Nanoscale Temperature Measurement of Phase Transition in Water Using Novel Optical Thermometry Techniques

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ABSTRACT

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Nanoscale Temperature Measurement of Phase Transition in Water Using Novel Optical Thermometry Techniques

Director of Dissertation: Hugh H. Richardson

Liquid to gas phase transition can be induced by the interaction of light with very small, but high absorbing particles. In the micro and nanoscale systems, this transition can be used for water purification\(^1\), equipment sensitizing\(^2\)\(^-\)\(^3\), drug delivery\(^4\)\(^-\)\(^5\), cancer cell destruction\(^6\)\(^-\)\(^7\), and biological imaging\(^8\)\(^-\)\(^10\), as well as for lithography of microstructure fabrications\(^11\). All the previously mentioned applications require some optimization to enhance their efficiency. Much has been done to investigate this process thoroughly, but previous studies were mostly based on theoretical calculations. A limited amount of experimental work has been reported on micro and nanoscale vapor nucleation\(^2\)\(^-\)\(^16\). This dissertation explores and investigates (liquid ↔ gas) phase transitions in a system where nanoparticle heaters drive the nucleation process using a Continuous Wave illumination. The aims of this study are: 1) to introduce a sub-micro thermometry technique that can be used to measure the temperature during a phase transition (liquid → gas) process with high accuracy. 2) Study the effect of the dissolved gases on the nucleation temperature. 3) Develop a new and non-invasive approach for high temperature measurement during a cycle of liquid-vapor nucleation (liquid ↔ gas).
Multiple objectives are accomplished in this study: first, erbium oxide nanoparticles (Er$_2$O$_3$) were fully characterized to act as a thermal sensor with a resolution that is only limited by the size of the nanoparticle. Using the optical tweezer technique, the thermal probe is successfully trapped in the solution and attached to a target, where the phase transition takes place. Through the excitation of Er$_2$O$_3$NPs using 532 nm light, the temperature is measured from the two thermally coupled energy states in the photoluminescence spectrum of the nanoparticles.

Additionally, due to the collective heating effect of the gold nanorod clusters, a huge amount of heat is generated, which is sufficient for a phase transition to occur. The temperature of the surrounding water is increased until vapor nucleation occurs through the dissipation of heat from the nanoparticle clusters to the water. The effect of the dissolved gases in the nucleation process is demonstrated by conducting multiple temperature measurements in two solutions (degassed and non-degassed).

Finally, NaYF$_4$: Er$^{3+}$, Yb$^{3+}$ upconverting nanoparticles (UCNPs) are synthesized and characterized in water using a 980 nm laser. The green emission of the UCNPs is used to measure the temperature of the system using the Fluorescence Intensity Ratio Technique. Silver nanoparticle clusters are used to generate heat under 405 nm laser excitation. The temperature during bubble nucleation and collapse is measured by tracking the green emission of the UCNPs using 980 nm light, while the amount of heat generated is controlled using the 405 nm laser.
To my parents, Abdulrahman Alaulamie and Norah Almutawa

To my husband, Abdullah Albrik

To my lovely daughter, Jory

It would not have been possible without you
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CHAPTER 1 : INTRODUCTION

Heat Generation in Plasmonic Nanoparticles

In the last decade, nanotechnology has significantly contributed to major revolutions in all areas of life through the development of small objects with unique and novel characteristics such as mechanical, magnetic and optical attributes.\textsuperscript{17} These unique characteristics allow nanotechnology to function more efficiently than the bulk material. However, behind all the achievements that may be described to date, there are many scientists and researchers who have worked on understanding and improving the performance of this technology. Until now, a great number of nanoscale phenomena have been introduced, discussed and understood, but there are many more to investigate. A significant component of this technology that needs further investigation is the aspect of nanoscale heat generation and transfer, which has a tremendous number of applications that could change the world in the near future.

Metallic nanoparticles, which are much smaller than the wavelength of light, show superior optical properties compared to many other types of nanoparticles. The unique characteristics of these particles result from their Surface Plasmon Resonance (SPR) effect.\textsuperscript{18} Metals are known to have a large number of free electrons in the conduction band. When incoming light at specific frequencies of electromagnetic radiation interacts with the metallic nanoparticles, the free electrons become polarized with respect to the ionic core\textsuperscript{19}. A charge difference forms on the particle surface, leading to electron cloud displacement, and collective coherent oscillations as shown in Figure 1.1. The number of applications that use plasmonic nanoparticles has seen a dramatic increase; this is due to the variety of
sizes and shapes of these particles, which gives rise to different optical properties. Metallic nanoparticles are known to be excellent light scatterers when their size approaches the wavelength of light. These particles are great probes for biological imaging applications because of their high scattering cross section. However, the scattering cross section is negligible when the nanoparticle is smaller than 40 nm. Researchers reported that metallic nanoparticles, such as gold and silver, have a high absorption cross section compared to many dyes that are known to be high absorbing molecules. More so, the quantum yield, number of emitted photons/number of absorbed photons, of these particles is very low ($10^{-6}$). As a result, these particles can be an efficient source of heat under optical illumination. It has been previously reported that the efficiency of light-to-heat conversion by gold nanoparticles is close to one. This implies that almost all of the light absorbed by these particles is completely converted to heat. The absorption cross section of a metallic nanoparticle is related to the change in temperature and it can be calculated using the following equation:

$$\Delta T_{\text{max}}(K) = \frac{C_{\text{abs}}(\lambda) I_0}{4 \pi k_m R_{\text{NP}}},$$  \hspace{1cm} (1.1)$$

where $I_0$ is the light intensity, $k_m$ is the thermal conductivity of the medium, $C_{\text{abs}}$ is the absorption cross-section of the particle, and $R_{\text{NP}}$ is the nanoparticle radius.
There are two types of metallic nanoparticles that are used in this dissertation as the main source of heat generation: gold nanorods and silver nanoparticles. Gold and silver are the most common metallic nanoparticles and have been extensively studied and used for two reasons: they are significantly inert (do not easily oxidize in air) and they are relatively biocompatible (have less toxicity) compared to other semiconductor nanocrystals. The Surface Plasmon Resonance of gold and silver nanoparticles can be easily tuned based on the nanoparticle size and shape. Gold nanorods are one of the most interesting nanoparticles because of their anti-symmetric shape that gives rise to two modes, transverse and longitudinal modes, with different plasmon resonances (see Figure 1.2A). The transverse mode is due to the electron cloud oscillations along the short axis and it always appears in the visible region of the spectrum. On the other hand, the longitudinal mode, which has an aspect ratio dependence, appears further in the Near
Infrared Region (NIR) and it results from the electron oscillations along the long axis. Even though the absorption cross section of the transverse mode in the nanorods is orders of magnitude lower than the absorption cross section of the longitudinal mode, as shown in Figure 1.2A, a significant amount of heat can be generated when the transverse mode is excited with an appropriate light frequency.

Based on the dielectric function, different metal nanoparticles give rise to different extinction cross sections as described by Lorenz-Mie Theory. The extinction cross section for a spherical particle in a homogeneous medium can be expressed as:

$$\sigma_{ext} = \frac{24 \pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon''(\lambda)}{\varepsilon'(\lambda)+2 \varepsilon_m+\varepsilon''(\lambda)}$$

(1.2)

where $R$ is the nanoparticle radius, $\varepsilon_m$ is the dielectric constant of the medium, and $\varepsilon''$ and $\varepsilon'$ are the real and imaginary parts of the dielectric constant of the metal, respectively. Unlike nanorods, silver nanospheres, have only one mode with a surface plasmon resonance that is shifted to a much higher energy (see Figure 1.2B). Heat generation using these particles is possible if the incident light has a wavelength that is in resonance with SPR frequency (i.e. a 405 nm laser).
Figure 1.2 (A) An absorption spectrum of gold nanorods colloidal solution. The nanorods have an aspect ratio of 4. The Plasmon resonance of the transverse mode is at 518 nm and the longitudinal mode is at 810 nm. (B) A calculated absorption spectrum of 20 nm silver nanoparticle on a glass substrate and immersed in water. The Plasmon resonance appears at a wavelength of ~400 nm.

A previous study has suggested that the heat generated by two interacting nanoparticles that are close to each other differs from the heat that is generated by two separated single nanoparticles. This is due to the collective heating effect, which depends on the nanoparticles’ arrangement and on the inter-particle distance in the cluster. The collective heating effect results from the accumulation of heat that is generated by each particle inside the cluster and from the additional electric field enhancement from the neighboring particles. In this dissertation, clusters of gold nanorods and silver nanoparticles have been used as heat generators instead of a single nanoparticle since the ultimate goal of using these particles is to generate a huge amount of heat that is sufficient for a liquid to vapor phase transition.
Heat Transfer from Nanoparticles to the Surrounding Medium

There are three common mechanisms of heat transfer: thermal conduction, thermal convection, and thermal radiation. The heat generated by a nanoparticle can be delivered to the surrounding medium via the thermal conduction process. Heat dissipation from a nanoparticle to the surrounding medium has a strong dependence on the thermal conductivity of that medium as described by Fourier’s Law:

\[ q = KA \left( \frac{dx}{dt} \right) \],

where \( q \) is the heat flux (heat dissipation), \( A \) is the area that heat transfers (m\(^2\)), \( k \) is the thermal conductivity of the material in a unit of W\( \cdot \)m\(^{-1}\)\( \cdot \)K\(^{-1}\), and \( \left( \frac{dx}{dt} \right) \) is the thermal gradient. If the nanoparticle’s surrounding medium is air, the heat mainly dissipates to the substrate since the thermal conductivity of air is very low (\( K = 0.024 \) W\( \cdot \)m\(^{-1}\)\( \cdot \)K\(^{-1}\)). On the other hand, when the nanoparticle is surrounded by a medium that has a higher thermal conductivity than air, such as water, one more channel will be open for heat dissipation besides the substrate. In this case, as shown in Figure 1.3, the heat transfers to the surrounding water leading to a rise in the water temperature. The heat generated by metallic nanoparticles is huge and sufficient for phase transformation processes, such as ice melting\( ^{32} \), polymer matrices melting\( ^{28} \), and water evaporation\( ^{1-3, 13, 33} \). The ability to transform water into a vapor in the micro and nanoscale has enabled many novel applications in multiple disciplines. For instance, vapor bubbles formed by water heating using plasmonic nanoparticles is used for therapeutic applications\( ^{6, 8, 34} \). When vapor bubble forms and collapses, it creates a lot of force on the neighboring cell or membrane.
Depending on the laser power and the size of the formed bubble, this effect can be used for cell destruction\(^6\), or for drugs and macromolecules delivery.\(^{35}\) Bubble pen lithography is another recent technique that has been introduced based on nanoscale heat transfer. In this technique, microbubble formation on a plasmonic substrate enables the fabrication of 2D and 3D patterns of nanoparticles.\(^{11}\)

![Figure 1.3 A schematic illustrating heat dissipation from optically heated metallic nanoparticle to two different surrounding mediums with different thermal conductivities. The thermal conductivities of air and water are 0.024 and 0.58 W·m\(^{-1}\)·K\(^{-1}\), respectively.](image)

**Liquid – Vapor Phase Transition**

It is known that liquid water boils when the water temperature reaches 100 Celsius or 373.15 in Kelvin scale under 1-atmosphere pressure. However, under specific conditions water can be heated to a temperature above the saturation temperature without boiling.\(^{36}\) This phenomenon is called water superheating. The transition from liquid to gas can be described using the Helmholtz free energy curve. At a temperature that is above the boiling point, as shown in Figure 1.4, the gas phase is more stable than the liquid phase. This is because the vapor’s free energy is lower than that of the liquid. Therefore, in this case, a
phase transition can take place and the formation of the gas phase is preferred. However, the liquid can be converted to a gas only if the system possesses enough energy to overcome the energy barrier between the two phases. The height of this barrier represents the difference in the Gibbs free energy between the liquid and gas phase ($\Delta g_{l\rightarrow g}$). If the energy barrier is high, then the liquid will be trapped in a metastable state for a period before it is converted to a vapor. Liquid superheating, or in other words nucleation delay, occurs in the absence of the nucleation centers, which have an essential role in catalyzing the nucleation process. These nucleation centers can be impurities, cracks or cavities on the wall’s surface, or some dissolved gas pockets.\(^{37}\)

![Helmholtz free energy curve](image)

**Figure 1.4** Helmholtz free energy curve as a function of phase density. The gas phase is more stable with lower free energy minimum. The liquid is trapped in the metastable state for a finite time. The needed energy to overcome the barrier is the difference in the Gibbs free energy between the liquid and gas phase ($\Delta g_{l\rightarrow g}$).

