j - 2)\Delta z/\cos(f_{\text{ref}}^{E \rightarrow L}(\theta)) \right]$$  \hfill (4.12)

$$p_{E \rightarrow P(D)}^{(t)}(\theta, j) = \exp \left[ -\alpha_L \left( f_{\text{ref}}^{E \rightarrow L}(\theta) \right) N_L \Delta z/\cos(f_{\text{ref}}^{E \rightarrow L}(\theta)) \right. - \alpha_p(j - 2 - N_L)\Delta z/\cos(f_{\text{ref}}^{E \rightarrow P}(\theta)) \right]$$  \hfill (4.13)

$$p_{L \rightarrow E(D)}^{(t)}(\theta, i) = \exp \left[ -\alpha_L(\theta)(i - 1.5)\Delta z/\cos \theta \right]$$  \hfill (4.14)

$$p_{L \rightarrow L(D)}^{(t)}(\theta, i) = \exp \left[ -\alpha_L(\theta)(|i - j| - 0.5)\Delta z/\cos \theta \right]$$  \hfill (4.15)

$$p_{L \rightarrow P(D)}^{(t)}(\theta, i, j) = \exp \left[ -\alpha_L(\theta)(N_L + 1.5 - i)\Delta z/\cos \theta \right. \right.$$

$$- \alpha_p(j - N_L - 2)\Delta z/\cos(f_{\text{ref}}^{L \rightarrow P}(\theta)) \right]$$  \hfill (4.16)

$$p_{P \rightarrow E(D)}^{(t)}(\theta, i) = \exp \left[ -\alpha_L \left( f_{\text{ref}}^{P \rightarrow L}(\theta) \right) N_L \Delta z/\cos(f_{\text{ref}}^{P \rightarrow L}(\theta)) \right. \right.$$

$$- \alpha_p(i - N_L - 1.5)\Delta z/\cos \theta \right]$$  \hfill (4.17)
\[ p^{(1)}_{P\rightarrow L(D)}(\theta, i, j) = \exp \left[ -\alpha_L \left( f_{\text{ref}}^{P\rightarrow L}(\theta) \right) (N_L + 1 - j) \Delta z / \cos \left( f_{\text{ref}}^{P\rightarrow L}(\theta) \right) \right. \]

\[ \left. - \alpha_p (i - N_L - 1.5) \Delta z / \cos \theta \right] \] (4.18)

\[ p^{(1)}_{P\rightarrow P(D)}(\theta, i, j) = \exp(-\alpha_p |i - j| - 0.5) \Delta z / \cos \theta \] (4.19)

The transmission probabilities for transitions involving a single mirror reflection can be calculated similarly, according to Equations 4.20–4.28.

\[ p^{(1)}_{E\rightarrow E(R1)}(\theta) = \exp \left[ -2\alpha_L \left( f_{\text{ref}}^{E\rightarrow L}(\theta) \right) N_L \Delta z / \cos \left( f_{\text{ref}}^{E\rightarrow L}(\theta) \right) \right. \]

\[ \left. - 2\alpha_p N_p \Delta z / \cos \left( f_{\text{ref}}^{E\rightarrow P}(\theta) \right) \right] \] (4.20)

\[ p^{(1)}_{E\rightarrow L(R1)}(\theta, j) = \exp \left[ -\alpha_L \left( f_{\text{ref}}^{E\rightarrow L}(\theta) \right) (2N_L + 1 - j) \Delta z / \cos \left( f_{\text{ref}}^{E\rightarrow L}(\theta) \right) \right. \]

\[ \left. - 2\alpha_p N_p \Delta z / \cos \left( f_{\text{ref}}^{E\rightarrow P}(\theta) \right) \right] \] (4.21)

\[ p^{(1)}_{E\rightarrow P(R1)}(\theta, j) = \exp \left[ -\alpha_L \left( f_{\text{ref}}^{E\rightarrow L}(\theta) \right) N_L \Delta z / \cos \left( f_{\text{ref}}^{E\rightarrow L}(\theta) \right) \right. \]

\[ \left. - \alpha_p (N_L + 2N_p + 1 - j) \Delta z / \cos \left( f_{\text{ref}}^{E\rightarrow P}(\theta) \right) \right] \] (4.22)

\[ p^{(1)}_{L\rightarrow E(R1)}(\theta, i) = \exp \left[ -\alpha_L(2N_L + 1.5 - i) \Delta z / \cos \theta \right. \]

\[ \left. - 2\alpha_p N_p \Delta z / \cos \left( f_{\text{ref}}^{L\rightarrow P}(\theta) \right) \right] \] (4.23)

\[ p^{(1)}_{L\rightarrow L(R1)}(\theta, i, j) \]

\[ = \exp \left[ -\alpha_L(2N_L + 2.5 - i - j) \Delta z / \cos \theta \right. \]

\[ \left. - 2\alpha_p N_p \Delta z / \cos \left( f_{\text{ref}}^{L\rightarrow P}(\theta) \right) \right] \] (4.24)
\[ p_{L \rightarrow P(R1)}^{(1)}(\theta, i, j) = \exp \left[ -\alpha_L(\theta)(N_L + 1.5 - i)\Delta z/\cos \theta \right. \]
\[ \quad - \alpha_p(N_L + 2N_p + 1 - j)\Delta z/\cos \left( f_{ref}^{L \rightarrow P}(\theta) \right) \]  \hspace{1cm} (4.25) 

\[ p_{P \rightarrow E(R1)}^{(1)}(\theta, i) = \exp \left[ -\alpha_L \left( f_{ref}^{P \rightarrow L}(\theta) \right) N_L\Delta z/\cos \left( f_{ref}^{P \rightarrow L}(\theta) \right) \right. \]
\[ \quad - \alpha_p(N_L + 2N_p - i + 1.5)\Delta z/\cos \theta \]  \hspace{1cm} (4.26) 

\[ p_{P \rightarrow L(R1)}^{(1)}(\theta, i, j) = \exp \left[ -\alpha_L \left( f_{ref}^{P \rightarrow L}(\theta) \right) (N_L + 1 - j)\Delta z/\cos \left( f_{ref}^{P \rightarrow L}(\theta) \right) \right. \]
\[ \quad - \alpha_p(N_L + 2N_p - i + 1.5)\Delta z/\cos \theta \]  \hspace{1cm} (4.27) 

\[ p_{P \rightarrow P(R1)}^{(1)}(\theta, i, j) = \exp(-\alpha_p(2N_L + 2N_p + 1.5 - i - j)\Delta z/\cos \theta) \]  \hspace{1cm} (4.28) 

Transition probabilities for direct (D) and single-reflection (R1) transitions can be calculated by integrating the product of \( dp^{(e)}(\theta) \), \( p^{(1)}(\theta, i, j) \), and \( p^{(2)}(\theta) \) over the range \( 0 \leq \theta \leq \theta_{\text{lim}} \). For transitions that do not involve any refractions, i.e., transitions within a certain medium, or transitions from a lower refractive index medium to a higher refractive index medium, \( \theta_{\text{lim}} = \pi/2 \). However, for transitions from a higher refractive index to a lower refractive index, \( \theta_{\text{lim}} = \theta_{\text{crit}}^{n_1 \rightarrow n_2} = \sin^{-1}(n_2/n_1) \).

Calculating the transition probabilities for transitions involving multiple reflections via total internal reflection (TIR) is considerably more complex due to the infinite number of possible transitions. The total probability of TIR transitions between two arbitrary layers at a given emission angle can be calculated by considering an infinite series of exponentially decreasing transmission probabilities.
\[ p_{ji}^{(\text{TIR})}(\theta, i, j) = \int_0^{\theta_{\text{lim}}} \left[ dp^{(e)}(\theta) \sum p_{\text{TIR}}^{(1)}(\theta, i, j) p^{(a)}(\theta) \right] \quad (4.29) \]

The contrasting refractive indices of the luminophore and PV media results in two distinct TIR modes: (1) reflections between the E-L interface and the bottom mirror, and (2) reflections between the L-P interface and the bottom mirror. Thus, the total transmission probability along a given emission angle can be expressed as

\[ \sum p_{\text{TIR}}^{(1)}(\theta, i, j) = \sum p_{\text{TIR1}}^{(1)}(\theta, i, j) + \sum p_{\text{TIR2}}^{(1)}(\theta, i, j). \quad (4.30) \]

The transition probabilities corresponding to each mode can be further divided into four groups depending on the directions of emission and absorption as shown in Equations 4.31 and 4.32.

\[ \sum p_{\text{TIR1}}^{(1)}(\theta, i, j) \]
\[ = \sum p_{\text{TIR1}}^{(\uparrow \downarrow)}(\theta, i, j) + \sum p_{\text{TIR1}}^{(\downarrow \uparrow)}(\theta, i, j) + \sum p_{\text{TIR1}}^{(\downarrow \downarrow)}(\theta, i, j) \quad (4.31) \]

\[ \sum p_{\text{TIR2}}^{(1)}(\theta, i, j) \]
\[ = \sum p_{\text{TIR2}}^{(\uparrow \downarrow)}(\theta, i, j) + \sum p_{\text{TIR2}}^{(\downarrow \uparrow)}(\theta, i, j) + \sum p_{\text{TIR2}}^{(\downarrow \downarrow)}(\theta, i, j) \quad (4.32) \]

Equations 4.33–4.35 provide a detailed description of the individual terms that make up each TIR transmission probability.

\[ f_{\text{TIR1}}^{L}(\theta) = (N_{\text{L}} \alpha_{\text{L}}(\theta) d\theta) / \cos \theta + (N_{\text{p}} \alpha_{\text{p}}) / \cos \left( f_{\text{ref}}^{\text{L-P}}(\theta) \right) \quad (4.33) \]

\[ f_{\text{TIR1}}^{P}(\theta) = \left( N_{\text{L}} \alpha_{\text{L}} \left( f_{\text{ref}}^{\text{P-L}}(\theta) \right) d\theta \right) / \cos \left( f_{\text{ref}}^{\text{P-L}}(\theta) \right) + (N_{\text{p}} \alpha_{\text{p}}) / \cos \theta \quad (4.34) \]

\[ f_{\text{TIR2}}(\theta) = (N_{\text{p}} \alpha_{\text{p}}) / \cos \theta \quad (4.35) \]
$$\sum_{p_{L \rightarrow L}^{(\text{TIR1})\uparrow}}(\theta, i, j)$$

$$= \exp \left[ -\alpha_L(\theta)(i + N_L - j - 0.5)\Delta z/\cos \theta \right. $$

$$\left. - \alpha_p N_p \Delta z/\cos (f^L_{\text{ref}, P}(\theta)) \right] \exp \left( -f^L_{\text{TIR1}}(\theta) \right)$$

$$/ \left[ 1 - \exp \left( -2f^L_{\text{TIR1}}(\theta) \right) \right]$$

(4.36)

$$\sum_{p_{L \rightarrow L}^{(\text{TIR1})\uparrow}}(\theta, i, j)$$

$$= \exp \left[ -\alpha_L(\theta)(i + j - 3.5)\Delta z/\cos \theta \right] $$

$$/ \left[ 1 - \exp \left( -2f^L_{\text{TIR1}}(\theta) \right) \right]$$

(4.37)

$$\sum_{p_{L \rightarrow L}^{(\text{TIR1})\downarrow}}(\theta, i, j)$$

$$= \exp \left[ -\alpha_L(\theta)(2N_L + 2.5 - i - j)\Delta z/\cos \theta \right. $$

$$\left. - 2\alpha_p N_p \Delta z/\cos (f^L_{\text{ref}, P}(\theta)) \right] \exp \left( -f^L_{\text{TIR1}}(\theta) \right)$$

$$/ \left[ \exp \left( -2f^L_{\text{TIR1}}(\theta) \right) - 1 \right]$$

(4.38)

$$\sum_{p_{L \rightarrow L}^{(\text{TIR1})\downarrow}}(\theta, i, j)$$

$$= \exp \left[ -\alpha_L(\theta)(n_L + j - i - 0.5)\Delta z/\cos \theta \right. $$

$$\left. - \alpha_p N_p \Delta z/\cos (f^L_{\text{ref}, P}(\theta)) \right] \exp \left( -f^L_{\text{TIR1}}(\theta) \right)$$

