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Photothermal studies of single molecules and gold nanoparticles : vapor nanobubbles and conjugated polymers

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Steady state of a vapor nanobubble in liquid around a continuously laser-heated gold nanoparticle

***Abstract**– We provide a simple model of the thermodynamic properties of vapor nanobubbles in liquid around a continuously laser-heated gold nanosphere, assuming the system is under steady state. We calculate the minimal boiling temperature and pressure for different sizes of vapor nanobubbles, the optical power to be delivered into the system for vapor nanobubble formation, and the optical signal change due to the scattering by the bubble.*

2.1. Introduction

Fluid dynamics and phase transitions have been extensively studied since the time of Gibbs [3]. They are both fundamentally important and practically useful. When temperature and pressure of a liquid reach and cross the coexistence saturation curve where two phases are in equilibrium, transformation from liquid to vapor can take place, and vapor bubbles can form in the liquid. In the phase diagram, there also exists a region where liquid and vapor can be in "metastable" states. The limit to which a metastable liquid can be superheated without boiling is called "liquid spinodal line", while the limit to which metastable vapor can be "subcooled" is called "vapor spinodal line" [36]. Superheated liquids are found to be extremely unstable, and homogeneous nucleation and explosive boiling are often observed [64]. The maximum superheating temperature measured experimentally is about 88-90% of the critical temperature, in good agreement with the temperature predicted by classical nucleation theory [12]. In this chapter, we will focus on the first-order phase transition from liquid to vapor and vapor bubble formation at the surface of a continuously laser-heated gold nanosphere. We assume that liquid and vapor are in equilibrium. We provide a simple model to describe the thermal properties of a vapor nanobubble under steady state.

2.2. The boiling temperature T_b as a function of bubble radius

Our system is described as follows, as is shown in the scheme Fig.2.1(a). A gold nanosphere is immersed in a liquid. A continuous-wave (CW) laser with a wavelength close to the absorption maximum of the gold nanosphere is focused on the gold particle. Due to the high optical absorption, the gold nanoparticle becomes hot and can bring the surrounding liquid to ebullition if the illumination power is high enough. Then, a vapor shell can form around the particle. We set out our discussions with a few assumptions. First, the vapor nanobubble has a spherical symmetry; Second, the vapor and liquid phases are in equilibrium; Third, thermal parameters of liquid and vapor are taken from their macroscopic values; Last, the thermal conductivity of gold is approximated as infinite. We assume that the radius of the vapor bubble is just equal to the radius of the gold nanoparticle. Under steady state, there is equilibrium between the vapor and the surrounding liquid. That is, the pressure inside the vapor bubble should be equal to the liquid pressure plus the Laplace pressure induced by the surface tension:

$$P_{vapor}(T) = P_0 + \frac{2\gamma(T)}{R_{bubble}} \quad (2.1)$$

2.2. The boiling temperature T_b as a function of bubble radius

$P_0 = 1$ atm is the ambient pressure. For two liquids, water and n-pentane, the temperature- dependent vapor pressure $P_{vapor}(T)$ and surface tension $\gamma(T)$ are plotted in Fig.2.1 (b) and (c). Data are taken from Ref.[65]. According to Eq.2.1, we get the minimum (critical) temperature required for the boiling as a function of the bubble/particle radius (the bubble size is just equal to the size of particle), as shown in Fig.2.1 (d). Below the critical temperature, there is no vapor bubble. The particle is surrounded by a temperature gradient of hot water. We call this steady state regime I. Above a critical temperature, we expect to reach a second steady state, regime II, with a steam bubble around the nanoparticle. Close to the critical temperature, we can see that the boiling temperature is significantly shifted to a higher value with respect to the boiling temperature at ambient pressure (For water, the normal boiling point is 373.12 K; for pentane, it is 309.21 K, as shown by the dashed lines in Fig.2.1 (d), due to the large Laplace pressure of small bubble sizes. Similarly, the critical pressure for vapor nanobubble formation can be calculated and is plotted in Figure 2.2. For small particles, diameter < 10 nm, the interface approaches the critical temperature (647 K for water, 469.8 K for n-pentane), and no clear interface appears anymore [66].