Liquid metastability is generated because there is an energy required to create an interface between the liquid and the vapor phase i.e. creating a stable state from a
metastable state. The classical nucleation theory (CNT) suggests that for a spherical vapor bubble to form, the vapor embryo needs to exceed a critical size \( r^* \) to compensate for the energy that is required for vapor formation. If the size of the bubble embryo is large enough, the bubble will grow. Below that size, the bubble is not stable and it will be re-dissolved in the liquid again. The change in the Gibbs free energy \( \Delta G \) has a strong dependence on the embryo size as shown in the equation below:

\[
\Delta G_v = \frac{4}{3} \pi r^3 \Delta g \quad \text{and} \quad \Delta G_s = 4\pi r^2 \gamma
\]

\[
\Delta G_{total} = \Delta G_v + \Delta G_s
\]

In Equation (1.4), the two terms, \( \Delta G_v \) and \( \Delta G_s \), compete with each other. The first term \( \Delta G_v \) is a bulk term and it represents the volume free energy (the difference in the free energy between the liquid and gas). It is the term that drives the nucleation process and it decreases as \( r^3 \). On the other hand, \( \Delta G_s \) is the surface energy term, which is responsible for creating the interface between the two phases. The dependence of the change in the Gibbs free energy on the nuclei size is shown in Figure 1.5. The volume free energy term \( \Delta G_v \) has negative values (orange curve) while the surface energy term has positive values (green curve). The blue curve represents the total free energy \( \Delta G_{total} \) that is the sum of the two terms. When the embryo size reaches the critical size \( r^* \), the bubble becomes stable and can grow.
Figure 1.5 A diagram showing the dependence of the Gibbs free energy on the embryo radius. The critical size (black dashed line) that is needed for making a stable bubble takes place at $\Delta G$ maximum. Surface energy and bulk energy terms are shown with green and orange curves respectively. The blue curve represents the total free energy, which is the sum of the two terms.

The limit of the metastable state is the spinodal and it is the region where the system becomes unstable. The spinodal region is shown in the energy phase diagram (see Figure 1.6 A). The metastable state is surrounded by two curves; the binodal curve (orange) where the two phases are in equilibrium, and the spinodal curve (green), which is the limit of the metastable phase.\(^{41}\) Figure 1.6 B shows the binodal and the spinodal in a free energy diagram. The binodal points are located in the free energy minima of both the liquid and gas phases; on the other hand, the spinodal is located at a much higher free energy. However, if the temperature of the system increases beyond the spinodal point and until it reaches the critical temperature ($T_c$), the energy barrier disappears and the spinodal and binodal curves are merged.
Figure 1.6 (A) (B) phase diagrams showing the binodal (orange curve, orange dots), the spinodal (green curve, green dots) and the metastable state (the area between the two curves). In the binodal region, the system is stable and it is in equilibrium. Inside the spinodal region, the system is unstable and small perturbations cause phase separation.

Micro/Nanoscale Thermometry

Studying heat transfer at the nanoscale becomes more challenging and critical as the number of applications grows dramatically. Multiple micro and nanothermometry techniques have been introduced to provide an advanced understanding and solutions for serious problems in different disciplines.42-56 One can classify these techniques as luminescent and non-luminescent. Luminescence occurs when an electron in the excited state relaxes back to the ground state, releasing the absorbed energy as photons. In luminescent-based techniques, the temperature can be determined by studying the change in the luminescence bandwidth, lifetime, intensity, spectral position, or band shape.57 The Fluorescence Intensity Ratio Technique (FIRT) is one technique that has received much attention.58-63 In this technique, the temperature can be measured by monitoring the change in the relative intensities of a luminescent material. This method is non-invasive and measures the temperature with high sensitivity.64 Another great advantage of this technique
is that the temperature is not measured based on the overall change in the luminescence intensity (number of counts), but rather on the intensity ratio between two thermally related bands in the luminescent material. This is important because the overall intensity can be affected by many other factors other than the temperature such as the Förster Resonance Energy Transfer (FRET) that causes quenching or enhancement, non-radiative processes, laser intensity, or luminescent concentration. Different luminescent materials have been used as thermal probes including organic dyes, quantum dots, and lanthanide ions (Ln\(^{3+}\)). However, lanthanide ions have proven to be excellent temperature sensors compared to the other traditional probes. These particles do not show a background fluorescence signal, have sharp emission peaks, high chemical stability, a low level of toxicity, and they do not undergo photobleaching or blinking.

**Rare-Earth Elements and Temperature Sensor**

Rare earth elements (Lanthanides) occupy the F-block of period six in the periodic table. The series starts with Lanthanum (La) and ends with Lutetium (Lu). The entire elements group form trivalent cations (Ln\(^{3+}\)). Recently, much attention has been paid to Erbium with an atomic number of 68. The electronic configuration of Er is [Xe] 4f\(^{12}\) 6s\(^{2}\) and [Xe] 4f\(^{11}\) for the trivalent erbium ion. When the Er\(^{3+}\) ion absorbs specific wavelengths of visible light, the outer electrons are promoted to an excited state. After a very short time, the excited electrons relax back to the ground state releasing the energy as emitted photons (photoluminescence). The photoluminescence (PL) of the trivalent erbium ion shows multiple peaks in the visible and near-infrared region of the spectrum. Researchers reported that the PL of Er\(^{3+}\) has a temperature dependence. The Richardson group at
Ohio University has used $\text{Er}^{3+}$ ions as a temperature sensor in the form of an Aluminum Gallium Nitride film doped with Erbium (Al$_{0.94}$Ga$_{0.06}$N: Er$^{3+}$) and several temperature measurements have been successfully made using this fabricated film.$^{23, 30, 69-71}$ However, the measured temperature using this film is not local and a scaling parameter called an Optical Transfer Function (OTF) is needed to determine the true temperature (this is further discussed in Chapter 3.).$^{30}$ A great alternative to the film sensor is Erbium Oxide nanoparticles (Er$_2$O$_3$), which are commercially available at a low cost. Using these nanoparticles, the local temperature can be measured with a higher resolution compared to the erbium-doped film. This is because the thermal probe size has been reduced to the nanometer scale. In the nanoparticle sensor, the measured temperature is local and it is not limited by the diffraction of the optics, but by the size of the temperature sensor (particle size). The second advantage of these temperature nanosensors is the ability to optically trap them and selectively place them on the site where the temperature measurement takes place. In both the Al$_{0.94}$Ga$_{0.06}$N: Er$^{3+}$ film and the Er$_2$O$_3$ nanoparticles, the PL emission results from the excited state relaxation after the absorption of 532 nm light by the Er$^{3+}$ ions. Because of the two excited energy levels that are thermally coupled, two emission bands are expected in the visible region due to the transition of $^4S_{3/2}$ to $^4I_{15/2}$ and $^2H_{11/2}$ to $^4I_{15/2}$ state (see Figure1.7).
Upconverting nanoparticles have proven to be a promising tool for sub-micro scale thermometry. These particles have been given significant attention because of their ability to emit a photon at a shorter wavelength (higher energy) than the absorbed photon. This is a non-linear process, described as upconversion and it can be considered as anti-stock emission. UCNPs consist of three main components with each having an essential role to play: crystalline host, dopant lanthanide ion (phosphors), and lanthanide ion (sensitizer). The crystalline host is an inorganic material such as NaYF₄, and it acts as a matrix that holds everything together. The choice of the host material is critical since it determines several factors such as the distance between the dopant ions, and the ions’ position. It is necessary to have a crystal host with low phonon energy; otherwise, the number of radiationless relaxation will be high, leading to a decrease in the final
emission. The activator, a dopant lanthanide ion, represents the luminescent center in the crystal and it requires an intermediate long-lived excited state. Er\(^{3+}\) ion is an excellent candidate to act as a dopant ion inside the crystal. The long lifetime of the excited state in this ion, which is on the order of micro to milliseconds, leads to sequential excitations in the excited states. This is due to the nature of the electronic transitions (4f-4f) inside the Ln\(^{3+}\) ions that are dipole forbidden based on the Laporte selection rules. Even though many lanthanides ions can be utilized as phosphors, Er\(^{3+}\) ion is the most commonly used, especially in thermometry applications. This is because, as described previously, Er\(^{3+}\) ion shows two bands in the visible region, whose relative intensity has a temperature dependence. The sensitizer, which is usually a Yb\(^{3+}\) ion, plays a significant role in enhancing the luminescence efficiency by transferring the energy to the luminescence center (Er\(^{3+}\) ion). This is because a Yb\(^{3+}\) ion has an absorption cross section that is orders of magnitude greater than that of an Er\(^{3+}\) ion. The upconversion process in the NaY\(_{4}\): Yb\(^{3+}\), Er\(^{3+}\) nanoparticles can be described as shown in the energy diagram below (see Figure 1.8). First, as the Yb\(^{3+}\) ion absorbs a photon from the 980 nm laser; it is promoted from the ground state (\(^2F_{7/2}\)) to the excited state (\(^2F_{5/2}\)). The excited state (\(^2F_{5/2}\)) in the Yb\(^{3+}\) ion is in resonance (has the same energy) with one of the excited states (\(^4I_{11/2}\)) in the Er\(^{3+}\) ion, so there is an energy transfer occurring from the Yb\(^{3+}\) to the Er\(^{3+}\) ion. Because of two successive energy transfers from the Yb\(^{3+}\) ion, the Er\(^{3+}\) ion is promoted from the ground state (\(^4I_{15/2}\)) to an intermediate state (\(^4I_{11/2}\)), which has a long lifetime, and then finally to the excited state (\(^4F_{7/2}\)). The population of (\(^4F_{7/2}\)) excited state in the Er\(^{3+}\) ion can occur by the Excited State Absorption (ESA) process that results from the transition of (\(^4I_{11/2}\) to the
Another possibility is the population via the energy transfer (ET) process from Yb\(^{3+}\) (\(^{2}F_{5/2}\)) to Er\(^{3+}\) (\(^{4}I_{11/2}\)). On the other hand, the intermediate excited state (\(^{4}I_{11/2}\)) can be populated either through the Energy Transfer (ET) from Yb\(^{3+}\) (\(^{2}F_{5/2}\)) to Er\(^{3+}\) (\(^{4}I_{15/2}\)) or by the Ground State Absorption (GSA) process that leads to a transition from (\(^{4}I_{15/2}\)) to (\(^{4}I_{11/2}\)) in the erbium ion as a result of 980 nm absorption. Some Non-Radiative (NR) relaxation takes place that leads to the population of (\(^{4}S_{3/2}\)) and (\(^{2}H_{11/2}\)) energy levels. The transitions from (\(^{4}F_{7/2}\)) to (\(^{2}H_{11/2}\)) and (\(^{2}H_{11/2}\)) to (\(^{4}S_{3/2}\)) are non-radiative. Then, the transition from the (\(^{2}H_{11/2}\)) and (\(^{4}S_{3/2}\)) excited states to the ground state (\(^{4}I_{15/2}\)) is responsible for the green light emission in the UCNPs. In addition, there is another emission band in the red region that is due to the NR relaxation from (\(^{4}S_{3/2}\)) to (\(^{4}F_{9/2}\)), and then the de-excitation from that state to the ground state (\(^{4}I_{15/2}\)) (see Figure 1.9). However, the green emission in these particles is more interesting for the thermometry applications. The two levels (\(^{4}S_{3/2}\) and \(^{2}H_{11/2}\)) are only separated by several hundreds of wavenumbers. Therefore, the populations of these two levels as we described before depend on the temperature following Boltzmann’s distribution relation\(^{58}\):

\[
R = \frac{N(H)}{N(S)} = A \exp\left(-\frac{\Delta E}{kT}\right),
\]

where \(N(H)\) and \(N(S)\) are the population of the \(^{2}H_{11/2}\) and \(^{4}S_{3/2}\) energy levels respectively, \(\Delta E\) is the energy gap between the two levels in cm\(^{-1}\), \(K\) is the Boltzmann constant, \(T\) is the absolute temperature in Kelvin, and \(A\) is a constant that depends on the degeneracy of states, the emission cross section, and the angular frequency of the \(^{2}H_{11/2}\) and \(^{4}S_{3/2}\) to \(^{4}I_{15/2}\) transitions.\(^{73}\)
Figure 1.8 Energy level diagram showing the NIR energy transfer from the sensitizer $\text{Yb}^{3+}$ ion to the dopant $\text{Er}^{3+}$ ion. Four mechanisms can occur in the upconversion process: Energy transfer (ET), excited state absorption (ESA), ground state absorption (GSA) and non-radiative relaxation (NR).