$$/ \left[ 1 - \exp \left( -2f^L_{\text{TIR1}}(\theta) \right) \right]$$

(4.39)
\[ \sum_{\theta, i, j} p^{(\text{TIR1})\uparrow\downarrow}_{L\rightarrow P}(\theta, i, j) \]
\[ = \exp \left[ -\alpha_L(\theta)(i - 1.5)\Delta z/\cos \theta \right. \]
\[ \left. - \alpha_p(N_L + N_P + 1 - j)\Delta z \right] \exp \left( -f_{\text{L-P}}^{\text{L-P}}(\theta) \right) \]
\[ / \left[ 1 - \exp \left( -2f_{\text{L-P}}^{\text{L-P}}(\theta) \right) \right] \] (4.40)

\[ \sum_{\theta, i, j} p^{(\text{TIR1})\downarrow\uparrow}_{L\rightarrow P}(\theta, i, j) \]
\[ = \exp \left[ -\alpha_L(\theta)(i - 1.5 + N_L)\Delta z/\cos \theta \right. \]
\[ \left. - \alpha_p(j - N_L - 2)\Delta z/\cos \left( f_{\text{ref}}^{\text{L-P}}(\theta) \right) \right] \exp \left( -f_{\text{L-P}}^{\text{L-P}}(\theta) \right) \]
\[ / \left[ 1 - \exp \left( -2f_{\text{L-P}}^{\text{L-P}}(\theta) \right) \right] \] (4.41)

\[ \sum_{\theta, i, j} p^{(\text{TIR1})\downarrow\downarrow}_{L\rightarrow P}(\theta, i, j) \]
\[ = \exp \left[ -\alpha_L(\theta)(N_L + 1.5 - i)\Delta z/\cos \theta \right. \]
\[ \left. - \alpha_p(2N_L + 2N_P + 1 - j)\Delta z/\cos \left( f_{\text{ref}}^{\text{L-P}}(\theta) \right) \right] \exp \left( -f_{\text{L-P}}^{\text{L-P}}(\theta) \right) \]
\[ / \left[ \exp \left( -2f_{\text{L-P}}^{\text{L-P}}(\theta) \right) - 1 \right] \] (4.42)

\[ \sum_{\theta, i, j} p^{(\text{TIR1})\uparrow\downarrow}_{L\rightarrow P}(\theta, i, j) \]
\[ = \exp \left[ -\alpha_L(\theta)(2N_L + 1.5 - i)\Delta z/\cos \theta \right. \]
\[ \left. - \alpha_p(N_P + j - N_L - 2)\Delta z \right] \exp \left( -f_{\text{L-P}}^{\text{L-P}}(\theta) \right) \]
\[ / \left[ 1 - \exp \left( -2f_{\text{L-P}}^{\text{L-P}}(\theta) \right) \right] \] (4.43)
\[ \sum p_{P \rightarrow L}^{(TIR1)\uparrow \uparrow}(\theta, i, j) = \exp \left[ -\alpha_L f_{ref}^{P \rightarrow L}(\theta) (2N_L + 1 - j)\Delta z / \cos (f_{ref}^{P \rightarrow L}(\theta)) - \alpha_p(N_p + i - N_L - 1.5)\Delta z / \cos \theta \right] \exp \left( -f_{TIR1}^P(\theta) \right) \left[ 1 - \exp \left( -2f_{TIR1}^P(\theta) \right) \right] \]

(4.44)

\[ \sum p_{P \rightarrow L}^{(TIR1)\uparrow \uparrow}(\theta, i, j) = \exp \left[ -\alpha_L f_{ref}^{P \rightarrow L}(\theta) (N_L + j - 2)\Delta z / \cos (f_{ref}^{P \rightarrow L}(\theta)) \right] \left[ 1 - \exp \left( -2f_{TIR1}^P(\theta) \right) \right] \]

(4.45)

\[ \sum p_{P \rightarrow L}^{(TIR1)\uparrow \uparrow}(\theta, i, j) = \exp \left[ -\alpha_L f_{ref}^{P \rightarrow L}(\theta) (N_L + 1 - j)\Delta z / \cos (f_{ref}^{P \rightarrow L}(\theta)) \right] \left[ \exp \left( -2f_{TIR1}^P(\theta) \right) \right] \left[ 1 - \exp \left( -2f_{TIR1}^P(\theta) \right) \right] - 1 \]

(4.46)

\[ \sum p_{P \rightarrow L}^{(TIR1)\downarrow \downarrow}(\theta, i, j) = \exp \left[ -\alpha_L f_{ref}^{P \rightarrow L}(\theta) (j - 2)\Delta z / \cos (f_{ref}^{P \rightarrow L}(\theta)) \right] \left[ \exp \left( -f_{TIR1}^P(\theta) \right) \right] \left[ 1 - \exp \left( -2f_{TIR1}^P(\theta) \right) \right] \]

(4.47)
\[
\sum_{p_{P \to P}^{(TIR1)\uparrow\downarrow}(\theta, i, j)} = \exp \left[ -\alpha_L \left( f_{\text{ref}P \to L}(\theta) \right) N_L \Delta z / \cos \left( f_{\text{ref}P \to L}(\theta) \right) \right. \\
\left. - \alpha_p(i - j + N_p - 0.5) \Delta z / \cos \theta \right] \exp \left( -f_{TIR1}^P(\theta) \right) \hspace{1cm} \text{(4.48)}
\]

\[
\sum_{p_{P \to P}^{(TIR1)\uparrow\downarrow}(\theta, i, j)} = \exp \left[ -2\alpha_L \left( f_{\text{ref}P \to L}(\theta) \right) N_L \Delta z / \cos \left( f_{\text{ref}P \to L}(\theta) \right) \right. \\
\left. - \alpha_p(i + j - 2N_L - 3.5) \Delta z / \cos \theta \right] / \left[ 1 - \exp \left( -2f_{TIR1}^P(\theta) \right) \right] \hspace{1cm} \text{(4.49)}
\]

\[
\sum_{p_{P \to P}^{(TIR1)\uparrow\downarrow}(\theta, i, j)} = \exp \left[ -\alpha_p(2N_L + 2N_p + 2.5 - i - j) \Delta z / \cos \theta \right] \hspace{1cm} \text{(4.50)}
\]

\[
\sum_{p_{P \to P}^{(TIR1)\uparrow\downarrow}(\theta, i, j)} = \exp \left[ -\alpha_L \left( f_{\text{ref}P \to L}(\theta) \right) N_L \Delta z / \cos \left( f_{\text{ref}P \to L}(\theta) \right) \right. \\
\left. - \alpha_p(N_p - i + j - 0.5) \Delta z / \cos \theta \right] \exp \left( -f_{TIR1}^P(\theta) \right) \hspace{1cm} \text{(4.51)}
\]

\[
\sum_{p_{P \to P}^{(TIR2)\uparrow\downarrow}(\theta, i, j)} = \exp \left[ -\alpha_p(i - j + N_p - 0.5) \Delta z / \cos \theta \right] \exp(-f_{TIR2}(\theta)) \hspace{1cm} \text{(4.52)}
\]
∑_{P\rightarrow P} p_{P\rightarrow P}^{(TIR2)\uparrow}(\theta, i, j) \\
= \exp[-\alpha_p(i + j - 2N_L - 3.5)\Delta z/\cos \theta] / [1 - \exp(-2f_{TIR2}(\theta))] \quad (4.53)

∑_{P\rightarrow P} p_{P\rightarrow P}^{(TIR2)\downarrow}(\theta, i, j) \\
= \exp[-\alpha_p(2N_L + 2N_P + 2.5 - i - j)\Delta z/\cos \theta] / [\exp(-2f_{TIR2}(\theta)) - 1] \quad (4.54)

∑_{P\rightarrow P} p_{P\rightarrow P}^{(TIR2)\downarrow\downarrow}(\theta, i, j) \\
= \exp[-\alpha_p(N_P - i + j - 0.5)\Delta z/\cos \theta]\exp(-f_{TIR2}(\theta)) / [1 - \exp(-2f_{TIR2}(\theta))] \quad (4.55)

To model the current extracted from the PV cell, a dedicated non-radiative pathway is incorporated into the Markov chain transition diagram (Figure 4.1b). The allocation of transition probability for this external pathway involves an approach similar to the treatment of non-radiative losses in section 3.2.2. The total probability of radiative transitions from each PV layer is scaled down to make accommodate the probability of a photon being extracted through the external circuit, \( P_{\text{alt}} \). This transformation is described mathematically according to Equations 4.56 and 4.57 where \( N_L \) represents the number of layers in the luminophore medium.

\[
p_{ji}^{(\text{mod})} = (1 - P_{\text{alt}}) p_{ji} \quad \text{for } N_L + 1 \leq i \leq N_L + N_P + 1; \ j > 1 \quad (4.56)
\]

\[
p_{bi}^{(\text{mod})} = (1 - P_{\text{alt}}) p_{ji} + P_{\text{alt}} \quad \text{for } N_L + 1 \leq i \leq N_L + N_P + 1 \quad (4.57)
\]

The steady-state population distribution of the system is obtained by determining the eigenvector of the modified transition matrix \( P_{\text{mod}} \) corresponding to an eigenvalue of 1 and
normalizing it such that the population of the environment layer equals the total integrated solar flux.

For a given value of $P_{alt}$, the voltage of the cell ($V$) is calculated based on the total emission from the PV layer according to the correlation between radiative emission and cell voltage used in the detailed balance analysis (Equation 2.4). The total emission from an arbitrary PV layer $i$ is given by

$$n_{emit}^{(i)} = d_S^{(i)} (1 - P_{alt}) \left[ \sum_{j=1}^{N_L+1} p_{ji} + \sum_{j=N_L+2}^{N_L+N_P+1} p_{ji}^{(TIR1)} \right] \quad (4.58)$$

where $d_S^{(i)}$ represents the normalized steady-state population of layer $i$ and $p_{ji}^{(TIR1)}$ represents the probability of a photon transitioning from layer $i$ to layer $j$ through TIR mode 1. Thus, the total PV emission be calculated by summing up the individual contributions from each PV layer according to

$$n_{emit} = \sum_{i=N_L+2}^{N_L+N_P+1} n_{emit}^{(i)} \quad (4.59)$$

In this study, a least-squares-fit method was utilized to fit the calculated PV emission to Equation 2.4 in order to determine the cell voltage. However, in theory, it may be possible to derive an analytical expression for $V$ in terms of $n_{emit}$.

The current density ($J$) from the cell can be varied by adjusting the probability of PV-to-environment transitions along the external pathway ($P_{alt}$). By tuning this probability through the full range, $0 \leq P_{alt} \leq 1$, and calculating the voltage at each point, a correlation between the current density and the voltage, i.e., the J-V characteristic curve, can be established. In order to determine the power conversion efficiency of a given system, the
maximum power obtained from the J-V plot is divided by the total incident power, following the same approach employed in the detailed balance calculations (Chapter 2).

4.3. Results and Discussion

4.3.1. Reproducing Standard Shockley-Queisser Results

To assess the accuracy of the Markov chain-based evaluation of PV performance, the limiting power conversion efficiency of a flat-plate solar cell was calculated as a function of bandgap energy, both with and without perfect angle restriction (Figure 4.2). The primary objective of this exercise was to confirm that the efficiencies calculated using the Markov chain approach agreed with the detailed balance results presented in Chapter 2. As shown in Figure 4.2, the Markov chain model perfectly replicates the efficiency trends calculated using the standard detailed balance method.

![Figure 4.2](image)

**Figure 4.2.** Limiting efficiencies for a flat plate cell (orange trace) and a flat plate cell with perfect angle restriction (green trace) calculated using the Markov chain method. The corresponding efficiency curves calculated using the standard detailed balance approach are shown by the dashed purple and blue curves, respectively. The flat plate cases were modeled using an AM1.5 G spectrum while the angle-restricted cases assume an AM1.5 D spectrum.

The observed agreement between the Markov chain and the detailed balance results comes as no surprise, considering the inherent conservation of detailed balance in Markov
chain models. However, it is worth noting that the two methods differ in their treatment of the solar cell J-V characteristics. In the conventional detailed balance approach, the extracted current density is calculated as a function of cell potential. Conversely, the Markov chain model treats the voltage as a dependent variable while adjusting the current.

4.3.2. Aligned Nanorod Layer Placed Above a Flat Plate Solar Cell

This section delves into the performance analysis of the proposed "luminescent solar funnel" using the Markov chain approach. The initial calculations focus on demonstrating the theoretical benefits of this novel device geometry by determining the optimal conversion efficiency of the device. However, as shown in the subsequent discussion, the performance of the device is contingent upon a host of parameters such as the luminophore concentration, the refractive index of the luminescent medium, and the degree of angle-restriction of emission. Therefore, a careful examination of these dependencies is required for a comprehensive understanding of the underlying photophysics of the device.