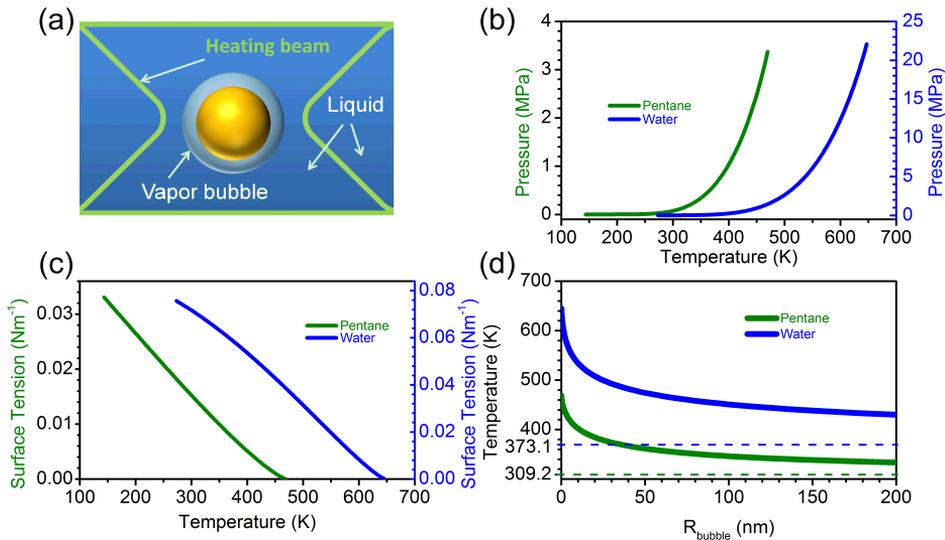


Figure 2.1: Phase diagram of a vapor nanobubble. (a): Scheme of the system under study; (b): Temperature-dependent pressure of the vapor phase at saturation for two different liquids, water and pentane; (c): Surface tensions of the two liquids at saturation as a function of temperature; (d): Minimum (critical) temperature to reach the boiling as a function of bubble/particle radius, assuming the size of the vapor bubble is just equal to the size of the particle.

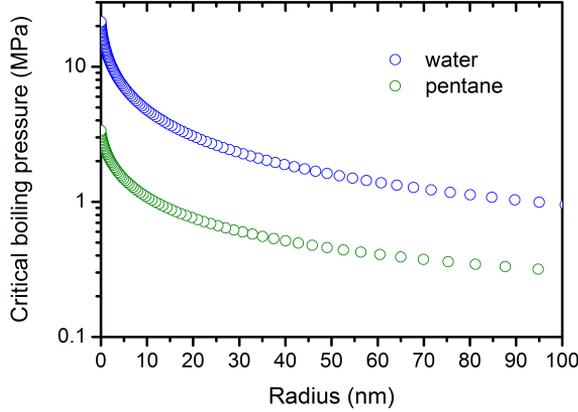


Figure 2.2: Critical boiling pressure for vapor nanobubble formation as a function of particle/bubble radius.

2.3. Temperature profiles under different absorbed powers

Under steady state, the temperature distribution can be calculated by solving the Poisson equation. We assume the temperature inside the gold particle to be homogeneous, because the thermal conductivity of gold is much higher than the thermal conductivities of liquid water and water vapor. Below the critical boiling temperature, there is no vapor bubble around the gold nanoparticle, the temperature distribution around a gold nanoparticle is written as follows [44, 67]:

$$T(r) = \begin{cases} T_0 + \frac{P_{abs}}{4\pi\kappa_l r_p} & \text{for } r \leq r_p \\ T_0 + \frac{P_{abs}}{4\pi\kappa_l r} & \text{for } r > r_p \end{cases} \quad (2.2)$$

where κ_l is the thermal conductivity of the liquid, T_0 the ambient temperature and P_{abs} is the power absorbed by the gold nanoparticle. Using this equation, we can calculate the minimal (critical) power that is required to reach the boiling by setting the bubble radius equal to the particle radius and demanding that the bubble temperature is equal to the minimal (critical) temperature in Fig.2.1 (d). The results are shown in Fig.2.3. Above the critical temperature, a vapor bubble can form around the gold nanoparticle, and the thermodynamic properties of a vapor bubble are governed by the following two equations:

$$\begin{cases} p_0 + \frac{2\gamma(T_b)}{r_b} = p_{vap}(T_b) \\ T_b = T_0 + \frac{P_{abs}}{4\pi\kappa_l r_b} \end{cases} \quad (2.3)$$

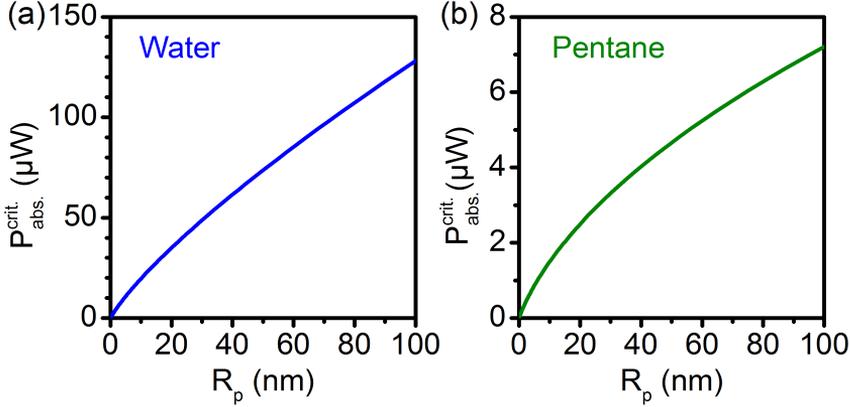


Figure 2.3: Minimal (critical) absorbed powers for the boiling as a function of particle radius, (a) in water; (b) in pentane.

where r_b is the radius of the vapor bubble, p_0 is the ambient pressure, $p_{vap}(T_b)$ is the temperature dependent vapor pressure, $\gamma(T_b)$ is the bubble-temperature dependent surface tension, and T_b is the temperature of the vapor bubble for vanishing thickness, the same as the minimum/critical boiling temperature.