Figure 1.9 A photoluminescence spectrum of UCNPs showing the two thermally coupled bands in the visible region at 525 nm and 550 nm. Another band appears in the near infrared region at 662 nm.
Optical Trapping

Optical trapping, also called the optical tweezer, is a powerful tool that was introduced by Ashkin in 1970 when he demonstrated that a micro size particle could accelerate toward a beam of light and remain trapped.\textsuperscript{74} Using a tightly focused laser beam, it is possible to manipulate a dielectric particle suspended in a solution based on the difference in the refractive index between the particle and the surrounding medium (refractive index mismatch).\textsuperscript{75} For that to occur, the refractive index of the particle should be higher than that of the solution.\textsuperscript{76} In general, the trapping process results from two types of forces: the scattering force and the gradient force. The gradient force leads to the attraction of the particle toward the focus of the laser beam, while the scattering force is created by the change in the light’s momentum because of the light scattering by the particle.\textsuperscript{77} This scattering force tends to destabilize the particle; therefore, stable trapping requires that the gradient force be larger than the scattering force. In addition to that, the trapping force has to overcome the random motion of the particle in the solution; this phenomenon is also called Brownian motion.\textsuperscript{77} This non-contact technique has been used in the direct writing of optical nanostructure patterns\textsuperscript{78} and in many potential biological applications such as the investigation of the mechanical properties of a cell membrane\textsuperscript{79} and DNA stretching using an optically trapped bead\textsuperscript{80}. In this dissertation, the optical tweezer technique is used to manipulate a targeted nanothermal sensor ($\text{Er}_2\text{O}_3$ NPs) to measure the local temperature of the surrounding water at selective sites in the sample.
CHAPTER 2 : EXPERIMENTAL PROCEDURES

(Part of this Chapter is reprinted from “Targeted Nanoparticle Thermometry: A Method to Measure Local Temperature at the Nanoscale Point Where Water Vapor Nucleation Occurs” by Arwa A. Alaulamie et al., 2016. Small, 13, 1601989, Copyright [2016] by WILEY-VCH Verlag GmbH & Co).

Temperature Measurement Using Erbium Oxide Nanoparticles

Preparation of Gold Nanorod Sample

A glass substrate was immersed in a beaker of acetone and sonicated for 10 minutes. Then the sample was removed, dried with nitrogen, and treated with plasma cleaner for 3 minutes to ensure removal of organic contaminants. A dilute solution (~10^10 particles/mL) of 25 nm diameter x 100 nm length gold nanorods (NANOPARTZ) was made with 18 MΩ water and the solution was then spin coated onto the cleaned glass substrate. The substrate was then cleaned of any residual water or dust with nitrogen gas.

Preparation of Erbium Oxide Nanoparticle Solution

Dilute solution of erbium oxide nanoparticles (~1 mM concentration) was prepared by dissolving erbium oxide nanoparticle powder (~50 nm) purchased from Nanostructured and Amorphous Materials INC in 18 MΩ water with stirring and sonication. Disperbyk®-190 and sodium citrate were added as a surfactant and stabilizer, respectively in order to ensure the dispersion of the particles. Finally, a syringe filter of 450 nm diameter was used to exclude the large clusters from the solution.
Photoluminescence - Temperature Calibration Measurement of Erbium Oxide Nanoparticles

To determine the temperature using an optically trapped erbium oxide nanoparticle as a thermal sensor, a measurement was performed to calibrate the photoluminescence of the \( \text{Er}_2\text{O}_3 \) NPs as a function of temperature. A diluted solution of \( \text{Er}_2\text{O}_3 \) NPs was spin coated over a clean glass cover slip and a droplet of 18 M\( \Omega \) water was added to the sample. The cover slip was placed over a peltier heater and a thermocouple was placed inside the water droplet close to the excited erbium oxide nanoparticles. A schematic illustration of the setup is shown in Figure 2.1. Under the optical microscope, using a 60x immersion lens and a 532 nm laser, the \( \text{Er}_2\text{O}_3 \) NPs were excited and the photoluminescence spectrum of these particles was obtained. The temperature, using an applied voltage, was varied between 291 and 316 K. At each temperature, the corresponding photoluminescence spectrum was collected. The change in 539 nm band which corresponds to the \( ^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2} \) transition and 564 nm band, which corresponds to the \( ^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2} \) transition was monitored while varying the temperature. The natural logarithm of the relative intensity between the two peaks was plotted as a function of the inverse temperature as shown in Figure 2.2.
Figure 2.1 A schematic diagram showing the setup for the photoluminescence–temperature calibration measurement of erbium oxide nanoparticles in water. A 532 nm laser is used to excite the Er$_2$O$_3$ NPs on the sample. A thermocouple connected to a digital reader is immersed inside the water droplet and close from the excited particles. Using the peltier cooler, the temperature is varied and a single spectrum of the Er$_2$O$_3$ photoluminescence is recorded at each temperature.

Figure 2.2 A plot of the natural logarithm of the ratio between the $^2$H$_{11/2}$ and $^4$S$_{3/2}$ bands area as a function of the inverse temperature in Kelvin. The slope ($\frac{\Delta E}{K}$) is -1135 ± 39 with an intercept of 1.85 ± 0.13.
Experimental Setup for Temperature Measurements Using Trapped Erbium Oxide Nanoparticles

The optical measurements were made using a WITec α-SNOM300s microscope (see Figure 2.3). The glass cover slip with the spin-coated gold nanorod clusters was placed under the microscope and a very small amount of Er$_2$O$_3$NP solution was added on top of the coverslip followed by the addition of pure water to dilute the solution and a droplet was placed on top of the coverslip. A Nikon 60x water immersion lens (NA 1.00) was then focused onto the surface of the substrate. Through dark-field illumination, the suspended Er$_2$O$_3$NPs in the solution were located and selectively an erbium oxide nanoparticle cluster was trapped and irradiated with a CW 532 nm Nd: YAG laser with adjustable power. The sample stage was moved very slowly and carefully to the region with nanorod clusters seen under dark-field illumination. The trapped erbium oxide nanoparticle cluster was deposited over a cluster of gold nanorods. The 532 nm laser excites the Er$_2$O$_3$NPs and heats the nanorod cluster simultaneously. The photoluminescence from the Er$_2$O$_3$ was collected with 100µm optical fiber connected to a charge-coupled device (CCD) spectrograph that is used for temperature measurements. Dynamic measurements of the temperature were performed to determine the nucleation temperature in the non-degassed and the degassed water. Degassed water was prepared from ultrapure 18.2 MΩ water by boiling the water for 10 minutes followed by sonication and repeating the process at least two times. The nanorods were excited (heated) in non-degassed and degassed water and the temperature change over the time was monitored by collecting the resulting photoluminescence from the Er$_2$O$_3$NPs at an integration time of 0.1 seconds. The laser intensity was increased stepwise throughout
the time measurements in order to determine the nucleation temperature. The spectrum, as well as a video, were collected simultaneously using a trinocular to determine the nucleation event and the corresponding temperature for the nucleation event. A large number of measurements were performed on several clusters of gold nanorods for both non-degassed and degassed water.

Figure 2.3 (A) An image of Near-Field Scanning Optical Microscope (WITec α-SNOM300s) used for data collection. (B) LED white light ring used for bubble dark-field imaging. (C) Corresponding diagram of the internal setup of the NSOM. 1. Bandpass filter 2.Dichroic mirror 3. Focusing objective (60x) 4. Sample.
Absorption Measurement of Gold Nanorod Clusters

An absorption spectrum of gold nanorod clusters over a glass substrate and immersed in water is collected using a WITec α-SNOM300s microscope. The sample is prepared by drop casting a gold nanorod solution on a cover slip, drying and placing the sample under a water immersion lens. Using white light source (halogen lamp), the sample is illuminated from the bottom and the transmitted light was collected from the top using 60x objective. The collected light is sent to a CCD camera using a 25µm collection fiber. An absorption image spectrum (10 x10 µm) is acquired by scanning over a group of gold nanorod clusters with an integration time of 0.03 s. The background spectrum (reference) is taken from the image spectrum outside the gold cluster. The absorbance is calculated using the Beer-Lambert law.

Method of Bubble Video Recording and Video Analysis

Some of the data presented here were collected by simultaneously recording the bubble growing movie and the erbium oxide photoluminescence time spectrum. For this purpose, a trinocular is used to divide the collected light such that half of the light is sent to the CCD detector to generate a spectrum, and the other half is sent to the camera as shown in the diagram (Figure 2.4). However, this causes a reduction in the number of acquired counts. For this reason, data collected using this trinocular show a low signal to noise ratio. All movies are collected with a frame rate of 25 frames/second.
Figure 2.4 A schematic diagram showing the modified setup for a simultaneous bubble video recording and spectrum collection. The red arrow points to the trinocular that splits 50% of the light to the camera and the other 50% to the CCD.

Bubble videos are analyzed using the ImageJ software. After converting the colored movies to grayscale, the threshold of the bubble in all frames is adjusted based on the difference in the contrast between the bubble and the background (see Figure 2.5 A and B). By processing, particle analyzing, and depending on the adjusted threshold, the total area of the bubble is acquired for every frame. At the time when the bubble does not form yet, the area is zero as shown in Figure 2.5C.
Figure 2.5 Panel A and B show the bubble image before and after adjusting the threshold respectively. (C) A plot of the bubble diameter (calculated from the area) as a function of time results from the analyzed video. The arrow points to the time when the bubble initially forms. The blue highlighted plot is the magnified region from 13.5 to 14.5 seconds (the region where bubble forms).

Temperature Measurement Using Upconverting Nanoparticles

Synthesis of \((NaYF_4: Er^{3+}, Yb^{3+})\) Upconverting Nanoparticles

The upconverting nanoparticles are synthesized using the thermal decomposition method as previously described in the literature.\(^8\) This method is based on the thermal decomposition of metallic trifluoroacetate. Sodium trifluoroacetate is added to a solution
of two mixed solvents that have been used for different purposes, octadecene, which has a high boiling point and is necessary for providing the suitable temperature for the reaction. The second solvent is oleic acid and it works as a capping agent to prevent the nanoparticles from aggregation. The synthesized particles are 300 nm and a Transmission Electron Microscopy (TEM) image of the particles is shown below.

![TEM image](image)

Figure 2.6 TEM image of synthesized NaYF₄: Er³⁺, Yb³⁺ upconverting nanoparticles using thermal decomposition method. The panel on the right is a zoomed in image of a single nanoparticle. The nanoparticle has a hexagonal shape with a diameter of ~ 300 nm.

**Preparation of Silver Nanoparticles Sample**

A colloidal solution of 20 nm silver nanoparticles purchased from TED PELLA, INC (BBinternational) is diluted, sonicated and drop casted over a previously a clean glass substrate. Using a hot plate, the water is allowed to evaporate lifting the particles behind on the coverslip. The clusters of silver nanoparticles can be examined under a dark-field microscope as shown in Figure 2.7.
Figure 2.7 Dark-field image of silver nanoparticle clusters in water.