Figure 4.3 illustrates the efficiency of an integrated module with a layer of vertically aligned NRs positioned directly on top of a PV cell. Variations in efficiency of the proposed device (red trace) is plotted as a function of PV bandgap, and compared with the performance of a single-junction flat plate cell (blue trace). Both cases assume direct sunlight (AM1.5 D spectrum) and unity photoluminescence quantum yield (PLQY) for both the luminophore medium and the PV cell. The refractive index of the luminescent medium is assumed to be 1.
The results clearly indicate that the proposed module consistently outperforms an ideal flat plate solar cell across all bandgap energies. This efficiency enhancement is primarily attributed to the recycling of PV emission facilitated by the absorption and reemission from NRs. This effect increases the chemical potential within the PV material, enabling higher cell voltages and thereby improved efficiencies.

The linearly polarized absorption of the vertically aligned NRs allows them to transmit incident solar radiation with very little absorption. However, it is worth noting that due to the small but finite angular range of incident sunlight \(0 \leq \theta < 0.267^\circ\), a minute fraction of the incident photon flux is absorbed by the NR medium, leading to a slight decrease in current density. Nevertheless, this loss can be considered negligible in most cases, unless the NR dispersion reaches an exceedingly high concentration.

Although the advantage of incorporating the NR layer is apparent across all PV bandgap energies, the impact is particularly pronounced at lower bandgap values. This can be explained by the fact that when the bandgap is lower, a greater portion of the solar
spectrum can be effectively absorbed by the cell. Consequently, the photon recycling effects are scaled proportionately to the total incident flux, leading to a more noticeable increase in efficiency.

Building upon the demonstrated efficiency benefits of the proposed integrated device, the subsequent exploration delves deeper into the dependencies of efficiency on various system parameters. This section focuses specifically on the effects of varying the absorptivity and refractive index of the luminescent medium.

Figure 4.4a shows the variations in efficiency of the proposed PV module as a function of luminophore absorptivity of varying values of luminophore refractive index. In this context, the absorptivity of the luminescent layer is directly correlated to the volume density or concentration of dipole emitters in the medium. When the refractive index is equal to that of free-space \((n_L = 1)\), the efficiency initially increases with rising absorptivity, reaching a peak value of 36.8% at approximately \(A_0 = 2 \times 10^7 \text{ m}^{-1}\). This initial efficiency enhancement can be attributed to the photon recycling facilitated by the dipole-emitting luminophores, resulting in higher cell voltages. However, as the absorptivity continues to rise beyond a certain threshold, the efficiency begins to decrease. This decline is attributed to the absorption of incident solar flux by the high luminophore concentration, leading to decreased current densities from the cell and an overall reduction in efficiency, despite the voltage benefits due to photon recycling.
Figure 4.4. (a) The efficiency of the proposed device as a function of luminophore absorptivity for different values of luminophore refractive index. (b) Efficiency as a function of refractive index for different values of absorptivity. In both cases, the bandgap of the PV is held constant (1.12 eV).

For refractive index values greater than 1, similar efficiency trends are observed, but with consistently higher efficiencies at each absorptivity value. This phenomenon is due to the occurrence of total internal reflection caused by the refractive index contrast between the luminescent medium and free space. The greater the contrast, the narrower the escape cone from the luminescent medium to the environment, resulting in additional photon recycling within the cell, augmenting the effects of the dipole emitters.
Additionally, a notable observation is that the maximum efficiency occurs at higher absorptivities for materials with higher refractive indices. This effect can be attributed to the stronger refraction of incident solar radiation, which modifies the angular range of incoming light to a narrower cone. As a result, the degree of absorption losses mentioned previously is minimized, allowing for a higher threshold absorptivity before losses begin to dominate.

Figure 4.4b illustrates the variation of efficiency as a function of luminophore refractive index for different values of luminophore absorptivity. The refractive index ranges up to a maximum value of 4, corresponding to the refractive index of the PV cell.

In the absence of a NR layer, the efficiency of the device increases with increasing refractive index, in agreement with the trends observed in Figure 4.4a. This behavior can be attributed to the narrowing of the escape cone for photons emitted from the cell, which leads to increased light trapping within the luminescent medium, and thereby, increased cell voltages.

In the presence of NRs, similar trends are observed, with efficiency increasing as the refractive index rises. Notably, for higher absorptivity values, the overall efficiency trends are consistently higher. However, it is worth mentioning that at higher absorptivities, the system appears to be less sensitive to changes in refractive index. In other words, the influence of higher absorptivity outweighs the impact of refractive index contrast.

The trends observed in Figure 4.4 highlight the intricate interplay between luminophore absorptivity, refractive index, and overall efficiency of the device. These findings underscore the importance of carefully optimizing the luminophore concentration and refractive index to achieve the highest possible efficiency in the proposed PV module.
Further investigations into the underlying photophysics and design parameters are warranted to unlock the full potential of this novel device architecture.

4.3.3. **Efficiency Benefits in a Real GaAs Solar Cell**

Thus far, the analysis has predominantly focused on systems with ideal performance, assuming no losses. However, real materials are susceptible to various types of loss mechanisms such as non-radiative losses (non-unity PLQY) and losses due to Auger recombination. This section shifts the focus to modeling the performance of a realistic PV material, specifically GaAs, by accounting for the non-unity quantum yield and Auger losses.

![Flowchart](image)

**Figure 4.5.** Flowchart describing the recursive algorithm used to calculate Auger recombination losses in a GaAs solar cell. The entire procedure is repeated for each value of $P_{alt}$. 

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Accounting for the non-unity quantum yield in the Markov chain implementation is relatively straightforward and has been demonstrated in Chapter 3. However, incorporating Auger recombination poses a challenge as the magnitude of Auger losses depends on the cell voltage (Equation 2.12), which is a dependent variable in the Markov chain model. Defining a probability for Auger loss transitions from the PV to the environment without prior knowledge of the cell voltage is not feasible. To overcome this challenge, a recursive algorithm is employed, initially estimating an Auger loss transition probability, and iteratively improving the estimate until it aligns with the expected value based on the resulting voltage. As illustrated by the flowchart in Figure 4.5, this iterative process is repeated for each value of $P_{alt}$ in order to generate a complete J-V curve for GaAs with accounted Auger losses.

Using the approach described above, the efficiency of a realistic GaAs cell was calculated, as illustrated in Figure 4.6. The analysis investigates the effects of restricting the angular range of emission and having a refractive index contrast between the luminophore medium and the environment on the overall efficiency of the device.
Figure 4.6. The efficiency of a 3 µM-thick GaAs solar cell plotted vs the angular range of emission. The solid traces represent an ideal GaAs slab with no Auger losses while the dashed traces represent the calculations that account for Auger losses. The black traces show just the GaAs cell with no NRs. The orange and green traces correspond to systems with a NR layer that has refractive indices 1 and 1.5, respectively.

The trends shown in Figure 4.6 align with expected behavior, demonstrating the impact of the angular range of emission on the efficiency of the GaAs cell. Consistently, it is observed that as the angular range becomes stricter, the efficiency of the cell increases. However, when Auger losses are considered, this enhancement diminishes at higher degrees of angle-restriction, and the efficiency of the device saturates at a relatively lower value as the system approaches perfect angle restriction ($\theta_{\text{emit}} = 0.267^\circ$). To assess the practical advantages of the proposed strategy, the performance of a device comprising a realistic GaAs cell and a layer of aligned NRs (dashed orange and green traces) is compared to that of a realistic GaAs cell without NRs (dashed black trace). The trends clearly demonstrate that when the degree of angle restriction is relatively low ($\sim 20^\circ \leq \theta_{\text{emit}} < 90^\circ$), the NR-integrated device outperforms the flat plate cell, even when accounting for Auger losses. Furthermore, increasing the refractive index of the luminescent medium improves both the
efficiency enhancement as well as the dynamic range of angle-restriction over which efficiency benefits can be realized.

The implementation of angle-restriction in the Markov chain model requires the angular range of certain transitions to be modified. Specifically, it alters (1) the lower bound of the angular range for TIR1 transitions and (2) the upper bound of the angular range for direct and mirror-reflected transitions from either medium to the environment. Imposing angle restriction results in the narrowing of escape cones for PV and luminophore emission, leading to an overall increase in light trapping within the device.

4.4. Conclusion

In conclusion, the proposed integrated device, consisting of a realistic GaAs cell and a layer of aligned NRs, demonstrates significant improvements in conversion efficiency compared to a single-junction flat-plate solar cell or a conventional LSC. While this method may not achieve the peak efficiencies observed in geometric concentrators or angle-restriction schemes, its implementation offers notable advantages in terms of ease and cost-effectiveness.

Despite its significant benefits, the proposed strategy is subject to certain limitations. The efficiency benefits of this device are contingent on sunlight striking the module surface at near-normal incidence. Due to the preferential absorption of light polarized parallel to the long axis of the NRs, photons arriving at more oblique angles will be initially absorbed by the NRs, leading to a reduction in PV absorption which results in lower current densities. Therefore, similar to the implementation of geometric solar concentrators or angle-restriction schemes, precise solar tracking is required for optimal functionality of the proposed device. It is worth noting, however, that increasing the refractive index of the NR
medium reduces the zenith angle of incident light passing through the medium, and alleviates the dependence on solar tracking to a certain extent.

Overall, this chapter highlights the versatility of the Markov chain approach in modeling complex PV systems. The novel design of a "luminescent solar funnel" presented here takes advantage of the non-equivalence between the angle-dependences of absorptivity and emissivity outside of thermodynamic equilibrium, resulting in superior conversion efficiencies. Although this work focuses specifically on dipole-emitting semiconductor NRs, in principle, this concept can be extended to luminescent materials with arbitrary radiation profiles.

While the Markov chain model does not assume an equivalence between the angle-dependences of the bulk absorptivity and emissivity, it does enforce the principle of microscopic reversibility, wherein the absorptivity and emissivity of a single luminophore have identical angular distributions. Exploring the potential of non-reciprocal material systems within this framework would be an exciting prospect for future research, offering new insights and promising avenues for further exploration.
5. ALIGNMENT OF COLLOIDAL SEMICONDUCTOR NANORODS USING AC ELECTRIC FIELDS

5.1. Introduction

Aligning large populations of nanorods (NRs) can be achieved through several techniques that either (1) take advantage of the self-assembling tendency of colloidal NRs into superlattices\(^6\),\(^{111-113}\) or (2) rely on external stimuli such as mechanical rubbing\(^{114}\), electric fields\(^{103,115-117}\), or magnetic fields\(^{118}\) to induce alignment along a preferred axis.

To date, there has been significant progress studying the AC field-driven alignment of colloidal SC NRs as a strategy for producing functional materials with strong electrooptic modulation of optical anisotropy, typically in the 0.5–10 kHz frequency regime.\(^{103,119}\) The underlying mechanism is based on torquing the electrostatic dipole moment in NRs—largest along the long axis—by means of an externally applied electric field, leading to collective alignment of NRs parallel to the field direction.\(^{103}\) Previous studies have attributed this electrostatic dipole moment in Cd chalcogenide NRs to an intrinsic permanent dipole moment that arises due to their non-centrosymmetric wurtzite crystal structure.\(^{120}\) Additionally, in the presence external electric fields, semiconductor NRs are susceptible to induced dipole moments that may also contribute to the overall electrostatic dipole moment.\(^{103}\)

A colloidal dispersion of NRs oscillates between aligned and randomly oriented configurations in the presence of an external AC field due to the alternating magnitude of

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field strength. Since NRs preferentially absorb light with polarization that is parallel to their long axes, the ensemble alignment and relaxation can give rise to periodic changes in absorbance,\textsuperscript{103,119,121} up to a relative change of 53\% as demonstrated by Mohammadimasoudi et al.\textsuperscript{103} In a typical geometry where the sample is excited with light that is polarized perpendicular to the applied electric field, the absorbance of the sample decreases with increasing degree of alignment. The magnitude of the AC field-driven ordering in the time-dependent absorbance signal can be used to quantify the ordering in a NR ensemble.