Water Degassing Process

In this measurement, water is degassed via a Freeze-Pump-Thaw method. The setup consists of a sealed glass tube, a vacuum pump, and a glass syringe with a long needle that connects the vacuum pump to the sealed tube. The process starts with fast freezing of 18 MΩ deionized water in the sealed tube using liquid nitrogen. When the water is completely converted to ice, the vacuum pump is turned on and pumps off the gases for a couple of minutes. The vacuum valve is then closed and the tube immersed in a water bath. As the ice starts melting, the valve is opened again. The same process is repeated for five to seven times or until the gases disappear from the liquid.
Figure 2.8 The water-degassing process using the Freeze-Pump-Thaw method is shown. (A) Freezing the water inside the glass tube using liquid nitrogen and pumping off the gases for about 2 minutes. (B) Melting ice using a water bath and pumping off gases simultaneously. (C) An image of frozen water before degassing. (D) An image shows some gases evolve from the liquid. (E) An image of the frozen water after 3 cycles of degassing.

Upconverting Photoluminescence - Temperature Calibration Measurement

The setup and the process of the photoluminescence - temperature calibration measurement of UCNPs is similar to that previously described in the Er2O3NPs photoluminescence calibration measurement. The natural logarithm of the ratio between the two bands as a function of the inverse temperature for the upconverting nanoparticles is shown in Figure 2.9.
Figure 2.9 A plot of the natural logarithm of the intensity ratio between the two bands ($^4S_{3/2}$) and ($^2H_{11/2}$) as a function of the inverse temperature. The slope of the line is $-1343 \pm 37$ and the intercept is $1.84 \pm 0.123$.

Experimental Setup of Two Color Lasers Temperature Measurement

As previously described, the temperature measurement is conducted using a WITec α-SNOM300s microscope; however, some major changes are done to accommodate the purpose of this study. The prepared sample of silver nanoparticles (see Figure 2.7) is placed under the microscope and an 18 MΩ water droplet is added to the sample followed by the addition of a very small droplet of the prepared diluted UCNP solution (using a syringe needle). The UCNP solution is passed through a 450 nm syringe filter to ensure that the solution only carries single UCNP and not large clusters. After a period, the water droplet is removed from the sample and the sample is completely dried using Nitrogen gas. Another water droplet is added to the sample. Using 60x immersion lens, a 980 nm
wavelength laser is illuminated from the top to excite the UCNPs that are placed on the silver nanoparticle cluster surface. The green emission from these particles (see Figure 2.10) is collected by the same objective and sent to the charge-coupled device (CCD camera) using a 100 µm collection fiber. For heating the silver nanoparticles, 405 nm laser is illuminated from the bottom through a 50x objective. A representative diagram of the setup is shown in Figure 2.11. The intensity of the 980 nm is held at a constant value where it is adjusted to provide a good signal to noise ratio, without causing water heating (this will be discussed later in Chapter 5). The 405 nm laser intensity is increased during the collection of the time spectrum until bubble forms. When bubble forms, the intensity of the 405 nm is reduced gradually until to the point where the bubble collapses.

Figure 2.10 An image showing the green emission from UCNP cluster on a glass substrate using 980 nm laser with a spot size of 4µm.
Figure 2.11 A schematic illustration and images to show the setup of the two-laser colors temperature measurement. The 980 nm laser is used from the top with a 60x immersion lens to excite the UCNPs over the silver nanoparticle clusters. The 405 nm laser is illuminated from the bottom using a 50x lens to heat the silver nanoparticles on the glass substrate. The green emission from the UCNPs is collected by the same 60x lens and sent to the CCD camera.
CHAPTER 3: ERBIUM OXIDE NANOPARTICLES CHARACTERIZATION FOR NANOSCALE THERMOMETRY

(A major part of this Chapter is reprinted from “Targeted Nanoparticle Thermometry: A Method to Measure Local Temperature at the Nanoscale Point Where Water Vapor Nucleation Occurs” by Arwa A. Alaulamie et al., 2016. Small, 13, 1601989, Copyright [2016] by WILEY-VCH Verlag GmbH & Co).

Introduction

A number of new optical techniques have been introduced that can measure temperature in different micro and nanoscale environments. Measuring temperature with high spatial resolution is important for many potential applications such as mapping temperature inside living cells, micro/nanofluidic, the semiconductor industry, and microcircuit temperature mapping. A major limitation with nanoscale temperature measurements is that it is difficult to obtain absolute local temperature measurements with a spatial resolution that is not diffraction limited.

Previously, we have developed optical probes to measure the local temperature around a nanoscale hotspot. An amorphous Al$_{0.94}$Ga$_{0.06}$N thin film doped with a small amount of Er$^{3+}$ was used to measure the temperature of a single optically excited gold nanostructure. The temperature is extracted by measuring the ratio of photoluminescence peak intensities of Er$^{3+}$ where the relative peak intensities are given by a Boltzmann relationship. The limitation of this technique is a large temperature gradient occurs within the collection volume and scaling of the measured temperature was necessary to infer the local temperature of the nanostructure. The spatial resolution using this thin film approach is inherently diffraction limited (\(\sim\lambda/2NA\)). Sub-diffraction-limited temperature
measurements are possible if the thermal sensor size is smaller than the diffraction limit. In this type of measurement, the optical emission is used to determine the temperature from an emitting object whose size is smaller than the diffraction limit. Based on this principle, we have used Er$_2$O$_3$ nanoparticle emitters as the local temperature probes. This method uses erbium oxide nanoparticles to measure the absolute local temperature around the nanoparticle with a resolution that is limited by the size of the nanoparticle or nanoparticle cluster (50 - 450 nm). Using this new tool, it is possible to measure a local temperature for different systems by simply trapping the thermal nanosensor and attaching it to the site where the temperature measurement takes place.

Here, we characterized a new nanothermometry technique that uses a targeted approach where a cluster of Er$_2$O$_3$ nanoparticles is laser-trapped, moved and attached to the spot where the temperature measurement is collected. We attach the Er$_2$O$_3$ nanoparticles to a cluster of gold nanorods that is optically heated with a 532 nm laser. The temperature dependent photoluminescence of Er$_2$O$_3$ nanoparticles is characterized and these novel local temperature sensors are used to characterize the temperature where bubble formation occurs in water.

**Results and Discussion**

*Characterization of Erbium Oxide Nanoparticle Temperature Sensors*

The excitation of erbium oxide nanoparticles using a 532 nm light populates the $^2$H$_{11/2}$ and $^4$S$_{3/2}$ energy levels in Er$^{3+}$ ion as shown in Figure 3.1A. Relaxation to the ground state $^4$I$_{15/2}$ results in emission from the $^2$H$_{11/2}$ and $^4$S$_{3/2}$ energy levels. Because these energy levels ($^2$H$_{11/2}$ and $^4$S$_{3/2}$) are thermally coupled, any change in the temperature causes...
a change in the populations of these two levels and as a result, a change in the relative intensity of the two emission bands (see Figure 3.1B).\textsuperscript{114,115} The ratio of band areas (R) is given by $A \exp\left(-\frac{\Delta E}{kT}\right)$ as we described previously in Chapter 1. The expected Boltzmann relationship for an erbium oxide nanoparticle photoluminescence with temperature is confirmed by heating the nanoparticles and recording the PL spectrum at different temperature intervals (see erbium oxide photoluminescence calibration measurement in Chapter 2). Figure 3.2A shows a plot of the natural logarithm of R as a function of the reciprocal temperature. This plot results in a straight line with a slope of $-1135 \pm 39$ and an intercept of $1.85 \pm 0.13$. The slope represents the value of $(\frac{\Delta E}{k})$ and is in agreement with a peak separation of 788 cm$^{-1}$, i.e., 1135 K$\times$ 0.695 cm$^{-1}$/K = 788 cm$^{-1}$. The intercept is related to the density of states between the $^2H_{11/2}$ and the $^4S_{3/2}$ levels. The density of states shows up in the band area and the intercept value depends upon how much band area is included in determining the ratio R. Measuring the photoluminescence spectrum of erbium oxide nanoparticle cluster that has been attached to a cluster of nanorods and then excited with 532 nm laser tests this temperature calibration. Attaching the thermal sensor to a nanorod cluster is accomplished by laser trapping an Er$_2$O$_3$NP cluster, moving it, and placing it on the gold nanorod cluster. After the nanoparticle is placed on the nanorod cluster, the laser intensity is increased until the nanoparticle cannot be moved even when the sample is moved. Figure 3.2B plots the temperature difference obtained from the temperature calibration against laser intensity. A linear relationship is expected with an intercept that goes through the origin. We observed a linear relationship but the slope is
displaced above the origin. This is probably due to the interaction between the gold nanorod cluster and the erbium oxide nanoparticle. However, the linear relation that is observed between $\Delta T$ and laser intensity confirms that this interaction does not affect the accuracy of our temperature and calibration measurements. A new calibration curve is obtained that includes this interaction by shifting our original calibration so the slope goes through the origin. This shifting changes the intercept value from 1.85 to 2.01. We used this value for the intercept for all subsequent temperature measurements in this dissertation.

Figure 3.1 (A) An energy level diagram of an Er$^{3+}$ ion. The populations of the two energy levels $^2H_{11/2}$ and $^4S_{3/2}$ are temperature dependent. (B) Photoluminescence spectrum of an Er$_2$O$_3$NP at a temperature of 330 K (shown in black) and at 520 K (shown in red). The 539 nm band represents the $^2H_{11/2} \rightarrow ^4I_{15/2}$ transition and the 564 nm band corresponds to the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition. The difference in energy between these two transitions represents the value of $\Delta E$. $\Delta E$ divided by the Boltzmann constant ($k$) is $\sim 1135$ K.
Figure 3.2 (A) A plot of the natural logarithm of the ratio between the $^2H_{11/2}$ and $^4S_{3/2}$ bands area as a function of the inverse temperature in Kelvin. The slope ($\frac{\Delta E}{K}$) is $-1135 \pm 39$ with an intercept of $1.85 \pm 0.13$. (B) A plot of temperature change in (K) as a function of laser intensity in W/m$^2$. Temperature change (shown in blue) is calculated using the slope and the intercept values that resulted from the calibration measurement. Temperature change (shown as red data) is moved by an offset to give a linear trend with a zero temperature change at no laser power.

**Band Area Determination of ($^2H_{11/2} / ^4S_{3/2}$) Peak and Baseline Correction**

The photoluminescence spectrum of the Er$_2$O$_3$NPs over a cluster of gold nanorods has an underlying band that needs to be baseline corrected. Without baseline correction, a different wavelength region for calculating the band area leads to different intercept values and ultimately may lead to under or overestimate the temperature. We first performed baseline correction of the spectra using WITec software by fitting a mask to the area under the peaks with (537 – 540 nm), (544.7 – 557 nm), and (558.9 – 566.2 nm) wavelength (see Figure 3.3B). It should be noted that to calculate the band ratio, we only integrated the emission band from 535-540 nm, which is attributed to the $^2H_{11/2} \rightarrow ^4I_{15/2}$ transition and the emission band from 560-570 nm, which is attributed to $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition (the
highlighted areas in Figure 3.3A). Although the group of peaks between 545 to 557 nm is a part of the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition, we excluded these peaks in our calibration and temperature measurements. Fitting a mask to the area under these peaks will be more difficult and it is expected to be associated with a large error since a significant change in the baseline is observed when a bubble forms. This baseline becomes extremely pronounce in the region having a wavelength of 545 nm to 557 nm.

![Figure 3.3](image)

Figure 3.3 (A) Photoluminescence spectrum of Er$_2$O$_3$NPs. The highlighted peaks $^2H_{11/2}$ and $^4S_{3/2}$ represent the areas that used to calculate the ratio for the calibration temperature measurement. (B) Photoluminescence spectrum of an Er$_2$O$_3$NP over a cluster of gold nanorods before and after baseline correction shown in red and blue spectrum respectively.

Local Temperature Measurement from Nanoscale Hot Spot in Water

Figure 3.4A-C shows an illustration of the procedure for collecting the temperature in a nanoscale hot spot in liquid water. A cluster of gold nanorods is deposited on a glass coverslip and immersed in water. The cluster dimensions are much larger than the laser
spot size (~500 nm) so the size of the optically excited hot spot is limited by the laser spot size. Collective heating of the nanorods ensures that the heated area of the cluster has a relatively uniform temperature profile. An Er$_2$O$_3$NP cluster (see Figure 3.5) is laser-trapped, moved and attached to the gold nanorod cluster by moving the stage under the sample as shown in the inverted dark-field images in Figure 3.4D-F. In Figure 3.4D, the circle labeled 1 is a cluster of nanorods, circle 2 is the laser spot and circle 3 is a cluster of erbium oxide nanoparticles. The cluster of Er$_2$O$_3$NPs is moved and trapped using a 532 nm laser. As a result, the laser spot becomes brighter as shown with the circle labeled 2, 3 in figure 3.4E. After trapping, the stage under the sample is moved slowly until the trapped particle and the gold nanorod cluster co-align. Finally (as shown in Figure 3.4F, circles labeled 1, 2, 3), the laser-trapped Er$_2$O$_3$NP cluster is attached to the nanorods by increasing the laser intensity. After attaching the nanoparticle cluster, the laser position is fixed and the photoluminescence spectrum collected as the laser intensity is increased. The change in the temperature of the gold nanorod cluster as a function of laser power is shown in Figure 3.6A. Figure 3.6B shows the change in the relative intensity of the Er$_2$O$_3$NPs as a result of heating the gold nanorod cluster at three different laser powers.
Figure 3.4 A schematic illustration of the optical temperature measurement using laser-trapped erbium oxide nanoparticle cluster. (A) Optical trapping of Er$_2$O$_3$NPcluster using 532 nm laser. (B) Attaching the laser-trapped Er$_2$O$_3$NPs onto the gold nanorod cluster. (C) Measuring the local temperature of the system inside the bubble by tracking the change in the photoluminescence of the Er$_2$O$_3$NPs as a function of time. (D, E, F) A series of color inverted dark-field images showing the sequence of trapping a cluster of Er$_2$O$_3$NPs and attaching it to a gold nanorod cluster. (D) Gold nanorod cluster, laser spot, and erbium oxide nanoparticle cluster are labeled 1, 2, and 3 respectively. (E) Shows the bright laser spot after trapping the Er$_2$O$_3$NP cluster. The red dashed arrow indicates the direction of the sample stage movement toward the trapped cluster of Er$_2$O$_3$NPs. (F) The trapped Er$_2$O$_3$NP cluster is deposited over the nanorod cluster by a slight increase in the laser power.
Figure 3.5 Transmission Electron Microscope (TEM) image of (45 ~ 50 nm) erbium oxide nanoparticles.

Figure 3.6 (A) A plot of the local temperature in Kelvin taken from a single spectrum as a function of 532 nm laser power (mW). (B) Photoluminescence spectra of erbium oxide nanoparticles over a gold nanorod cluster at different laser powers 16.7, 9.4 and 6.1 mW.

Figure 3.7 shows the change in temperature in degassed water measured using the Al$_{0.94}$Ga$_{0.06}$N film doped with Er$^{3+}$ as well the Er$_2$O$_3$NPs as a function of the ratio of laser intensity divided by the critical laser intensity (I/Ic), where Ic is the critical intensity at
which the spinodal temperature is observed. In our previous work, we measured the nucleation temperature in degassed water by optical heating of single gold nanostructure over the Er$^{3+}$ doped film as shown in the black data. The optically measured temperature using a diffraction-limited spot is much lower than the real temperature of the optically excited gold nanostructure. Diffraction limited temperature measurements suffer from a lack of spatial resolution needed to clearly resolve the correct temperature.

Figure 3.7 Temperature change as a function of the ratio of laser intensity divided by the critical laser intensity. The critical laser intensity is the intensity that drives the optical heater to the spinodal decomposition temperature. The temperature change shown on the left axis is measured using an Al$_{0.94}$Ga$_{0.06}$N thin film doped with Er$^{3+}$ (shown in black) and the temperature change shown on the right axis is from optically trapped Er$_2$O$_3$NPs (shown in red).
Figure 3.8. A comparison between Al$_{0.94}$Ga$_{0.06}$N:Er$^{3+}$ film sensor (left) and Er$_2$O$_3$NP sensor (right). The collected emission from the film sensor is an averaged emission from the cold (blue) and the hot (red) region. The Er$_2$O$_3$NPs size ranges from 150 to 450 nm size.

A scaling factor is needed to adjust the measured temperature to the correct local temperature. This effect is illustrated in Figure 3.8. Figure 3.9 shows the measured thermal profile that is simulated with a two-dimensional convolution of a normalized sub-diffraction Gaussian thermal profile (FWHM of 114 nm, labeled A) with the point-spread function of the microscope (labeled B). The point-spread function is approximated as a two-dimensional Gaussian with a FWHM of 500 nm and the sub-diffraction thermal profile is approximated as a two-dimensional Gaussian. The “true” thermal profile is expected to drop with temperature as 1/distance away from the local hot spot. The convolution is shown in Figure 3.9C. The convolution results in an image whose maximum is approximated 10 times lower than the sub-diffraction thermal profile. Figure 3.9D shows a one-dimensional cross-section through the maximum from the sub-diffraction thermal image (labeled A), the convoluted image (labeled C) and the convoluted image scaled by
10.2 (green profile). The optical transfer function (a scalar in this case) that relates the measured image to the “true” image is 10.2. Previously, we found that an optical transfer function (OTF) of 10.2 can be used to scale the measured diffraction limited temperature to the local temperature (real sub-diffraction-limited temperature profile).\textsuperscript{30} In Figure 3.7, the measured temperature using a diffraction-limited spot needs to be multiplied by a factor of 10.2 to determine the local temperature of the nanostructure. This first-order scaling does not take into account the size or shape of the optically excited gold nanostructure and assumes a point heat source that spreads out spherically from the point source. This approach of using a single scaling factor for the OTF is only necessary if the spatial resolution cannot adequately resolve the true thermal image. Using small thermal sensor particles will provide the necessary spatial resolution to fully determine the correct local temperature circumventing the need for an OTF scaling parameter. The red squares in Figure 3.7 represent the temperature measured with an Er\textsubscript{2}O\textsubscript{3}NP cluster attached to a nanorod cluster surrounded by degassed water. The critical laser intensity was determined by the intensity that caused a large temperature spike in the step-wise optical heating of the nanorod cluster. The temperature spike is caused by an insulating cocoon of vapor surrounding the hot spot in water. We have previously shown that the temperature needed to promote vapor nucleation in degassed water is spinodal decomposition of water. This temperature is \(~\text{90}\%\) of the critical temperature of water. The temperature scales are shown in Figure 3.7 differ by a factor of 10, \textit{i.e.}, the nanoparticles thermal sensor measured $\Delta T$ is 10 times larger than the film measured $\Delta T$. Mapping the film measured $\Delta T$ onto the
nanoparticle measured $\Delta T$ required an OTF of 10 in agreement with our previous expectations.

Figure 3.9 Two-dimensional convolution of the local temperature change of a heated gold nanostructure with the point spread function (PSF) of the optical microscope. (A) Normalized sub-diffraction two-dimensional (2-D) Gaussian thermal profile with FWHM of 114 nm. (B) 2-D Gaussian of the point spread function with FWHM of 500 nm. (C) 2-D Gaussian of the convoluted image; the measured thermal profile is ~10 times lower than the sub-diffraction thermal profile. (D) One-dimensional cross-section through the maximum from the sub-diffraction thermal image labeled A (blue line) and the convoluted image labeled C (orange line). The orange profile is scaled by the optical transfer function of 10.2 to give the profile shown in green.

Temperature Uncertainty Using Er$_2$O$_3$ Nanoparticles

To evaluate the sensitivity of the temperature measurement, we analyzed the time variation in temperature. The temperature time variation is shown in Figure 3.10A and is
collected at 0.06 s integration time. The standard deviation in the temperature decreases with increasing the laser power, as expected. We found that the measured temperature using this technique has a noise floor of 0.28 K Hz$^{-1/2}$ with 0.06 s integration time and 8.2 mW laser power. This value is comparable to previously published work where the temperature was measured using a single diamond crystal with a noise floor of 0.3 K Hz$^{-1/2}$ at 1 s integration time. Figure 3.10B is a plot of the standard deviation (SD) (calculated from the temperature-time spectrum) as a function of laser power. The slope and the intercept of the linear relation in Figure 3.10B are used to calculate the noise floor at different laser powers.

$$SD = -0.14 \text{ Power (mW)} + 2.32$$

$$\text{Noise floor} = \frac{SD \text{ (K)}}{\text{int time (s)}^{-1/2}}$$

For 0.06 s integration time:

$$\text{Noise floor (K/Hz}^{1/2}) = -0.0344 \text{ Power (mW)} + 0.569$$
Technique Limitations and Challenges

Some challenges were faced in the process of this study. As the particle size is reduced, the trapping process becomes more difficult and laser power becomes a critical parameter. For optimum and stable optical trapping, the laser power should be relatively high. However, if the gold nanoparticle clusters nucleate at that laser power, attaching the particles becomes difficult since the formed bubble will repel the particle away from the laser beam focus. The electrostatic attraction between the trapped Er₂O₃NPs and the substrate surface is another critical challenge. In many cases, the trapped particle sticks to the substrate surface before it is attached to the target place. This effect can be minimized by coating the substrate surface with the opposite charge.
Conclusion

A sensitive method using an erbium oxide nanoparticle cluster that measures local temperatures is introduced. The optically trapped nanothermal sensor measures the temperature from a cluster of gold nanorods immersed in water. The nanoparticle uses the photoluminescence intensities from $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition at 539 nm and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition at 564 nm to measure spatially resolved temperature that is within the size of the nanoparticle cluster. This new and non-invasive temperature technique shows a noise floor of $\sim 0.28 \text{ K Hz}^{-1/2}$. 
CHAPTER 4: LOCAL TEMPERATURE MEASUREMENT OF VAPOR NUCLEATION AND DISSOLVED GAS EFFECT

(A major part of this Chapter is reprinted from “Targeted Nanoparticle Thermometry: A Method to Measure Local Temperature at the Nanoscale Point Where Water Vapor Nucleation Occurs” by Arwa A. Alaulamie et al., 2016. Small, 13, 1601989, Copyright [2016] by WILEY-VCH Verlag GmbH & Co).

Introduction

Replacing power stations that use fossil fuels with a pollution free sustainable source of energy is becoming more feasible as solar thermal-energy-power plants around the world are becoming more efficient.\textsuperscript{116} Water is the only substance that exists in the ecosphere in all three states of matter. Almost 70\% of it is in solid form and the entire accessible liquid water on Earth is recycled by the hydrological cycle of evaporation-precipitation ~37 times annually. The breadth of physical and chemical phenomena underlying this massive natural purification plant is staggering. Central to the hydrological cycle lies the issue of phase transformations. Improving heterogeneous supports that convert light to heat is important in improving the efficiency and alternately reducing production costs of megawatt solar thermal power plants. Understanding the mechanism of nanoscale phase transformations is crucial for improving this conversion.

Vapor bubbles on order of micro or nanometer can be used as contrast agents in ultrasound imaging and as powerful tools in diagnostic and therapeutic applications.\textsuperscript{4, 6, 8, 117-119} Bubble properties make them excellent vectors for drug delivery as microsyringes where therapeutic payloads are attached to the bubble surface and released at the targeted area.\textsuperscript{5} However, there is still a tremendous amount of information that we do not understand
about bubble thermodynamics, nucleation, stability, and bubble surface interaction with solvated molecules. Discovering new bubble properties and dynamics is accelerating because of recent developments in optical techniques that measure *in situ* properties, which will greatly advance our understanding of bubble physics.