Recent studies have reported partial\textsuperscript{119} and quasi-complete\textsuperscript{103} alignment of colloidal NRs based on the magnitude of the field-induced relative change in absorbance. These reports, however, interpret data under the assumption that individual NRs are isolated from one another in solution, and that the ensemble optical response can be attributed to the collective behavior of the individual NRs. However, growing evidence suggest that more complex interactions may be involved in the dynamic alignment of NRs. For instance, colloidal semiconductor NRs have been shown to spontaneously self-assemble into aggregated microscale bundles in solution at concentrations as low as 1 µM.\textsuperscript{118} Moreover, several studies indicate that the energetics associated with aligning individual NRs in an externally applied field minimally counteract the thermal energy of free rotation, if at all.\textsuperscript{103,119} Instead, synergistic effects between NRs may be partially responsible for the observed alignment. In this alternative scheme, aggregated NR bundles are more polarizable by externally applied electric fields compared to individual NRs, thereby enabling the pronounced field-driven optical response that is observed.

Solution-phase self-assembly into bundles, while directly affecting the degree of alignment, is also likely to modify the absorption anisotropy and other optical properties of
colloidal NRs. For example, self-assembled NR bundles have shown increased linear dichroism when placed in strong magnetic fields, as demonstrated by Pietra et al.\textsuperscript{118} The spontaneous aggregation of NRs into bundles—even in the absence of any external fields—complicates interpretations of ordering during optical measurements. Thus, ascertaining the optical anisotropy of the predominant NR species, i.e., isolated NRs or NR bundles, is critical for accurate quantification of the degree of field-driven alignment.

The focus of this study is to investigate the alignment of colloidal CdSe/CdS core/shell NRs in the presence of AC electric fields by probing the field-driven optical response. The measured relative change in absorbance is used in conjunction with ensemble fluorescence anisotropy measurements and a statistical model based on a 3\textsuperscript{rd} order von Mises-Fisher distribution,\textsuperscript{122} i.e., a normal distribution describing 3-dimensional vector orientations, to determine the average NR orientation relative to the field axis. Additionally, this study examines how varying the NR concentration impacts the electro-optic response and ensemble anisotropy to gain further insight into the spontaneous mesoscale self-assembly.

5.2. Methods

5.2.1. Synthesis and Characterization of CdSe/CdS Nanorods

The colloidal CdSe/CdS dot-in-rod heterostructures used in this study were prepared using a seeded growth method adapted from Carbone et al.\textsuperscript{123} The as-synthesized NRs were precipitated with the addition of methanol and purified by centrifugation at 3000 RCF for 8 minutes. The resulting precipitate was further cleaned by resuspending in a mixture of hexane and methanol followed by centrifugation at 3000 RCF for 8 minutes. The final precipitate was resuspended in anhydrous hexane and stored under argon for further analysis.
Figure 5.1. (a) Transmission electron micrographs of CdSe/CdS NRs. Frequency distributions for NR length (b) and width (c) fitted with Gaussian functions (sample size = 25). The average length and width were calculated to be $(55.8 \pm 3.3)$ nm and $(5.1 \pm 0.4)$ nm, respectively. (d) Absorbance and photoluminescence (normalized) spectra for CdSe/CdS NRs (inset: PL emission from colloidal CdSe/CdS NRs). (e) X-ray diffraction (XRD) pattern of CdSe/CdS NRs. The black ticks on the bottom horizontal axes denote reflections of hexagonal CdS.
The materials properties of the CdSe/CdS NRs were characterized using transmission electron microscopy (TEM), powder X-ray diffraction (PXRD), UV-vis spectroscopy, and fluorescence anisotropy as summarized in Figure 5.1.

5.2.2. **AC Field-Driven Alignment of Colloidal Nanorod Dispersions**

The field-driven alignment of colloidal CdSe/CdS core/shell NRs was investigated by measuring their time-dependent optical response in the presence of alternating electric fields. Dodecane-based dispersions of CdSe/CdS NRs were loaded into 50 μM-thick sample cells (Figure 5.2) and exposed to uniform AC fields as depicted in Figure 5.3. A sufficiently high AC frequency (2 kHz) was chosen in order to avoid accumulation of NRs at the electrodes by ensuring that the dynamic alignment of NRs occurs at a faster time scale compared to the cell transit time of any charged species. The time-dependent optical transmittance of the samples was monitored concurrent to the field-driven alignment using a 405 nm collimated light source and a photoreceiver (Figure 5.4).

![Figure 5.2](image-url)

**Figure 5.2.** Schematic view of the sample cell used in the field-alignment studies. The cell is prepared by combining two patterned ITO-glass slides separated by a uniform spacing of 50 μm.
Figure 5.3. Schematic representation of the experimental setup used to measure the electro-optic response of colloidal CdSe/CdS NRs.

5.3. Results and Discussion

5.3.1. Interpreting the Time-Dependent Optical Response

Figure 5.4 shows the variation of optical transmission of a 2 µM dispersion of NRs in the presence of a ±7 V/µm AC field. The transmittance of the sample fluctuates in response to the periodic alignment and relaxation via rotation diffusion of NRs. At zero field strength (1), the NRs are randomly oriented in solution, and the transmittance is at a minimum (maximum absorbance). However, as the field strength gradually increases, the NRs begin to align parallel to the field direction—and perpendicular to the polarization of the incident laser beam—resulting in an overall decrease in absorbance (increase in transmittance). At peak field strength (2), the transmittance reaches a maximum, indicating that the system has reached a maximum degree of alignment corresponding to the magnitude of the applied field. The rapid alignment and relaxation of NRs which occur at a millisecond
time scale can be perceived by the naked eye as a time-averaged increase in optical transmission (Figure 5.5).

Figure 5.4. (a) Alignment of NRs in the presence of an AC field when the magnitude of the applied voltage is equal to (1) zero and (2) the peak voltage. (b) Variation of applied field strength (bottom) and concurrent percent optical transmittance (top) as a function of time for a 2 μM colloidal dispersion of CdSe/CdS NRs in the presence of a 2 kHz, ±7 V/μm AC electric field.

Figure 5.5. Overhead view of a 2 μM dispersion of CdSe/CdS NRs under UV illumination in the presence of (a) no applied field and (b) a ±24 V/μm AC field.
The magnitude of the periodic shift in absorbance is correlated with the degree of alignment in the NR ensemble: higher degrees of order lead to larger shifts in absorbance. The relative change in absorbance, \( \Delta A/A_0 \), has been proposed as a quantitative measure of ensemble alignment that is independent of external factors such as cell thickness, NR concentration, or laser power.\(^{103}\) Equation 5.1 describes \( \Delta A/A_0 \) in terms of the absorbance at peak voltage, \( A_{\text{peak}} \), and the absorbance at zero field strength, \( A_0 \).

\[
\frac{\Delta A}{A_0} = \frac{A_{\text{peak}} - A_0}{A_0}
\]  

(5.1)

**Figure 5.6.** Variation of \( \Delta A/A_0 \) as a function of field strength measured for samples with different NR concentration.

The variation of \( \Delta A/A_0 \) was recorded as a function of field strength for five different NR concentrations (Figure 5.6), and in each case, the magnitude of \( \Delta A/A_0 \) was found to increase with field strength and saturate at approximately 15 V/µm, showing excellent agreement with previous studies.\(^{103}\) However, the limiting magnitude of the optical response exhibits a strong dependence on NR concentration, with \( \Delta A/A_0 \) saturating at more negative values for samples with higher NR concentration, suggesting an overall improvement in
ordering. This trend can be attributed to inter-particle interactions that facilitate alignment, in particular, the spontaneous self-assembly of colloidal NRs into rafts or bundles, an effect that has been observed in similar colloidal systems. Increasing the NR concentration likely enhances the free-energy driving force for the formation of aggregates, resulting in an augmented electro-optic response. The existence of such aggregates can be verified through small-angle X-ray scattering (SAXS) measurements, as shown in Figure 5.7. Results show the emergence of a broad peak centered around $\sim 0.7$ nm$^{-1}$ as the NR concentration is increased, confirming the formation of aggregates, as reported by Pietra et al.

![SAXS patterns of CdSe/CdS NR colloids with varying concentration recorded at room temperature in dodecane.](image)

**Figure 5.7.** (a–c) SAXS patterns of CdSe/CdS NR colloids with varying concentration recorded at room temperature in dodecane. In order to promote aggregation of NRs, sample (c) was prepared using a 2:98 (v/v) mixture of 2-butanol (antisolvent) and dodecane. (d–f) Corresponding one-dimensional scattering plots obtained by azimuthal integration of the 2D patterns. The black traces represent the orientationally averaged form factor of NRs.

It is important to note that the field-induced optical response of NRs depends not only on their ordering in solution, but also on the ensemble optical anisotropy of the colloidal species. For example, given the same degree of order, NRs with a more ideal dipolar
absorption pattern would produce a larger shift in absorbance compared to NRs with a more isotropic absorption pattern. Therefore, quantitatively analyzing the absorption anisotropy of the colloidal species is crucial for accurate determination of the overall ordering.

5.3.2. Ensemble Optical Anisotropy Measurements

The optical anisotropy of semiconductor NRs is typically determined either by measuring the polarization-dependent PL emission from individual NRs\(^{36,38}\) or by measuring the ensemble fluorescence anisotropy\(^{36-38}\) of samples in solution. The latter approach is employed here, as it samples the entire NR ensemble\(^{36}\) and preserves any superstructures that may form in solution. In a typical experiment, a random ensemble of NRs is excited by a vertically polarized source that selectively excites transition dipoles based on the projection of these dipoles parallel to the polarization axis of excitation.\(^{36,38,58,59}\) The PL emission from excited NRs is measured at an angle of 90° relative to the excitation beam, through a vertical or horizontal polarizing filter. The ensemble fluorescence anisotropy \(r\) is defined as

\[
r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}
\]

where \(I_{\parallel}\) and \(I_{\perp}\) are the vertically and horizontally polarized emission intensities, respectively.\(^{58,59}\)

The anisotropy of a random ensemble of emitters can, in theory, range between −0.2 and 0.4 depending on (1) the intrinsic dipole moment of the optical transition and (2) depolarization due to mismatch of excitation and emission dipole moments—typically caused by rotational diffusion between the excitation and emission events. The latter effect, while prominent in dichroic dyes,\(^{58,59}\) can be regarded as negligible in semiconductor NRs since the rotational diffusion rate (\(> 1 \mu s\)), even in low-viscosity solvents at room temperature, is significantly slower compared to the fluorescence lifetime (10–50 ns).\(^{37}\)
Dilute solutions of CdSe/CdS NRs have been experimentally shown to exhibit a peak anisotropy of ~0.2 for near-band-edge excitation, and consistently lower values (~0.1) at higher energy excitation (Figure 2.3b).\textsuperscript{36-38} Samples with no optical anisotropy show values of $r = 0$, whereas ensembles of randomly oriented ideal dipoles show $r = 0.4$.\textsuperscript{58,59}

While conventional fluorescence anisotropy offers insight into the overall dipole nature of the collective absorption-reemission process, it does not, by itself, uniquely determine the independent absorption and emission anisotropies. This study introduces an alternative technique (see Appendix B) that complements conventional fluorescence anisotropy measurements, facilitating the unique characterization of the absorption dipole. This new method involves the excitation of a colloidal sample with circular-polarized light and collection of PL emission at an angle of 90° relative to the excitation axis. The ensemble anisotropy in this case ($r_{\circ}$) is calculated using the same expression as before (Equation 5.2). However, the contrasting photoselection of transition dipoles arising from the distinct polarization mode results in an altered dynamic range for anisotropy values. Random ensembles of isotropic ($r = 0$) and ideal dipole ($r = 0.4$) emitters would yield values of $r_{\circ} = 0$ and $r_{\circ} = 0.25$, respectively. Taken together, the values of $r$ and $r_{\circ}$ define a system of equations that can be solved for the absorption anisotropy and emission anisotropy independently (see Appendix B for complete derivation).

Figure 5.8a shows the conventional (solid blue markers) and circular-polarized (solid green markers) ensemble fluorescence anisotropy of CdSe/CdS NRs recorded as a function of NR concentration. The strong spectral dependence of anisotropy in semiconductor NRs requires that the ensemble anisotropy measurements be carried out at the same excitation wavelength (405 nm) as in the $\Delta A/A_0$ measurements. As evident from both trends, the
variation of ensemble anisotropy reveals a strong dependence on NR concentration which is interpreted here as three regimes of contrasting behavior.

In the dilute regime (≤ 0.125 μM), the anisotropy remains consistent and comparable to previously reported values, suggesting that NRs exist as individual isolated particles in solution. However, at intermediate concentrations (0.125–0.5 μM), both anisotropy values increase with increasing NR concentration. This positive correlation is attributed to the self-assembly of NRs leading to the formation of mesoscale structures that have more ideal transition dipoles compared to individual NRs. This hypothesis concurs with proposed colloidal-phase NR assemblies in which NRs are aggregated in a side-by-side manner so that their long axes are co-aligned. The decrease in anisotropy observed at higher concentrations (> 0.5 μM) can be attributed to multiple scattering and/or multiple reabsorption and reemission events, which are typical artifacts in ensemble anisotropy measurements when incident photons interact with more than one species before reaching the detector. In order to estimate the vertical- and circular-polarized anisotropies of the NR colloids independent of these artifacts intrinsic to the measurement, the trends observed in the 0.125–0.5 μM regime have been extrapolated (hollow markers) up to 2 μM. While this extrapolation aids further analysis provided below, it is not a rigorous assessment of the true anisotropy but, instead, a rough estimate pertaining to the limiting case where the anisotropy values continue to increase with increasing NR concentration. For the sake of simplicity, linear trendlines (on a logarithmic x-axis) were used to extrapolate the data in the high-concentration regime.
Figure 5.8. Variation of (a) ensemble fluorescence anisotropy of CdSe/CdS NRs at 405 nm and (b) corresponding absorption and emission dipole coefficients plotted against NR concentration.

While NRs exhibit strong linearly polarized absorption and emission, their optical behavior deviates from those of ideal dipoles, in part, due to features of their band structure. \cite{36} Previous studies have treated this non-ideal optical behavior by considering a linear combination of isotropic and dipole character. \cite{31,32} Using a similar approach, theoretical expressions can be derived (see Appendix B) for vertical- and circular-polarized ensemble anisotropy of NRs, where the dipole nature of absorption and emission is defined using the linear interpolation parameters $\chi_a$ and $\chi_e$ respectively. These parameters are mutually
independent and can each range from 0 to 1, with 0 representing isotropic absorption/emission and 1 representing ideal dipole absorption/emission. As detailed in Appendix B, the correlation between the ensemble anisotropies ($r$ and $r_\circ$) and the two dipole coefficients can be solved as a system of simultaneous equations to uniquely determine $\chi_a$ and $\chi_e$.

Figure 5.8b depicts the concentration-dependent trends of $\chi_a$ (purple markers) and $\chi_e$ (red markers), each calculated using measured (solid markers) as well as extrapolated (hollow markers) ensemble anisotropy data. In the dilute regime ($\leq 0.125 \mu$M), the two coefficients remain constant (~0.76) and approximately equal to one another. However, as the solutions become more concentrated—and presumably, more aggregated—$\chi_e$ begins to dominate, approaching near-unity at the highest concentration. The variation of $\chi_a$ follows a less conclusive trend: the calculated values decrease on average with increasing NR concentration, although the extrapolated values show a clear increase.

### 5.3.3. Quantifying the Degree of Order

The measured $\Delta A/A_0$ and ensemble anisotropy data were translated into a quantitative measure of the orientational order using a statistical model that correlates $\Delta A/A_0$ with (1) the intrinsic absorption anisotropy of the colloidal species and (2) the degree of field-driven macroscale ordering. In this context, the absorbing species could be either individual isolated NRs or self-assembled NR bundles: the model simply assumes an arbitrary luminophore defined by its intrinsic optical dipole.
Figure 5.9. (a) Orientation of an arbitrary emitter ($r$) and applied field direction ($\mu$) defined in terms of zenith ($\theta$) and azimuth ($\varphi$) angles based on a Cartesian coordinate system. The axis of optical excitation polarization lies along the X–Z plane. The emitter could be an individual isolated NR or a self-assembled NR bundle (inset). (b) Average deviation angle of emitters relative to the field axis (solid red trace) and standard deviation (shaded region) plotted as a function of the parameter $\kappa$ for an ensemble of NRs modeled using a 3rd order von Mises-Fisher distribution.

The collective ordering of absorbers along the axis of the driving AC field is modeled using a 3rd order von Mises-Fisher distribution. The probability ($f_p$) of an absorber being oriented along an arbitrary direction ($r$) can be expressed according to
\[ f_p(r; \mu, \kappa) = \frac{\kappa}{2\pi(e^\kappa - e^{-\kappa})} \exp(\kappa \mu^T r) \] 

(5.3)

where the parameters \( \mu \) and \( \kappa \) represent, respectively, the direction of the externally applied field and the so-called focus factor. The parameter \( \kappa \) can take on any value from 0 (randomly oriented ensemble of emitters) to infinity (perfectly aligned ensemble of emitters) and is directly correlated with the average deviation angle (\( \bar{\theta} \)) of the emitters relative to the unit vector \( \mu \) (Figure 5.9b).

According to Beer’s law, the absorbance (A) of a colloidal dispersion of nanoparticles can be expressed as

\[ A = \left( \frac{N A}{\ln 10} \right) \bar{\sigma} c l \] 

(5.4)

where \( c \) is the concentration, \( l \) is the path length, and \( \bar{\sigma} \) is the average attenuation cross section.\textsuperscript{124} This formalism can be adapted to calculate the absorbance of an ordered ensemble of NRs or NR bundles, considering the angle-dependent absorption cross section of individual absorbers. If each particle behaves as an ideal dipole absorber, the attenuation cross section (\( \sigma \)) of an arbitrarily oriented absorber excited by linearly polarized light (along the XZ plane in Figure 5.9a) is related to its zenith (\( \theta \)) and azimuth (\( \varphi \)) angles according to

\[ \sigma(\theta, \varphi) = k \sin^2 \theta \cos^2 \varphi \] 

(5.5)

where \( k \) represents a proportionality constant. The average attenuation cross section of an ensemble (\( \bar{\sigma} \)) can be calculated according to

\[ \bar{\sigma}(\kappa) = \int_0^{2\pi} \int_0^{\pi} f_p(\theta, \varphi) \sigma(\theta, \varphi) d\theta \, d\varphi \] 

(5.6)

by integrating the single-particle attenuation cross section (\( \sigma \)) weighted by the normalized probability density of orientation in 3D space (\( f_p \)). The angles \( \theta \) and \( \varphi \) represent the zenith
and azimuth angles of an arbitrary absorber, respectively. Combining Equations 5.4 and 5.6 gives

\[ A = \left( \frac{N_A c l}{\ln 10} \right) \int_0^{2\pi} \int_0^\pi f_p(\theta, \varphi)\sigma(\theta, \varphi)\,d\theta\,d\varphi \quad (5.7) \]

which describes the ensemble absorbance \( A \) in terms of concentration \( c \), path length \( l \), and single-particle cross section \( \sigma \).

Substituting for absorbance in Equation 5.1 negates the dependence on concentration and path length, giving the expression

\[ \frac{\Delta A}{A_0} = \frac{\sigma(\kappa) - \sigma(\kappa = 0)}{\bar{\sigma}(\kappa)} \quad (5.8) \]

which can be used to calculate the relative change in absorbance \( \Delta A/A_0 \) as a function of the focus factor \( \kappa \).

The predicted \( \Delta A/A_0 \) decreases with increasing order and saturates at a minimum value as the system approaches complete alignment \( (\kappa \to \infty) \), i.e., when the transition dipoles align perpendicular to the polarization axis of the excitation. For an ensemble of ideal dipoles, this limiting value of \( \Delta A/A_0 \) would be equal to \(-1\) due to the complete absence of an absorption cross section when fully aligned \((\bar{\sigma}(\infty) = 0)\). In the case of real NRs, however, the correlation between \( \kappa \) and \( \Delta A/A_0 \) is less trivial as their optical behavior deviates from that of ideal dipoles.

In order to approximate the angle-dependent absorption cross section of a real NR, the single-particle absorption cross section of an ideal dipole (Equation 5.5) can be modified according to

\[ \sigma(\theta, \varphi) = k [\chi_a \sin^2 \theta \cos^2 \varphi + 1 - \chi_a] \quad (5.9) \]
where the aforementioned parameter, \( \chi_a \) (0 \leq \chi_a \leq 1), describes the dipole character of an individual absorber, i.e., how closely its absorption resembles that of an ideal dipole (\( \chi_a = 1 \)) or an isotropic emitter (\( \chi_a = 0 \)).

The correlation between \( \Delta A/A_0 \) and \( \kappa \) (Equation 5.8) can be used to calculate the degree of order in each sample in terms of the average (\( \bar{\theta} \)) and statistical standard deviation (SD) of the deviation angle (\( \theta \)) of emitters relative to the field axis. Table 5.1 summarizes the limiting \( \Delta A/A_0 \), vertical- and circular- polarized ensemble anisotropy, and maximum degree of order for each sample. Additionally, for NR concentrations above 0.5 \( \mu \text{M} \), the values of \( \bar{\theta} \) and SD estimated using extrapolated ensemble anisotropy data (hollow markers in Figure 5.8a) are also included.

### Table 5.1. Summary of measured and extrapolated results.

<table>
<thead>
<tr>
<th>NR conc. (( \mu \text{M} ))</th>
<th>Limiting ( \Delta A/A_0 )</th>
<th>Anisotropy (vertical)</th>
<th>Anisotropy (circular)</th>
<th>( \bar{\theta} \pm \text{SD (°)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Extrapolated</td>
<td>Measured</td>
<td>Extrapolated</td>
</tr>
<tr>
<td>0.125</td>
<td>-0.142</td>
<td>0.1036</td>
<td>0.0982</td>
<td>0.0758</td>
</tr>
<tr>
<td>0.25</td>
<td>-0.170</td>
<td>0.1299</td>
<td>0.1406</td>
<td>0.1038</td>
</tr>
<tr>
<td>0.5</td>
<td>-0.210</td>
<td>0.1884</td>
<td>0.1830</td>
<td>0.1540</td>
</tr>
<tr>
<td>1</td>
<td>-0.293</td>
<td>0.1843</td>
<td>0.2254</td>
<td>0.1522</td>
</tr>
<tr>
<td>2</td>
<td>-0.424</td>
<td>0.1505</td>
<td>0.2678</td>
<td>0.1251</td>
</tr>
</tbody>
</table>

In the regime where anisotropy measurements are free of scattering artifacts (\( \leq 0.5 \mu \text{M} \)), the average deviation angle decreases with increasing NR concentration, suggesting that macroscopic field-driven ordering improves as the degree of mesoscale self-assembly is increased. That is, it appears that NR aggregates align more easily, and order more completely compared to individual isolated NRs.

At higher NR concentrations (\( > 0.5 \mu \text{M} \)), the ensemble anisotropy values—and thereby, the dipole coefficients—are affected by scattering and/or reabsorption of
fluorescent emission. While measures were taken to reduce the impact of these artifacts, specifically, by using a narrow cuvette with a shorter fluorescence path length (\(\sim 2\) mm), it should be noted that these artifacts may still influence the final analysis. To correct for this potential complication, the average deviation angles were re-calculated using extrapolated ensemble anisotropy data. As summarized in the last two columns of Table 5.1, this correction appears to lower the degree of ordering for NR concentrations above 0.5 \(\mu\)M relative to the corresponding fitted values. Nevertheless, the extrapolated degree of order continues to increase as a function of NR concentration.

The formation of NR bundles was further investigated by studying the effects of colloidal stability on the optical anisotropy of NR dispersions. In this study, three samples with the same exact NR concentration (2 \(\mu\)M) were prepared using varying solvent-to-antisolvent ratios in order to promote varying degrees of aggregation. The ensemble anisotropy of these samples was found to increase with increasing antisolvent concentration (decreasing colloidal stability), consistent with the dependence on NR concentration discusses above.

Overall, these results support the hypothesis that the electro-optic response arises due to separate contributions from (1) the optical anisotropy of mesoscale NR assemblies that form in the absence of applied fields and (2) macroscopic ordering imposed by the electrostatic forces of the driving AC field. The greater magnitude of \(\Delta A/A_0\) at higher NR concentrations is attributed simultaneously to an increase in the absorption anisotropy of the emitting species, i.e., the formation of NR bundles, as well as a greater susceptibility of these bundles to field-driven ordering. While the magnitude of the experimentally measured \(\Delta A/A_0\) in this study is comparable with previous reports,\(^{103}\) the calculated degree of NR
alignment is considerably lower. The disparity lies in the treatment of individual absorbers: instead of assuming colloidal NRs to be individual isolated particles, this analysis treats them as aggregated bundles with varying degrees of characteristic concentration-dependent optical anisotropy.