Classical nucleation theory reveals that bubble nucleation from nanometer-sized structures or flat surfaces should not occur at temperatures close to the boiling point but at large superheated temperatures (~0.90 of the critical temperature). Cavities nucleate better than posts. This behavior is in agreement with classical nucleation theory where the Young-Laplace equation, \[ P_v - P_l = \frac{2\sigma}{r}, \] describes the pressure difference across the surface of a vapor bubble. In this equation, \( P_v \) is the vapor pressure, \( P_l \) is the liquid pressure, \( \sigma \) is the surface tension, and \( r \) is the bubble radius of curvature. This trend has been recently verified experimentally using nanometer to micron-sized posts and cavities fabricated by e-beam lithography. Bubble nucleation is important in the energy conversion processes that use phase change materials. Recently, it has been observed that bubble nucleation from an array of heated gold nanoparticles occurs between 220 and 240 °C. Recently, we have shown that continuous wave excitation of an individual gold nanodot at a solid liquid interface does not preferentially induce bubble formation at the boiling point, but superheats the liquid around the nanodot to the spinodal decomposition temperature. We proposed a mechanism in which superheating of the liquid occurs because there is a barrier to vapor formation that traps the liquid in a metastable state. This barrier exists for temperatures as high as the spinodal decomposition temperature where the liquid is no longer metastable but spontaneously decomposes into thermodynamic stable states at that
temperature. This picture is in agreement with classical nucleation theory.\textsuperscript{120} We further proposed that increasing the number of nucleation centers either by heating a larger volume of water or introducing more nucleation centers (dissolve gases) should lower the nucleation temperature.

Here, we measure the local nucleation temperature and follow the temperature inside the bubble during bubble formation. The temperature inside the bubble spikes to over 1000 K because the heat source (optically heated nanorods) is no longer connected to liquid water and the heat dissipation is greatly reduced. We observe that dissolved gases in the solution lower the nucleation temperature compared to the solution of degassed water and we hypothesize that the dissolved gases work as nucleation sites that help nucleate vapor in water at a lower temperature compared to water without dissolved gases.

Results and Discussion

	extit{Characterization of Nanorod Optical Heaters}

Figure 4.1 shows a Scanning Electron Microscopy (SEM) image of a cluster of nanorods used as optical heaters. The left panel is a zoomed out image of a representative nanorod cluster used as a nanoheater to optically raise the nanoscale local temperature to the nucleation point. The panel on the right is a zoomed in image of the panel on the left. The white arrow points to a large $\text{Er}_2\text{O}_3\text{NP}$ cluster that is trapped and attached to an aggregate of gold nanorods before taking the SEM images. The erbium oxide nanoparticle cluster size is $\sim 600$ nm. The $\text{Er}_2\text{O}_3\text{NP}$ solution that is used here was not filtered with the 450 nm syringe filter that was used previously at the time of collecting the data. The gold nanorods are 25 nm in diameter and 100 nm long. As observed from these images, the
nano rod cluster consists of planar stacking of the nanorods. The absorption spectrum of a cluster of gold nanorods immersed in water over a glass substrate has a transverse and a longitudinal mode that observed at ~ 573 nm and 782 nm, respectively (see Figure 4.2). The absorption spectrum of these clusters is affected by the random aggregation of the nanorods in the cluster, the plasmon coupling between the nanorods, the substrate, and the surrounding medium. The 532 nm laser is in resonance with the transverse mode, which can be used to excite and heat these rods efficiently. Laser excitation of these clusters results in a relatively uniform temperature over the entire cluster due to collective heating effects.24, 70

Figure 4.1 SEM image for clusters of gold nanorods with an attached erbium oxide nanoparticle cluster on a silicon substrate. The nanorods are 25 nm in diameter and 100 nm long.
Figure 4.2 (A) Absorption image of clusters of gold nanorods immersed in water on a glass substrate. (B) An absorption spectrum of a gold nanorod cluster taken at the position shown by the white arrow in (A). The experimental data is shown as black scattered points and fitted with a red line. The transverse and the longitudinal modes are observed at ~ 573 and 782 nm respectively. The blue dashed line represents the excitation wavelength of the laser that is used to excite and heat the gold nanorod clusters.

Vapor Nucleation Temperature Measurement and Dissolved Gases Effect

Figure 4.3 shows the temperature-time spectra for heated gold nanorods immersed in non-degassed (red spectrum) and degassed water (black spectrum). In both spectra, the laser intensity is increased stepwise and the temperature increases gradually with increasing laser intensity. However, a sharp and sudden spike in temperature is observed at higher intensities on both spectra. In non-degassed water, this spike is observed at a significantly lower temperature (~394 K) than that for the degassed water (~540 K) as seen from the magnified region of the temperature-time spectrum. This spike in temperature is due to the nucleation and the temperature corresponding to this spike is assigned as the corresponding nucleation temperature. The temperature-time measurements were repeated in non-degassed as well as degassed water. The nucleation
temperatures from a number of measurements are plotted in the histograms shown in Figure 4.4. The distribution of nucleation temperatures for non-degassed and degassed water is shown in red and black, respectively. The average nucleation temperature is 460 K for non-degassed water and 560 K for degassed water. The temperature for vapor nucleation in degassed water is close to the spinodal decomposition temperature (SDT) of liquid water, which is in agreement with our previous measurements of the superheating of water from nanoscale hot spots.23, 70

Figure 4.3 Temperature-time spectra for an optically heated gold nanorod cluster immersed in non-degassed (red spectrum) and degassed water (black spectrum). Blue arrows indicate the onset of bubble formation.
Figure 4.4 Histograms of the nucleation temperatures in non-degassed (red) and degassed water (black). The solid red and black curves are the fitted normal distributions to the corresponding histogram.

Figure 4.5 shows the photoluminescence spectra of an Er$_2$O$_3$NP at different temperatures. In each spectrum, the photoluminescence intensity is normalized with respect to the most intense peak. The green, red and blue spectra represent the photoluminescence from erbium oxide at a temperature of ~340 K (below the boiling point), ~396 K (just before nucleation), and ~790 K (after nucleation), respectively. As seen in the figure, the intensity of 539 nm peak increases with respect to the 565 nm peak with increasing temperature and becomes much higher after the nucleation event suggesting that the nucleation event is accompanied by the sudden and sharp spike in temperature.
Figure 4.5 Temperature - time spectrum with the corresponding normalized photoluminescence spectra of Er$_2$O$_3$NP taken at the point in time indicated by the arrow. Spectra represent the photoluminescence from Er$_2$O$_3$NP at a temperature of $\sim$340 K (green, below the boiling point), $\sim$396 K (red, just before nucleation) and $\sim$790 K (blue, after nucleation) respectively.

Figure 4.6 shows the temperature change and the corresponding change in the bubble diameter as a function of time in a non-degassed water. The spectrum and the corresponding video were collected simultaneously with the microscope trinocular, which allowed for the splitting of the collected light. The higher noise in the temperature measurement is a result of the lower emission signal. At the beginning, the temperature (shown in black) increased gradually with increasing laser intensity. During that time, the recorded video shows no evidence of nucleation (so the bubble diameter is assigned as zero). However, at 118 seconds, there is a spike in the temperature that follows the simultaneous formation and growth of the bubble diameter from zero to 4.9 µm (as seen from the recorded video).
Vapor nucleation below the spinodal decomposition temperature is an activated process. Generally, bubble formation at the boiling point occurs with the help of nucleating agents which aid in the phase transformation process. Raising the temperature in the absence of these agents causes water to superheat and the liquid is trapped in a metastable state. Nucleation is an activated process and is inherently a stochastic process. The barrier to nucleation becomes smaller and eventually disappears at the spinodal decomposition temperature. Classical nucleation theory predicts that the time interval to have a nucleation event that varies exponentially with barrier height. If on
the other hand, the time interval is held constant, then the nucleation temperature varies stochastically and, for a normal distribution, yields a Gaussian profile.\textsuperscript{138, 139}

Recently, we proposed that the nucleation site has an important role in the nucleation process.\textsuperscript{70} For an optically heated gold colloidal solution, bubble nucleation was observed at the boiling point because the large volume of the heated water ensured that nucleation occurred heterogeneously. Alternately, for an optically excited single nanostructure, superheating occurred to the spinodal decomposition temperature because the volume of water heated from a single nanostructure is 9 orders of magnitude smaller than heating a colloidal solution. The probability of a nucleation center being in the superheated region decreases dramatically when comparing the single nanoscale heater to the colloidal solution of heaters. We tested this hypothesis by comparing the constant time interval nucleation temperature of degassed water to non-degassed water. In this comparison, the number of nucleation centers should be higher in non-degassed water than in degassed water. Figures 4.3 and 4.4 illustrate the difference in the nucleation temperature between the non-degassed and the degassed water. Figure 4.3 shows temperature-time traces of non-degassed water (red) and degassed water (black). Bubble formation is observed as a large temperature spike and the nucleation temperature is taken as the temperature before the spike. Figure 4.4 shows a histogram comparing the nucleation temperature of non-degassed and degassed water. The solid lines are a Gaussian fit to the histogram data. The average temperature is the temperature at the Gaussian maximum. The nucleation temperatures for non-degassed and degassed water are presented in red and black respectively. The average nucleation temperature in non-
degassed water is 460 K while the average nucleation temperature in degassed water is 560 K.

We have previously measured the superheating properties of degassed liquid water surrounding an optically heated single gold nanostructure and found that superheating occurs to 580 K ± 20 K.\textsuperscript{23,70} In that work, we assigned this temperature as the spinodal decomposition temperature of liquid water. The vapor spinodal decomposition temperature (temperature limit where the vapor is metastable) is expected to be around 320 K.\textsuperscript{126} The average nucleation temperature measurement for degassed water, shown in Figure 4.4, is in agreement with our previous measurements.\textsuperscript{23,70} Dissolving gas in water reduces the average nucleation temperature from 560 K to 460 K. This implies that dissolve gases have a role in the nucleation process.

The temperature spike in the temperature-time trace is believed to locate the onset of bubble nucleation. Figure 4.5 shows a temperature-time trace with spectra collected significantly before (green), immediately before (red) and after (blue) the temperature spike. The spectra have been normalized to the largest peak in the spectrum. The relatively larger increase in the band at 539 nm is caused by the increase in temperature. The noise in the temperature trace is larger at lower temperatures because the laser intensity is the lowest at this point. The laser intensity is increased as time advances and this causes an increase in temperature. This increase in temperature is observed as a change in the relative intensity of the 539 nm band compared to the intensity of the 564 nm band.

We believe that the temperature spike occurs at the onset of nucleation because gases accumulate at the heated interface, which inhibits heat dissipation into the bulk.
liquid. As the temperature of the liquid is increased, the gas solubility is decreased and small pockets of gas clusters coalesce to form larger gas pockets. This process is shown in Figure 4.7. The size of the gas pockets increases with temperature until a critical size occurs, triggering the nucleation process. In this model, the nucleation temperature is reduced when dissolved gases are in the water because the formation of critical-sized gas pockets is easier if there are gases dissolved in the water compared to the case where the gas pockets are created with water vapor.

Figure 4.7 A Schematic illustration of the proposed mechanism of lowering nucleation temperature by the presence of dissolved gases. As the temperature of the water around the gold nanorod cluster increases as in (B and C), the dissolved gases become less soluble in water, leading to the formation of larger clusters of gas pockets. A critical size gas pocket leads to bubble formation.

*Bubble Dynamic in Degassed and Non-Degassed Water*

Dissolved gases have shown not only a significant impact on the nucleation temperature, but also on the bubble dynamic, as shown in the dark-field images in Figure 4.8. Water has a large amount of dissolved gases, mainly oxygen and nitrogen with a concentration of ~0.27 and 0.5 mM, respectively. When gold nanoparticles are optically heated, the water temperature increases. If water temperature exceeds the boiling point and
it is ready to nucleate, the bubble initially forms from a thin layer of water vapor. However, in the non-degassed water, the dissolved gases will rapidly diffuse inside the bubble leading to the formation of a larger bubble. Following this, the bubble size will grow until it reaches a point where the bubble size becomes constant. Since the formed bubble is not only filled with water vapor but also with some incondensable gas, the bubble collapsing rate will be too slow. It can take ten seconds, a couple of minutes, or even a whole hour for the bubble to collapse completely depending on the bubble size. However, a bubble formed in degassed water will be completely filled with water vapor. This implies that as soon as the source of heat is turned off (laser in this case); the bubble is expected to collapse immediately within seconds or a fraction of a second. Figure 4.8 is a dark-field image that shows the bubble collapse taken from successive frames for the same cluster, and at the same laser intensity in degassed water (A) and non-degassed water (B). Two videos showing the complete cycle of bubble expansion and shrinkage are analyzed using Image J software (see Chapter 2). The resulting data (bubble diameter as a function of time) is plotted in Figure 4.9. Another impact of the dissolved gas in water is that the final size that the bubble reaches in non-degassed water is much larger than the one that forms in degassed water as can be clearly seen from the figure. The diameter of the bubble formed in non-degassed water reaches ~17 µm compared to only ~8 µm in degassed water.
Figure 4.8 Dark-field images showing bubble collapse in non-degassed (A) and degassed (B) water taken from successive frames.