5.4. Conclusion

In conclusion, this work demonstrates the AC field-driven mechanical alignment of colloidal CdSe/CdS NR dispersions by measuring concurrent changes in their optical transmission. Two distinct scales of interaction that give rise to the macroscopic optical response are identified in this study: (1) the spontaneous mesoscale self-assembly of colloidal NRs into bundles with optical anisotropy greater than that of ensembles of individual NRs and (2) the macroscale ordering of NR assemblies along the direction of the applied driving field. Ensemble optical anisotropy measurements show that aggregated NR assemblies are more anisotropic compared to isolated NRs and, therefore, provide an enhanced electro-optic response. A key insight from this study is that the field-driven relative change in absorbance depends not only on the degree of NR alignment, but also on the optical anisotropy of the absorbing species—i.e., isolated NRs or NR assemblies. By interpreting the field-driven optical response of NR ensembles using a statistical model, the degree of order in each case was calculated in terms of the average emitter orientation relative to the field axis. Results show a consistent improvement in macroscopic alignment with increasing NR concentration, with a minimum average deviation angle of 36.2° based on the extrapolated values for anisotropy. Additionally, there is evidence to suggest that NR bundles are more responsive to field-driven alignment compared to individual NRs. The insights from this work provide a fundamental basis for quantifying the AC field-driven
ordering of colloidal NRs and may further aid the design of optoelectronic devices with aligned anisotropic nanocrystals.
6. CONCLUSIONS

In summary, this dissertation has explored the utilization of optically anisotropic nanomaterials as a strategy to enhance the efficiency of photovoltaic (PV) energy conversion. The overarching theme is centered around leveraging the linearly polarized absorption and emission from luminescent semiconductor nanorods (NRs) to modify the entropy of the outgoing radiation field in a PV module. Through the exploration of four major chapters, each contributing to this theme, this dissertation outlines key theoretical and experimental results that provide insight into the ensemble optical anisotropy of aligned NR arrays as it pertains to their integration into next-generation PV devices.

Chapter 2 delved into a detailed balance analysis of a luminescent solar concentrator (LSC) featuring vertically aligned dipole-emitting NRs. This study demonstrated the potential for improving the efficiency of an LSC by modifying the angular distribution of radiation leaving the device through absorption and reemission from NRs. Specifically, the findings showed that Stokes shift losses in a conventional LSC can be partially overcome by using aligned dipole emitters. Moreover, the results underscored the anticipated efficiency improvements in realistic device implementations, while accounting for various losses associated with the PV material as well as non-idealities in the optical behavior of NRs.

Chapter 3 introduced a statistical method based on ergodic Markov chains to model absorption and photoluminescence in optical nanomaterials. This model provides valuable insight into the steady-state behavior of various optical systems, including cases where analytical solutions may not exist. This chapter demonstrates the application of the Markov chain method to investigate the attenuation of light intensity through an absorbing material (Beer-Lambert law) and the equivalence between the angle-dependent absorptivity and
emissivity in a medium at thermal equilibrium (Kirchhoff’s law). The versatility of this approach accommodates the incorporation of additional variables, enabling the characterization of more complex nanophotonic systems.

Chapter 4 focused on the utilization of the Markov chain model to analyze the performance of a NR-integrated “luminescent solar funnel”. In this novel device geometry, a layer of vertically aligned NRs is placed directly above the PV cell, in contrast to a conventional LSC where the luminophore medium is adjacent to the PV. The functionality of this device relies on the recycling of PV emission by the NR layer which enhances the cell voltage. This study highlighted the versatility of the Markov chain approach in being able to model complex optical systems that do not conform to an equivalence between the angle-dependent absorptivity and emissivity.

Chapter 5 investigated the AC electric field-driven alignment of colloidal NRs as a strategy for producing highly anisotropic optical nanocomposites. The main focus of the study was to quantify the degree of alignment by interpreting the field-induced optical response of NR dispersions in terms of their intrinsic optical anisotropy. This work highlighted the spontaneous solution-phase aggregation of NRs into mesoscale assemblies and its impact on the ensemble optical anisotropy and the degree of alignment. The results of this study provided valuable insight into the application of field-driven ordering in the design and fabrication of optoelectronic devices that utilize aligned anisotropic nanocrystals.

Overall, the findings presented in this dissertation highlight the role of manipulating the light-matter interaction at the nanoscale in developing ultra-high-efficiency PV technologies. This work contributes to the broader understanding of nanostructured PV systems and serves as a foundation for future innovations in the field.
REFERENCES


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81. van de Groep, J.; Sheldon, M. T.; Atwater, H. A.; Polman, A. Thermodynamic theory of the plasmolectric effect. Scientific Reports 2016, 6, 23283.


6.1. MATLAB Code for Calculating Detailed Balance Efficiency of NR LSCs

```matlab
% CONSTANTS & PARAMETERS
h = 6.62607004*10.^-34; % (J s)
c = 2.99792458*10.^8; % (m s^-1)
k_B = 1.38064852*10.^-23; % (J K^-1)
q = 1.6021765*10.^-19; % (C)
T_c = 300; % (K)
a = 1; % absorptivity of luminophore layer
e = 1; % emissivity of luminophore layer
theta_emit = deg2rad(0.267); % (rad)
dipole = 0; % 0 = isotropic; 1 = dipole
sol_spec = 1; % 0 = AM1.5G; 1 = AM1.5D
E_g = linspace(0.50*q,2.50*q,101); % band gap energy (J)
dE = linspace(0.000*q,0.000*q,1);

% COMMONLY USED EXPRESSIONS
int1 = integral(@(phi) phi.^0,0,2*pi);
int2 = integral(@(theta) cos(theta).*sin(theta),0,theta_emit);
if dipole == 1
    int3 = integral(@(theta) cos(theta).*(sin(theta)).^3,0,theta_emit);
    I = integral(@(theta) (sin(theta)).^2,0,theta_emit);
else
    int3 = int2;
    I=1;
end
const1 = (2*(k_B*T_c).^3)/(h.^3*c.^2); %[Commonly used constant]

% IMPORTING SOLAR SPECTRA
solardata = importsolardata('astmg173.xlsx');
wavelength = solardata(:,1);
if sol_spec == 0
    power = solardata(:,3);
elseif sol_spec == 1
    power = solardata(:,4);
end
photons = (power*1e-9.*wavelength)/(h*c);
photons_interp = interp1(wavelength,photons,280:0.001:4000);
power_interp = interp1(wavelength,power,280:0.001:4000);
tot_inc_power = trapz(280:0.001:4000,power_interp);

% CALCULATING I-V CHARACTERISTICS & EFFICIENCY
V_OC = zeros(length(E_g),length(dE)); % preallocating V_OC array
J_SC = zeros(length(E_g),length(dE)); % preallocating J_SC array
P_max = zeros(length(E_g),length(dE)); % preallocating max power array
eta = zeros(length(E_g),length(dE)); % preallocating efficiency array
for i = 1:length(E_g) % scanning bandgap energy values
    for j = 1:length(dE) % scanning dE values
        Eint = E_g(i)+dE(j); % intermediate energy
        x_g = E_g(i)/(k_B*T_c); % converting Eg (J) to xg
        x_g^int = Eint/(k_B*T_c); % intermediate xg
        L_int = (1e9*h*c)/Eint; % wavelength corresponding to intermediate energy (nm)
        L_g = (10.^9*h*c)/E_g(i); % (nm)
        N_abs_1 = a*trapz(280:0.001:L_int,interp1(wavelength,photons,280:0.001:L_int));
        if dE(j) == 0
            N_abs_2 = 0; %[Correcting for dE = 0 to avoid integral error]
        else
            N_abs_2 = I*a*trapz(L_int:0.001:L_g,interp1(wavelength,photons,L_int:0.001:L_g));
        end
        N_abs = N_abs_1 + N_abs_2; % total solar absorption flux
        fun1 = @(x) (x.^2)./(exp(x)-1);
```

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if dE(j) == 0
   N_amb_1 = 0; % correcting for dE = 0 to avoid integral error
else
   N_amb_1 = a*const1*int1*int3*integral(fun1,x_g,x_g_int);
end
N_amb_2 = a*const1*int1*int2*integral(fun1,x_g_int,Inf);
N_amb = N_amb_1 + N_amb_2; % total ambient absorption flux
J_SC(i,j) = N_abs*q; % short-circuit current density (A m^-2)
if sol_spec == 0
   V_app = linspace(E_g(i)/q-0.6,E_g(i)/q-0.1,5000); % cell voltage (V)
elseif sol_spec == 1
   V_app = linspace(0,E_g(i)/q+0.5,5000);
end
parfor k=1:length(V_app)
   x_c = (q*V_app(k))/(k_B*T_c);
   if E_g(i)-q*V_app(k) > k_B*T_c
      fun2 = @(x) (x.^2)./(exp(x-x_c)-1);
   else
      fun2 = @(x) (x.^2).*exp(x-x_c);
   end
   if dE(j) == 0
      Nemit_1 = 0; % correcting for dE = 0 to avoid integral error
   else
      Nemit_1 = e*const1*int1*int3*integral(fun2,x_g,x_g_int);
   end
   N_emit_2 = e*const1*int1*int2*integral(fun2,x_g_int,Inf);
   N_emit(k) = Nemit_1 + N_emit_2; % total emission flux
   J_tot(k) = q*(N_abs+N_amb-N_emit(k)); % total current density (A m^-2)
   abs_J_tot(k) = abs(J_tot(k)); % calculating absolute values of total current density (A m^-2)
end
index_Voc=find(abs_J_tot==min(abs_J_tot));
V_OC(i,j)=V_app(index_Voc); % open-circuit voltage (V)
P = V_app.*J_tot;
[abs_J_tot,ind] = max(P); % maximum power (J)
eta(i,j) = 100*(abs_J_tot/tot_inc_power); % efficiency (%)
end
eta_max_Eg(i) = max(eta(i,:)); % calculating maximum efficiency for each value of Eg
for j = 1:length(dE)
   eta_max_dE(j) = max(eta(:,j)); % calculating maximum efficiency for each value of dE
end
max_eff = eta(E_g_index, dE_index); % maximum efficiency
E_g_opt_eV = E_g(E_g_index)/q; % finding E_g (eV) corresponding to maximum efficiency
dE_opt_eV = 1000*dE(dE_index)/q; % finding dE (eV) corresponding to maximum efficiency
V_OC_opt = V_OC(E_g_index, dE_index); % finding V_OC corresponding to maximum efficiency
J_SC_opt = 0.1*J_SC(E_g_index, dE_index); % finding J_SC corresponding to maximum efficiency
6.2. MATLAB Code for Markov Chain Simulation of NR-PV Systems

% CONSTANTS & PARAMETERS
h = 6.62607015e-34; % Planck's constant (m^2 kg s^-1)
c = 299792458; % speed of light (m s^-1)
qu = 1.60217663e-19; % elementary charge (C)
k_B = 1.380649e-23; % Boltzmann constant (m^2 kg s^-2 K^-1)
a_L = @(t) 1e7*sin(t).*sin(t); % absorption coefficient of LSC [dipole] (m^-1)
a_P = 1e5; % absorption coefficient of PV (m^-1)
n_ref_E = 1; % refractive index of the environment
n_ref_L = 1; % refractive index of the LSC
n_ref_P = 4; % refractive index of the PV
t_Sun = deg2rad(0.267); % solar angle (radians)
t_AR = deg2rad(90); % angular range of absorption/emission (radians)
dz = 1e-5; % layer thickness (m)
n_L = 5; % number of LSC layers
nP = 5; % number of PV layers
n_tot = 1+n_L+n_P; % total number of layers
T_c = 300; % operating temperature of cell (K)
E_g_array = q*linspace(0.5,2.5,201); % bandgap (J)
P_alt_array = logspace(-6,0,2000); % PV current extraction probability
V_app_fit = linspace(0,1.5,1500); % voltage array (V)
QY_L = 1; % quantum yield of luminophores
QY_P = 1; % quantum yield of PV

% CRITICAL ANGLES
% REGIONAL INTERNAL REFLECTION FUNCTIONS
% IMPORTING SOLAR SPECTRUM
% REFRACTION FUNCTIONS
% TOTAL INTERNAL REFLECTION FUNCTION
% EMISSION PROBABILITY FUNCTIONS
% TRAVEL PROBABILITY FUNCTIONS

% END OF MATLAB CODE
\[
p_a_{E2P} = @(t) 1 \quad \text{EN} \to \text{PV (single reflection)}
\]
\[
p_a_{P2L} = @(t) 1 \quad \text{LSC} \to \text{ENV (direct)}
\]
\[
p_a_{L2L} = @(t, l) \exp(-(|d_z| \cdot a_L(t_{P2L})(t))/\cos(t)) \quad \text{LSC to LSC (direct)}
\]
\[
p_a_{L2P} = @(t, l, p) \exp(-(|d_z| \cdot a_L(t_E2L)(t))/\cos(t)) \quad \text{LSC to LSC (self-absorption)}
\]
\[
p_a_{P2P} = @(t) 1 \quad \text{PV to PV (single reflection)}
\]
\[
p_a_{P2E} = 1 \quad \text{PV to ENV (single reflection)}
\]
\[
p_a_{P2P} = @(t, p) \exp(-(|d_z| \cdot a_P(t_{E2P})(t))/\cos(t)) \quad \text{PV to PV (direct)}
\]
\[
p_a_{P2E} = @(t, p) \exp(-(|d_z| \cdot a_P(t_{E2L})(t))/\cos(t)) \quad \text{PV to ENV (direct)}
\]

\[
\begin{align*}
p_t_{P2P}_{\text{ref}_1} &= @(t, p) \exp(-(|d_z| \cdot a_P(t_{E2P})(t))/\cos(t)) \quad \text{absorption at PV} \\
p_t_{P2P}_{\text{dir}_1} &= @(t, p) \exp(-(|d_z| \cdot a_P(t_{E2L})(t))/\cos(t)) \quad \text{absorption at PV}
\end{align*}
\]

% ABSSORPTION PROBABILITY

\[
\begin{align*}
p_a_{E2L} &= 1 \quad \text{absorption at ENV} \\
p_a_{L2P} &= @(t) 1 \exp(-(|d_z| \cdot a_L(t_{P2L})(t))/\cos(t)) \quad \text{absorption at PV} \\
p_a_{L2P} &= @(t) 1 \exp(-(|d_z| \cdot a_L(t_{P2L})(t))/\cos(t)) \quad \text{absorption at PV}
\end{align*}
\]

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p_a_P2P_self = @(t) 2*(1-exp(-a_P*0.5*dz).*cos(t))); % self-absorption at PV

% DIRECT TRANSITION PROBABILITY MATRIX
P_dir = zeros(n_tot); % preallocating matrix

for i=1:n_L
    ... % calculations ...
end

% SINGLE-REFLECTION TRANSITION PROBABILITY MATRIX
P_ref_1 = zeros(n_tot); % preallocating matrix

for i=1:n_L
    ... % calculations ...
end
% (16) PV to LSC
[3,1] = ndgrid(2:n_L+1,n_L+2:n_tot);
tempvec = (2*pii)*integral(@(t) p_e_P(t).*p_t_P2L_ref_1(t,n_L+1-[J(:)],n_tot+n_P-[I(:)])+0.5).*p_a_P2L(t),0,t_c_P2L,'ArrayValued',true);
P_ref_1(2:n_L+1,n_L+2:n_tot) = reshape(tempvec,[n_L,n_P]);

% (17) PV to PV
[3,1] = ndgrid(n_L+2:n_tot,n_L+2:n_tot);
tempvec = (2*pii)*integral(@(t) p_e_P(t).*p_t_P2P_ref_1(t,2*n_tot+0.5-[I(:)]-[J(:)]).*p_a_P2P(t),0,pi/2,'ArrayValued',true);
P_ref_1(n_L+2:n_tot,n_L+2:n_tot) = reshape(tempvec,[n_P,n_P]);

% TOTAL INTERNAL REFLECTION MODE 1 TRANSITION PROBABILITY MATRIX

P_ref_TIR_1 = zeros(n_tot);

% (18) LSC to LSC
[3,1] = ndgrid(2:n_L+1,2:n_L+1);
P1 = (2*pii)*integral(@(t) p_e_L(t).*p_t_L2L_ref_TIR_1_UU(t,[I(:)]+n_L-0.5,n_P).*p_a_L2L(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
P2 = (2*pii)*integral(@(t) p_e_L(t).*p_t_L2L_ref_TIR_1_UD(t,[I(:)]+n_L-3.5).*p_a_L2L(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
P3 = (2*pii)*integral(@(t) p_e_L(t).*p_t_L2L_ref_TIR_1_DU(t,2*n_L+2.5-[I(:)],2*n_P).*p_a_L2L(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
P4 = (2*pii)*integral(@(t) p_e_L(t).*p_t_L2L_ref_TIR_1_DD(t,n_L+[J(:)]-0.5,n_P).*p_a_L2L(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
tempvec = P1+P2+P3+P4;
P_ref_TIR_1(2:n_L+1,2:n_L+1) = reshape(tempvec,[n_L,n_L]);

% (19) LSC to PV
[3,1] = ndgrid(n_L+2:n_tot,2:n_L+1);
P1 = (2*pii)*integral(@(t) p_e_L(t).*p_t_L2P_ref_TIR_1_UU(t,[I(:)]-1.5,n_tot-[J(:)]).*p_a_L2P(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
P2 = (2*pii)*integral(@(t) p_e_L(t).*p_t_L2P_ref_TIR_1_UD(t,n_L+[J(:)]-2.*p_a_L2P(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
P3 = (2*pii)*integral(@(t) p_e_L(t).*p_t_L2P_ref_TIR_1_DU(t,n_L+1.5-[J(:)],n_P+n_tot-[J(:)]).*p_a_L2P(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
P4 = (2*pii)*integral(@(t) p_e_L(t).*p_t_L2P_ref_TIR_1_DD(t,2*n_L+1.5-[J(:)],n_P+[J(:)]-n_L-2).*p_a_L2P(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
tempvec = P1+P2+P3+P4;
P_ref_TIR_1(n_L+2:n_tot,2:n_L+1) = reshape(tempvec,[n_P,n_L]);

% (20) PV to LSC
[3,1] = ndgrid(2:n_L+1,n_L+2:n_tot);
P1 = (2*pii)*integral(@(t) p_e_P(t).*p_t_P2L_ref_TIR_1_UU(t,2*n_L+1-[J(:)],n_P+[I(:)]-n_L-1.5).*p_a_P2L(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
P2 = (2*pii)*integral(@(t) p_e_P(t).*p_t_P2L_ref_TIR_1_UD(t,2*n_L+1-[J(:)],n_P+[I(:)]-n_L-1.5).*p_a_P2L(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
P3 = (2*pii)*integral(@(t) p_e_P(t).*p_t_P2L_ref_TIR_1_DU(t,2*n_L+1-[J(:)],n_P+[I(:)]-n_L-1.5).*p_a_P2L(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
P4 = (2*pii)*integral(@(t) p_e_P(t).*p_t_P2L_ref_TIR_1_DD(t,2*n_L+1-[J(:)],n_P+[I(:)]-n_L-1.5).*p_a_P2L(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
tempvec = P1+P2+P3+P4;
P_ref_TIR_1(2:n_L+1,n_L+2:n_tot) = reshape(tempvec,[n_L,n_P]);

% (21) PV to PV
[3,1] = ndgrid(2:n_L+1,2:n_L+1);
P1 = (2*pii)*integral(@(t) p_e_P(t).*p_t_P2P_ref_TIR_1_UU(t,[I(:)]-1.5,n_tot-[J(:)]).*p_a_P2P(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
P2 = (2*pii)*integral(@(t) p_e_P(t).*p_t_P2P_ref_TIR_1_UD(t,[I(:)]-1.5,n_tot-[J(:)]).*p_a_P2P(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
P3 = (2*pii)*integral(@(t) p_e_P(t).*p_t_P2P_ref_TIR_1_DU(t,[I(:)]-1.5,n_tot-[J(:)]).*p_a_P2P(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
P4 = (2*pii)*integral(@(t) p_e_P(t).*p_t_P2P_ref_TIR_1_DD(t,[I(:)]-1.5,n_tot-[J(:)]).*p_a_P2P(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
tempvec = P1+P2+P3+P4;
P_ref_TIR_1(2:n_L+1,2:n_L+1) = reshape(tempvec,[n_P,n_P]);

% TOTAL INTERNAL REFLECTION MODE 2 TRANSITION PROBABILITY MATRIX

P_ref_TIR_2 = zeros(n_tot);

% (22) PV to PV
[3,1] = ndgrid(2:n_L+1,2:n_L+1);
P1 = (2*pii)*integral(@(t) p_e_P(t).*p_t_P2P_ref_TIR_2_UU(t,[I(:)]-n_L+n_tot-1.5).*p_a_P2P(t),t_E2L(t_AR),pi/2,'ArrayValued',true);
\begin{verbatim}
P2 = (2*pi)*integral(@(t) p_e_P(t).*p_t_P2P_ref_TIR_2_UD(t,[I(:)]+[J(:)]-[n_L-3.5]*p_a_P2P(t),t_c_P2L,pi/2,'ArrayValued',true);
P3 = (2*pi)*integral(@(t) p_e_P(t).*p_t_P2P_ref_TIR_2_DU(t,2*n_tot-[I(:)]+[J(:)]-[n_L-3.5]*p_a_P2P(t),t_c_P2L,pi/2,'ArrayValued',true);
P4 = (2*pi)*integral(@(t) p_e_P(t).*p_t_P2P_ref_TIR_2_DD(t,n_tot-[I(:)]+[J(:)]-[n_L-1.5]*p_a_P2P(t),t_c_P2L,pi/2,'ArrayValued',true);
tempvec = P1+P2+P3+P4;
P_ref_TIR_2(n_L+2:n_tot,n_L+2:n_tot) = reshape(tempvec,[n_P,n_P]);

% CONSTRUCTING COMPLETE TRANSITION PROBABILITY MATRIX
P = P_dir + P_ref_1 + P_ref_TIR_1 + P_ref_TIR_2;

% CALCULATING STEADY STATE AND I-V CHARACTERISTICS
P_mod = P;
P_mod(:,2:n_L+1) = QY_L*P(:,2:n_L+1);
P_mod(1,2:n_L+1) = 1-QY_L+P(1,2:n_L+1);
P_mod_array = repmat(P_mod,[1,1,length(P_alt_array)]);
for i=1:length(P_alt_array)
P_mod_array(:,n_L+2:n_tot,i) = QY_P*(1-P_alt_array(i))*P_mod_array(:,n_L+2:n_tot,i);
P_mod_array(1,n_L+2:n_tot,i) = P_mod_array(1,n_L+2:n_tot,i)+1-QY_P*(1-P_alt_array(i));
end
em_prob_scaled = QY_P*(sum(P(1:n_L+1,n_L+2:n_tot))+sum(P_ref_TIR_1(n_L+2:n_tot,n_L+2:n_tot)))*P_mod_array(:,:,i);
eta = zeros(1,length(E_g_array));
J_SC = zeros(1,length(E_g_array));
V_OC = zeros(1,length(E_g_array));
for loop = 1:length(E_g_array)
E_g = E_g_array(loop);
E_L = 1e9*(h*c)/(E_g);
x_g = E_g/(k_B*T_c);
tot_inc_flux = trapz(280:0.001:E_L,interp1(wavelength,photons_DC,280:0.001:E_L));
n_emit_fit = zeros(1,length(V_app_fit));
parfor i=1:length(V_app_fit)
    x_c = (q*V_app_fit(i))/(k_B*T_c);
    if E_g-q*V_app_fit(i)>k_B*T_c
        fun = @(x) (x.^2)./(exp(x-x_c)-1);
    else
        fun = @(x) (x.^2).*exp(x_c-x);
    end
    n_emit_fit(i) = ((2*(k_B*T_c).^3)/(h.^3*c.^2))*pi*integral(fun,x_g,inf);
end
D_ss = zeros([n_tot,length(P_alt_array)]);
parfor i=1:length(P_alt_array)
    P_alt = P_alt_array(i);
    [V,EV] = eigs(P_mod_array(:,:,i),1);
    D_ss(:,i) = V*(tot_inc_flux/V(1));
end
n_emit = sum(D_ss(:,n_L+2:end))'*em_prob_scaled;
J_tot = sum(D_ss(:,n_L+2:end))'*P_altarray*QY_P;
[n_emit_grid,n_emit_fit_grid] = meshgrid(n_emit,n_emit_fit);
diff = abs(n_emit_grid-n_emit_fit_grid);
[diff,ind_min_diff] = min(diff);
V_app = zeros(1,length(P_alt_array));
parfor i=1:length(P_alt_array)
    V_app(i) = V_app_fit(ind_min_diff(i));
end
power = V_app.*J_tot;
max_power,ind_max_power) = max(power);
eta(loop) = 100*max_power/tot_inc_power;
J_SC(loop) = J_tot(length(P_alt_array));
V_OC(loop) = V_app(1);

End
\end{verbatim}
6.3. MATLAB Code for Quantifying the Degree of AC Field-Driven Alignment