Figure 4.9 Plots of bubble diameter as a function of time showing bubble growth and collapse in non-degassed (shown in red) and degassed water (shown in black). Blue and green arrows indicate the time when the laser is turned on and off, respectively.
Conclusion

A laser-trapped erbium oxide nanoparticle cluster is utilized to probe the temperature where bubble nucleation occurs for degassed and non-degassed water. Vapor nucleation is observed after superheating the liquid above the boiling point of water. The average nucleation temperature for non-degassed water is 460 K. Removing the gas from the water shifts the average nucleation temperature up 100 K to 560 K. We propose a mechanism describing the role that dissolved gases have in bubble nucleation where gas solubility is decreased with temperature and small pockets of gas clusters coalesce to form larger gas pockets that lead to a reduction in the nucleation temperature.
CHAPTER 5: UPCONVERTING NANOPARTICLES CHARACTERIZATION AND TEMPERATURE MEASUREMENT DURING BUBBLE NUCLEATION AND COLLAPSE

Introduction

From a simple process that we observe every day to more advanced and complex systems, the first order phase transitions of water have been extensively explored. The liquid to vapor phase transition can be used for power generation (i.e. electricity), and sterilization\(^3\), on the other hand, vapor condensation (gas→liquid) can be used as a potential method for water purification in developing countries.\(^{14}\) Water can exist in a liquid state for a large temperature range, that is (0 - 100 °C) or (273 – 373.15 Kelvin). At a temperature of 373.15 K and 1 atm pressure, the two phases (liquid and vapor) are stable and they both can coexist. If at this pressure, the temperature of the liquid increases beyond the boiling point, then the liquid is in a metastable state. As a result, the temperature of the liquid water can be extended to a temperature that is much higher than the boiling point until it reaches the spinodal point. On the other hand, based on a computational simulation, Cho et al. reported that water vapor can be supercooled to a temperature that is well below the boiling point of water, 318.15 K±10.\(^{126}\) This implies that water vapor can be trapped in a metastable state for a certain time before it is converted to liquid.

In this Chapter, we are introducing a new approach for high-temperature measurements in water, using upconverting nanoparticles that are characterized and utilized as a temperature sensor. Using this technique, the temperature is monitored during a complete cycle along with microbubble formation and collapse. Water vaporization is
achieved by the optical excitation of silver nanoparticle clusters in water using a 405 nm laser. The temperature is measured during bubble collapse by tracking the emission spectrum of the UCNPs using the 980 nm laser while controlling the amount of heat generated during that process using the 405 nm laser. Silver nanoparticles are used as nanoscopic heaters in this study for the reason that the plasmon resonance of these particles is shifted far to the blue region of the spectrum. This is important to avoid the possible absorption and thus the heating of the particles by the 980 nm laser. Although the study of liquid water superheating and water vapor supercooling has been discussed previously at the macroscale, this dissertation presents a new experimental approach to study the phase transitions inside microbubbles that are formed from heating a local area on the order of microns.

Results and Discussion

Temperature Measurement Sensitivity Using Upconverting Nanoparticles and Particle Size Effect

The sensitivity of the temperature measurement using upconverting nanoparticles is determined by conducting temperature – time spectrum measurements. ~ 1 micron cluster of UCNPs is excited using the 980 nm laser. Temperature – time spectra with an integration time of 0.5 s are collected at different laser powers. The calculated temperatures from the temperature – time traces are plotted in histograms and fitted to Gaussian curves as shown in Figure 5.1(A-G). The Full-Width Half Maximum (FWHM) of the Gaussian peak is clearly becoming smaller as a function of laser intensity. With a laser intensity of $8.03 \times 10^8$ W/m$^2$ and 0.5 s integration time, the sensitivity of the measurement reaches ~
1.3 K Hz$^{-1/2}$. In Figure 5.1H, the average temperature is calculated from each temperature – time spectrum and plotted as a function of laser intensity.

Characterizing the effect of the UCNP cluster size on the temperature is essential. An image scan of different particle sizes ranging from 1 to 9 µm is shown in Figure 5.2. The image is collected at room temperature. The temperature inside each cluster is averaged and plotted with standard deviation as shown in Figure 5.2 A. There is no significant difference in the temperature between the differently sized nanoparticle clusters. The average temperature ranges from 294.5 to 302.2 Kelvin. However, the small size cluster (cluster 7) has a large standard deviation compared to cluster 1. This is due to the low signal to noise ratio of the emission spectrum for cluster 7 (see Figure 5.2 C and D). It should be noted that these data are collected with 0.15 s integration time and low laser intensity. Using higher laser intensity and integration time, the standard deviation can be reduced significantly.
Figure 5.1 (A-G) Histograms fitted to Gaussian curves generated from temperature – time spectrum for ~1 micron size UCNP cluster irradiated with different 980 nm laser power. The maximum of the Gaussian peak represents the average temperature. The FWHM of the Gaussian peaks is reduced with increasing laser intensity. (H) A plot of the average temperature in Kelvin calculated from each time spectrum and plotted as a function of laser intensity (W/m²).
Figure 5.2. The temperature measured using different cluster sizes of UCNPs. (A) A plot of the average temperature for different cluster sizes. The different cluster sizes show relatively same temperatures with a large standard deviation for small clusters. (B) Image scan of different sizes of UCNP clusters collected at 0.15 s integration time. Each number in figure (A) represents the average temperature of the same-number labeled cluster in image (B). (C) and (D) show the photoluminescence spectrum of the small and the large cluster (cluster 7) and (cluster 1), respectively. The large signal-to-noise ratio in cluster 1 compared to cluster 7 leads to smaller error bars (low standard deviation value).

**Effect of 980 nm Laser on Water Heating**

The effect of the 980 nm laser on water heating has been discussed in previously published papers. Although water has a low absorption cross section at this wavelength, the absorption of the 980 nm by water can lead to water heating at specific
laser densities. In some cases, this heating impact can be negligible. However, in this study, the presence of a large background heating might affect the bubble dynamic and the bubble metastability. Therefore, knowing the amount of heat that the 980 nm laser is contributing to the process is necessary. To study this effect, the intensity of 980 nm is increased as a function of time in water, over a small cluster of UCNPs (there is no heater in the sample such as gold or silver nanoparticles). The temperature is calculated from the photoluminescence spectrum and plotted as a function of laser power as shown in Figure 5.3. There is a linear increase in temperature with power. The maximum temperature reaches 312 K at a power of 4.8 mW. This gives a temperature change of $\Delta T = 14$ K. However, at the time of data collection, we minimize this effect by adjusting the laser power to a value that gives a reasonable signal to noise ratio, but on the other hand, does not contribute to heating the system. Therefore, all the data presented here are collected at a laser power of 2.6 mW. This laser power generates a small amount of heat that is in the range of $\sim 306$ K ($\Delta T \sim 8$ K) as shown in Figure 5.3. This value is set as the background temperature for all analyzed data.
Figure 5.3 A plot of the measured temperature using UCNPs in water as a function of the 980 nm laser power. The temperature is increasing linearly with power. The meeting point of the two blue lines represents the background temperature that is expected at a laser power of 2.6 mW (the power that is used for collecting bubble cycle data).

Effect of Heating Laser and Bubble Formation on UCNPs Emission

The 405 nm laser, which is used to heat the AgNPs, and the formed bubble have an impact on the baseline of the upconverting nanoparticles (UCNP) emission spectrum. When the 405 nm laser power increases with time, this baseline gradually increases. However, when the bubble forms, this effect becomes very significant. Figure 5.4 (A-D) shows the emission spectra of UCNPs at four different stages of the bubble nucleation and collapse cycle. Figures 5.4 (A) and (B) are the emission of the UCNP without and with 405 nm laser heating, respectively. It is clear that the 405 nm has a large contribution to the emission’s baseline. On the other hand, bubble formation causes a large destruction to the emission spectrum (see Figure 5.4 (C)). We believe that this emission destruction is due to
one of the two reasons: when bubble forms, it blocks most of the green emission of the UCNPs from reaching back to the collection fiber, and the other possibility is that the 980 nm laser is not able to access the UCNPs because of the laser scattering by the formed bubble. At this stage, the bubble size is maximum and the temperature cannot be recorded due to the loss of signal. However, when the 405 nm laser power is decreased (the source of heat), the bubble size is reduced and the emission signal starts to recover as shown in Figure 5.4 (D). The temperature after this point can be calculated until the point where the bubble completely collapses.

Figure 5.4 An emission spectrum of UCNPs at different stages of the bubble formation cycle. (A) An emission spectrum before heating with blue light. (B) The emission spectrum after increasing the 405 nm laser power. (C) The emission spectrum after bubble nucleation. (D) The emission spectrum when 405 nm laser power is decreased and bubble starts to collapse.
Temperature of Vapor Bubble Nucleation and Collapse

Figure 5.5 shows the measured temperature using upconverting nanoparticles in water over a heated cluster of silver nanoparticles as a function of time. Figure 5.5A illustrates four successive events of bubble formation and collapse. In this measurement, the 980 nm laser power is kept constant, while the 405 nm laser power is increased gradually. This leads to an increase in the temperature of the silver nanoparticle cluster with time up to the point where vapor nucleation occurs. At that time, the power of the 405 nm laser is decreased gradually until the bubble is completely collapsed. In this Figure, the cycle is repeated four times. The black trace in Figures 5.5 (A) and (B) represents the temperature change as a function of time, while the red trace is the integrated area of the overall emission (area under S and H bands). Figure 5.5 (B) is a zoomed in plot for one of the four bubble cycles in Figure 5.5(A). The red trace is used to identify the time of bubble nucleation and collapse. In the beginning of the trace, between 9 and 12 seconds, a decrease in the emission of the UCNPs is observed along with the increase in temperature. With the continued increase in temperature, a sudden drop in the emission signal occurs at 12.5 seconds. This drop is assigned to bubble formation and this temperature is assigned to be the nucleation temperature. After bubble formation, the laser power is decreased leading to a reduction in the generated temperature. This reduction in the temperature is associated with an insignificant increase in the emission intensity. However, later in the trace, a sudden and dramatic increase in the emission intensity is observed at 22.5 seconds and this drop is assigned to bubble collapse.
The two events, bubble nucleation and collapse, are indicated by blue arrows in figure 5.5(B). This pattern of bubble nucleation and collapse is clearly reproducible as can be seen from the other three cycles in Figure 5.5(A).

Figure 5.5 (A) Temperature - time spectrum measured using UCNPs in water showing four successive cycles of bubble formation and collapsing overlaid with the change in the emission-integrated area as a function of time. (B) A zoomed in plot of the first bubble cycle in the temperature - time spectrum (figure A). The blue arrows point to the temperature at which bubble first nucleates and then collapses.
The vapor nucleation temperatures, determined from several temperature – time traces are plotted as a function of the bubble collapse temperatures as shown in Figure 5.6. Although vapor nucleation can be observed at a temperature of 373.15 K at 1 atm, this temperature varies depending on the bubble curvature. If the average bubble size is 10\(\mu\)m, the calculated pressure inside the bubble is 1.23 atm using the Young – Laplace equation \((\Delta P = \frac{2\gamma}{r})\), where \(\gamma\) is the water vapor surface tension at 373.15 K, and \(r\) is the bubble radius. At such a pressure, the vapor saturation temperature \((T_{sat})\) is slightly larger than the normal boiling point and it is \(\sim 379\) K (see Figure 5.7). However, bubbles that are smaller than 10 \(\mu\)m will have higher pressure and thus, the temperature will be even larger than the above-calculated value (379 K). The red dotted lines in Figure 5.6 represent the calculated vapor saturation temperature (379 K), taking into account the effect of the bubble curvature on the inner pressure. In this Figure, bubble nucleation is observed between 417 \(\pm\) 2 and 492 \(\pm\) 10 K. Bubbles that nucleate at low temperatures in the range of 417 - 440 K remained stable below the saturation temperature \((T_{sat})\). On the other hand, a much smaller number of nucleation events occur at higher temperatures. Bubbles with nucleation temperatures above 450 K, collapse at a temperature that is close to the \(T_{sat}\). In Chapter 4, we concluded that non-degassed water has a low nucleation temperature in comparison to degassed water; the presence of the dissolved gas pockets is catalyzing the nucleation process. Based on this conclusion, we can infer that bubbles that nucleate at low temperatures are filled with dissolved gases in addition to the water vapor. As a result, these bubbles collapse at lower temperatures. Conversely, bubbles that are believed to be filled with water vapor collapse at or above the \(T_{sat}\) with no chance for supercooling.
Figure 5.6. A plot of the bubble nucleation temperature as a function of the bubble collapse temperature. The data points represent an average temperature calculated from several temperature-time traces. The red dotted lines represent the vapor saturation temperature ($T_{\text{sat}}$) ~ 379 K calculated for 10 µm diameter bubble.

By considering a vapor bubble that is surrounded by liquid water, the temperature inside the bubble is significantly high and it might reach 500 K. On the other hand, as a result of the thermal interfacial resistance at the vapor-liquid interface, the temperature of the water molecules at the vapor-liquid interface is expected to be a close or equal to $T_{\text{sat}}$. When the heat is reduced inside the bubble, the temperature decreases along with a reduction in the bubble size, keeping the inner pressure relatively constant until the temperatures inside and outside the bubble become equal. At this temperature ($T_{\text{sat}}$), there are two suggested possible paths for bubble collapse based on the partial pressures of the water vapor, and the gases inside the bubble (see Figure 5.7). For a bubble that is made of
water vapor, any further reduction in the temperature below the $T_{\text{sat}}$ causes vapor to condensate by crossing the vapor-liquid boundary; this, in turn, causes the bubble to collapse. This is shown as path (A) in Figure 5.6. However, this is not the case for bubbles that are filled with a mixture of water vapor and other incondensable gases. The total pressure inside these bubbles is the sum of the partial pressure of the water vapor and the partial pressure of the gas. For instance, if the temperature inside the bubble reaches 360 K, the water vapor partial pressure is 0.622 atm. Therefore, for the total pressure inside the bubble to be 1.23 atm, the gas pressure inside should be ~ 0.608 atm. As can be seen from path B in the Figure, this reduction in the water vapor partial pressure causes a slight decrease in the temperature below the saturation temperature until the point where the bubble is not stable and thus, the bubble collapses.
Figure 5.7. The phase diagram of water, showing the change in the vapor atmospheric pressure as a function of temperature. The red dotted lines represent the calculated vapor saturation temperature ($T_{\text{sat}}$) 379 K, for 10 $\mu$m bubble with an inner pressure of 1.23 atm. The green solid line illustrates the initial step of bubble collapse by reducing the temperature inside the bubble, while the pressure is relatively constant at 1.23 atm. The blue arrows indicate the two possible paths for bubble collapse, depending on the partial pressure of the water vapor and the gas inside the bubble.

*Effect of Temperature Rise on Upconverting Nanoparticles Luminescence*

The luminescence intensity of the UCNPs can be affected by different factors that might lead to either emission quenching or enhancement.\textsuperscript{144-146} The luminescence of the UCNPs has a significant dependence on the solvent.\textsuperscript{145} Particles that are dispersed in water undergo a high degree of quenching compared to the one in the organic solvent. Moreover, a previous study has shown that the luminescence intensity for uncapped water dispersed UCNPs is affected by the increase in temperature and the change in PH of the solution.\textsuperscript{146}
They reported a reversible quenching of the emission intensity with water temperature increase from 10 to 80 °C. On the other hand, there is an irreversible quenching when the PH solution is varied from 7 to 3 due to the particles size reduction and shape deformation. This temperature luminescence quenching effect is due to the increase in the water vibrations with temperature, which in turn has an effect on the Lanthanide-flouride bond in the crystal.\textsuperscript{146} Here, we observed that the temperature increase in water cause a quenching of the UCNPs luminescence. To verify this effect, temperature – time spectrum and video are collected simultaneously for UCNPs over a heated silver nanoparticle cluster in water using the 405 nm laser. Figure 5.8 (A, B) are images taken from the recorded video of UCNPs that shows the green emission before and after heating the cluster. The green emission of the UCNP cluster is clearly reduced. Figure 5.8 C is a plot of the measured temperature, overall emission intensity calculated from the spectrum, and overall emission intensity taken from the recorded video (analyzed using Image J) as a function of time. As the temperature of the particles increases with time, there is a decrease in the overall luminescence intensity. Both the emission brightness calculated from the video and the emission intensity from the spectrum are following each other as can be seen from the gray and the red traces. The emission intensity is decreased by ~ 42 % of its original intensity. This reduction in the luminescence of the particles with temperature increase might result from a chemical change that occurs on the surface of the organic ligand of the UCNPs. These particles are capped with oleate ligands to reduce the chance of particle aggregation. However, a further detailed investigation of this effect is needed to draw a plausible conclusion.
Figure 5.8 A reduction of the UCNP green emission intensity with increasing temperature. (A) and (B) show the UNCP clusters before and after irradiation with 405 nm laser, respectively. (C) A plot of UCNP overall emission intensity change taken from the spectrum (red) and video (black) with the temperature measured as a function of time.
Technique Limitations and Challenges

The temperature of bubble nucleation and collapse is achieved in this study; however, there are some challenges that should be highlighted. When the bubble forms, the suspended particles in the solution are always dragged toward the bubble during the time of the data collection, which lead to fluctuations in the emission signal. Therefore, using a solution that is free of any floating particles is strongly recommended. Another challenge is that at the time of bubble formation and collapse a huge stress takes place that leads to fragmentation of the surrounding clusters. Therefore, in most of the cases, there was an inability to either take a complete cycle measurement or reproduce the measurement on the same cluster.

Conclusion

A method has been developed for high-temperature measurement in water where two different laser colors are used to independently heat the silver nanoparticle clusters using 405 nm light and monitor the emission of the UCNPs using 980 nm light. The upconverting nanoparticles show the high-temperature sensitivity that is on the order of 1.3 K.Hz$^{1/2}$. The effect of the nanoparticle cluster size with respect to temperature is also investigated. Different sizes of the UCNPs (1-9 micrometer) show a relatively similar average temperature. Moreover, we observed that the temperature increase in water causes a quenching of the UCNP luminescence. This effect is likely due to the change in the chemistry of the fabricated particles’ surface. However, more investigation is required to understand and to demonstrate the origin of this effect. The temperatures at which the bubble nucleates and collapses are identified by tracking the change in the overall intensity
of the UCNPs. We propose a possible mechanism that illustrates the dependence of the bubble collapse temperature on the partial pressure of the water vapor inside the bubble. Bubbles that contain some amount of air were able to attain stability down to a temperature that is below the calculated saturation temperature, $T_{\text{sat}}$. On the other hand, a bubble with much less gas content nucleates and collapses at a much higher temperature.
CHAPTER 6 : SUMMARY AND FUTURE DIRECTIONS

There is always an urgent need to develop a thermometry technique and there are many ways to do it, but we are always looking for the best ways that offer inexpensive, easy, fast and more important accurate measurement techniques. This dissertation introduced two techniques to study liquid → gas and gas → liquid phase transitions at the nanoscale. In this study, two different thermometry particles were characterized and a temperature measurement was conducted under difficult circumstance, up to a very high temperature where the phase transition was observed.

In Chapter 3, we developed a new technique to measure the temperature in water from optically heated gold nanoparticles. With small and relatively cheap particles, the temperature can be measured with high accuracy using Er₂O₃NPs. This technique allows for targeting specific sites in the sample where the temperature measurement should take place by laser trapping and attaching the particles to the heater surface. We characterize the erbium oxide nanoparticles, study the validity of these particles as nanosensors, and calibrate the photoluminescence of these particles as a function of temperature. The particles show high stability and the ability to measure a very high temperature with a noise floor of 0.28 K Hz⁻¹/².

Chapter 4 discussed the measurement of vapor nucleation temperature for micro-bubbles using nanoparticle thermometry. Vapor nucleation results from a heated gold nanoparticle cluster in water using a 532 nm laser. The heat generated from the nanoparticles dissipated to the surrounding medium, leading to a rise in the water temperature, and when there is enough heat for vapor nucleation, a phase transition is
observed. The temperature at which vapor nucleation takes places is measured optically using a nanosize cluster of erbium oxide nanoparticles that is optically trapped in water and attached to the surfaces of the gold nanoheaters. The nucleation event is identified from the sudden and significant increases in temperature. This is due to the vapor layer that acts as a thermal barrier, inhibiting the heat dissipation from the particles to the surrounding water. The effect of the dissolved gases in the nucleation temperature was also studied. For degassed water, the nucleation temperature is shifted to a very high temperature compared to non-degassed water. A mechanism of vapor nucleation is proposed where dissolved gases work as activating sites, start to accumulate at a higher temperature and work as nuclei for the nucleation process.

Using the unique property of the upconverting nanoparticles, Chapter 5 discussed the validity of using these particles as a thermal sensor to measure the temperature during a phase transition. Using these particles, the temperatures at which vapor bubbles nucleate and collapse were determined. We show that the presence of the dissolved gas in the solution has an impact on the collapse temperature. Bubbles filled with air and water vapor were able to stay stable for a long time, even when the temperature of the water decreased to a temperature that is below the boiling point. Conversely, bubbles filled mostly with water vapor show low stability and the bubbles collapse immediately at high temperatures. This variation in the bubble collapse temperature is probably due to the difference in the water vapor partial pressure inside the bubble.
The two-laser experiment introduced in Chapter 5 can be expanded by combining the nanothermometry technique with Surface Enhancement Raman Scattering (SERS). A project will be proposed here that enables researchers to probe the heat dissipation from different molecules absorbed on the gold nanoparticles’ surface and to detect and identify these molecules through the SERS technique at the same time. This can be made possible using an optically trapped silver decorated erbium oxide nanoparticle (Er$_2$O$_3$NP-AgNPs). This particle can probe the temperature as well as enhance the Raman scattering signal. As the trapped particle (Er$_2$O$_3$NP-AgNPs) is brought close to the unknown molecules that dissipate the heat from the AuNPs, the thermometer will sense the differences in temperature. On the other hand, the proximity of the silver to the molecules’ surface leads to a signal enhancement. One laser will be used for the particle trapping and gold excitation, however, another laser in the near-infrared (NIR) region is required to shift the Raman scattering for the molecules of interest beyond the visible region. One of the challenges of this project would be that it is unknown how close the trapped particle can be brought to the molecules, and what effect this distance will have on the signal’s enhancement, compared to the other known methods.

Besides expanding the application of thermosensor optical trapping to measure the temperature and identify molecules through SERS simultaneously, the temperature sensing approach used in this research could also provide a way to identify when, and at what temperature the release of a liposome cargo takes place. Using optical trapping, UCNP can be attached to the outer surface of a temperature sensitive liposome with dye encapsulated. When the temperature surrounding the liposome increases, the temperature
along this heating process can be measured using the UCNP. If the absorption spectrum of the dye inside the liposome overlaps with the emission spectrum of the UCNPs, the luminescence of the particles will be quenched or enhanced at the time that the capsulated dye will be released from the liposome because of the energy transfer.\textsuperscript{147,148}

Despite some of the challenges that the researcher may face in building up these proposed projects if these projects are successfully developed, they will have a significant impact on the applications of thermal imaging and drugs delivery.
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