% CONSTANTS & PARAMETERS
========================================================================
B = 0.75;
rel_A_lim = -0.424; % limiting value of experimental dA/A0
n = 1; % number density of NRs
l = 50*1e-6; % path length (m)
k = log10(exp(1)); % constant

% SETTING UP PARAMETER SPACE ============================================
theta = linspace(-pi/2,pi/2,181);
phi = linspace(0,2*pi,361);
[theta,phi] = meshgrid(theta,phi);
K_array = logspace(-4,2,1001); % order parameter

for i = 1:length(K_array)
    % SETTING UP VON MISES–FISHER DISTRIBUTION =============================
    K = K_array(i);
    C3 = K/(2*pi*(exp(K)-exp(-K)));
    theta_mu = pi/2;
    phi_mu = 0;
    f1 = cos(theta_mu)*cos(phi_mu).*cos(theta).*cos(phi);
    f2 = cos(theta_mu)*sin(phi_mu).*cos(theta).*sin(phi);
    f3 = sin(theta_mu).*sin(theta);
    f_p = C3*cos(theta).*exp(K*(f1+f2+f3));
    f_p = f_p/sum(sum(f_p)); % normalized probability density function

    % CALCULATING MEAN DEVIATION ANGLE =====================================
    dev_ang = acos(f1+f2+f3); % deviation angle for all rod orientations
    mean_dev_ang = sum(sum(f_p.*dev_ang)); % mean deviation of rods from mean orientation
    var = sum(sum(f_p.*((dev_ang - mean_dev_ang).^2))); % variance
    stdev = sqrt(var);
    mean_dev_ang_deg(i) = rad2deg(mean_dev_ang);
    stdev_deg(i) = rad2deg(stdev);

    % CALCULATING RELATIVE CHANGE IN ABSORBANCE ===========================
    EPP = B*cos(theta).*cos(theta)+(1-B); % excitation photoselection probability
    sigma = sum(sum(EPP.*f_p));
    A(i) = k*sigma*n*l;
    rel_A(i) = (A(i) - A(1))/A(1);
end

% CALCULATING DEGREE OF ORDER ===========================================
for i = 1:length(K_array)
    diff(i) = abs(rel_A(i)-rel_A_lim);
end
[min_diff,ind] = min(diff);
K_lim = K_array(ind)
mean_dev_ang_deg_lim = mean_dev_ang_deg(ind)
stdev_deg_lim = stdev_deg(ind)
APPENDIX B

This section outlines the derivation of theoretical expressions for the ensemble fluorescence anisotropy of ideal/non-ideal dipole emitters under (1) vertical- and (2) circular-polarized excitation. These derivations follow the work of Lakowicz\textsuperscript{59} with modifications to accommodate non-ideal dipole absorption and emission.

6.4. Derivation of Theoretical Expression for Vertical-Polarized Ensemble

Anisotropy

![Diagram](image)

**Figure S1.** Excitation of an arbitrary emitter by linearly (vertical) polarized light.

6.4.1. Ideal Dipole Absorption and Emission

Excitation photoselection probability:

\[
d f_\uparrow(\theta, \varphi) = \cos^2 \theta \, d\theta \tag{S1}
\]

Relative emission intensities from an excited luminophore:

\[
I_\parallel(\theta) = \cos^2 \theta \tag{S2}
\]

\[
I_\perp(\theta, \varphi) = \sin^2 \theta \cos^2 \varphi \tag{S3}
\]

Total emission intensities accounting for excitation photoselection:
\[
I_{\parallel}^{\text{tot}} = \int_0^{2\pi} \int_0^{\pi} f_1(\theta) I_{\parallel}(\theta) \sin \theta \, d\theta \, d\varphi = \int_0^{2\pi} \int_0^{\pi} \cos^4 \theta \sin \theta \, d\theta \, d\varphi = \frac{12\pi}{15} \quad (S4)
\]

\[
I_{\perp}^{\text{tot}} = \int_0^{2\pi} \int_0^{\pi} f_1(\theta) I_{\perp}(\theta) \sin \theta \, d\theta \, d\varphi
\]

\[
= \int_0^{2\pi} \int_0^{\pi} \cos^2 \theta \sin^2 \theta \cos^2 \varphi \sin \theta \, d\theta \, d\varphi = \frac{4\pi}{15} \quad (S5)
\]

Ensemble anisotropy:

\[
r = \frac{I_{\parallel}^{\text{tot}} - I_{\perp}^{\text{tot}}}{I_{\parallel}^{\text{tot}} + 2I_{\perp}^{\text{tot}}} = \frac{(12\pi/15) - (4\pi/15)}{(12\pi/15) + 2(4\pi/15)} = 0.4 \quad (S6)
\]

6.4.2. Non-Ideal Dipole Absorption and Emission

Excitation photoselection probability:

\[
df_1(\theta, \varphi) = \left[ \chi_a \cos^2 \theta + (1 - \chi_a) \right] d\theta \quad (S7)
\]

Relative emission intensities from an excited luminophore:

\[
I_{\parallel}(\theta) = \chi_e \cos^2 \theta + (1 - \chi_e) \quad (S8)
\]

\[
I_{\perp}(\theta, \varphi) = \chi_e \sin^2 \theta \cos^2 \varphi + (1 - \chi_e) \quad (S9)
\]

Total emission intensities accounting for excitation photoselection:

\[
I_{\parallel}^{\text{tot}} = \int_0^{2\pi} \int_0^{\pi} f_1(\theta) I_{\parallel}(\theta) \sin \theta \, d\theta \, d\varphi
\]

\[
= \int_0^{2\pi} \int_0^{\pi} \left[ \chi_a \cos^2 \theta + (1 - \chi_a) \right] \left[ \chi_e \cos^2 \theta \right.
\]

\[
+ \left(1 - \chi_e \right] \sin \theta \, d\theta \, d\varphi = \frac{4\pi}{15} \left( 8 \chi_a \chi_e - 10 \chi_a - 10 \chi_e + 15 \right) \quad (S10)
\]

\[
I_{\perp}^{\text{tot}} = \int_0^{2\pi} \int_0^{\pi} f_1(\theta) I_{\perp}(\theta) \sin \theta \, d\theta \, d\varphi
\]

\[
= \int_0^{2\pi} \int_0^{\pi} \left[ \chi_a \cos^2 \theta + (1 - \chi_a) \right] \left[ \chi_e \sin^2 \theta \cos^2 \varphi \right.
\]

\[
+ \left(1 - \chi_e \right] \sin \theta \, d\theta \, d\varphi = \frac{4\pi}{15} \left( 6 \chi_a \chi_e - 10 \chi_a - 10 \chi_e + 15 \right) \quad (S11)
\]
Ensemble anisotropy:

\[ r = \frac{I_{\parallel}^{\text{tot}} - I_{\perp}^{\text{tot}}}{I_{\parallel}^{\text{tot}} + 2I_{\perp}^{\text{tot}}} \]

\[ r = \frac{(4\pi/15)[(8\chi_a\chi_e - 10\chi_a - 10\chi_e + 15) - (6\chi_a\chi_e - 10\chi_a - 10\chi_e + 15)]}{(4\pi/15)[(8\chi_a\chi_e - 10\chi_a - 10\chi_e + 15) + 2(6\chi_a\chi_e - 10\chi_a - 10\chi_e + 15)]} \]

\[ = \frac{2\chi_a\chi_e}{20\chi_a\chi_e - 30(\chi_a + \chi_e) + 45} \]

6.5. Derivation of Theoretical Expression for Circular-Polarized Ensemble Anisotropy

Figure S2. Excitation of an arbitrary emitter by circular-polarized light.

6.5.1. Ideal Dipole Absorption and Emission

Excitation photoselection probability:

\[ df_{\ell}(\theta, \varphi) = (\sin^2 \theta \sin^2 \varphi + \cos^2 \theta) d\theta \]

Relative emission intensities from an excited luminophore:

\[ I_{\parallel}(\theta) = \cos^2 \theta \]

\[ I_{\perp}(\theta, \varphi) = \sin^2 \theta \cos^2 \varphi \]
Total emission intensities accounting for excitation photoselection:

\[
I_{\parallel}^\text{tot} = \int_0^{2\pi} \int_0^\pi f_\odot(\theta) I_{\parallel}(\theta) \sin \theta \, d\theta \, d\varphi \\
= \int_0^{2\pi} \int_0^\pi (\sin^2 \theta \sin^2 \varphi + \cos^2 \theta) \cos^2 \theta \sin \theta \, d\theta \, d\varphi = \frac{16\pi}{15} 
\]  
(S16)

\[
I_{\perp}^\text{tot} = \int_0^{2\pi} \int_0^\pi f_\odot(\theta) I_{\perp}(\theta) \sin \theta \, d\theta \, d\varphi \\
= \int_0^{2\pi} \int_0^\pi (\sin^2 \theta \sin^2 \varphi + \cos^2 \theta) \sin^2 \theta \cos^2 \varphi \sin \theta \, d\theta \, d\varphi = \frac{8\pi}{15} 
\]  
(S17)

Ensemble anisotropy:

\[
r_\odot = \frac{I_{\parallel}^\text{tot} - I_{\perp}^\text{tot}}{I_{\parallel}^\text{tot} + 2I_{\perp}^\text{tot}} = \frac{(16\pi/15) - (8\pi/15)}{(16\pi/15) + 2(8\pi/15)} = 0.25 
\]  
(S18)

6.5.2. Non-Ideal Dipole Absorption and Emission

Excitation photoselection probability:

\[
df_\odot(\theta, \varphi) = \left[ \chi_a (\sin^2 \theta \sin^2 \varphi + \cos^2 \theta) + (1 - \chi_a) \right] d\theta 
\]  
(S19)

Relative emission intensities from an excited luminophore:

\[
I_{\parallel}(\theta) = \chi_e \cos^2 \theta + (1 - \chi_e) 
\]  
(S20)

\[
I_{\perp}(\theta, \varphi) = \chi_e \sin^2 \theta \cos^2 \varphi + (1 - \chi_e) 
\]  
(S21)

Total emission intensities accounting for excitation photoselection:

\[
I_{\parallel}^\text{tot} = \int_0^{2\pi} \int_0^\pi f_\odot(\theta) I_{\parallel}(\theta) \sin \theta \, d\theta \, d\varphi \\
= \int_0^{2\pi} \int_0^\pi \left[ \chi_a (\sin^2 \theta \sin^2 \varphi + \cos^2 \theta) + (1 - \chi_a) \right] \left[ \chi_e \cos^2 \theta \right. \\
+ (1 - \chi_e) \sin \theta \, d\theta \, d\varphi = \frac{4\pi}{15} (4\chi_a \chi_e - 5\chi_a - 10\chi_e + 15) 
\]  
(S22)
\[ I_{\perp}^{\text{tot}} = \int_{0}^{2\pi} \int_{0}^{\pi} f_{\perp}(\theta) I_{\perp}(\theta) \sin \theta \, d\theta \, d\varphi \]
\[ = \int_{0}^{2\pi} \int_{0}^{\pi} \left[ \chi_a (\sin^2 \theta \sin^2 \varphi + \cos^2 \theta) + (1 - \chi_a) \right] \left[ \chi_e \sin^2 \theta \cos^2 \varphi + (1 - \chi_e) \sin \theta \, d\theta \, d\varphi \right] \]
\[ = \frac{4\pi}{15} (2\chi_a\chi_e - 5\chi_a - 10\chi_e + 15) \]  (S23)

Ensemble anisotropy:

\[ r_{\bigcirc} = \frac{I_{\parallel}^{\text{tot}} - I_{\perp}^{\text{tot}}}{I_{\parallel}^{\text{tot}} + 2I_{\perp}^{\text{tot}}} \]
\[ = \frac{(4\pi/15) \left[ (4\chi_a\chi_e - 5\chi_a - 10\chi_e + 15) - (2\chi_a\chi_e - 5\chi_a - 10\chi_e + 15) \right]}{(4\pi/15) \left[ (4\chi_a\chi_e - 5\chi_a - 10\chi_e + 15) + 2(2\chi_a\chi_e - 5\chi_a - 10\chi_e + 15) \right]} \]
\[ = \frac{2\chi_a\chi_e}{8\chi_a\chi_e - 15\chi_a - 30\chi_e + 45} \]  (S24)

The absorption (\(\chi_a\)) and emission (\(\chi_e\)) dipole coefficients can be uniquely determined by solving the expressions for vertical- and circular-polarized anisotropy (Equations S12 and S24), substituting experimentally measured values for \(r\) and \(r_{\bigcirc}\).