The steady-state temperature profile when a vapor bubble forms around the particle under various absorbed powers is given by [30]:

$$T(r) = \begin{cases} T_0 + \frac{P_{abs}}{4\pi r_b} \left(\frac{1}{\kappa_l} - \frac{1}{\kappa_v} \right) + \frac{P_{abs}}{4\pi\kappa_v r_p} & \text{for } r \leq r_p \\ T_0 + \frac{P_{abs}}{4\pi r_b} \left(\frac{1}{\kappa_l} - \frac{1}{\kappa_v} \right) + \frac{P_{abs}}{4\pi\kappa_v r} & \text{for } r_p \leq r \leq r_b \\ T_0 + \frac{P_{abs}}{4\pi\kappa_l r} & \text{for } r \geq r_b \end{cases} \quad (2.4)$$

where the first line describes the temperature inside the gold particle, the second line describes the temperature in the vapor bubble and the third line describes the temperature outside the vapor bubble. In this equation κ_v is the thermal conductivity of the vapor, assumed to take its macroscopic value (the heat conduction in the thin high-pressure vapor shell reaches the Knudsen regime only at thicknesses less than 10 nm [68]). The thermal conductivities that were used in the calculations are given in table 2.1 and their slight temperature dependence was neglected. Figure 2.4 shows calculated temperature profiles for particles in water and pentane heated above or below the critical heating powers. At the critical power, the particle is surrounded by a hot liquid layer with temperature higher than the boiling point at ambient pressure. Thermal energy is thus stored in this hot liquid layer. Once the bubble forms, we can see

2. Steady state of a vapor nanobubble in liquid around a continuously laser-heated gold nanoparticle

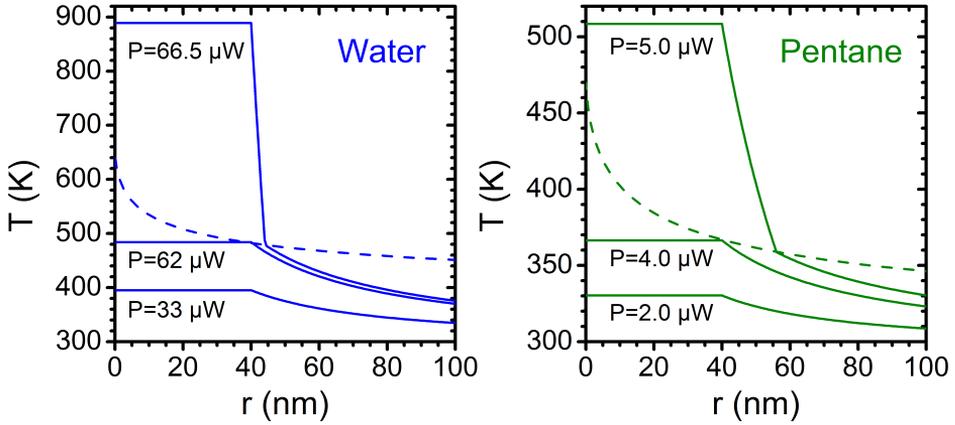


Figure 2.4: Temperature profiles around a gold nanosphere with 80 nm diameter under various absorbed powers in two liquids: (a) in water; (b) in pentane. The dashed curves in (a) and (b) are the temperatures of the boiling phase transition as a function of particle radius.

that the temperature of the nanoparticle rises by hundreds of Kelvin due to the poor thermal conductivity of the steam with respect to the liquid. This high temperature might degrade or cause surface melting of the nanoparticle. So the heating power should be carefully tuned in the experiment to ensure the reproducibility.

Table 2.1: Thermal conductivity of water and pentane in liquid and vapor phase

| ($\text{Wm}^{-1}\text{K}^{-1}$) | κ_l | κ_v |
|-----------------------------------|------------|------------|
| Water | 0.65 | 0.03 |
| Pentane | 0.11 | 0.019 |

Based on the above results, we can briefly discuss the stability of vapor nanobubbles. Below the critical boiling temperature, there is no vapor bubble formation. The temperature decreases as the inverse distance r in the liquid. As the absorbed power increases, the surrounding liquid becomes hotter and hotter, and approaches the threshold temperature (the dashed curve in Fig.2.4) for vapor bubble formation. Once the absorbed power is high enough, the surrounding liquid could cross the liquid-vapor saturation curve and a vapor bubble can form around the particle. Under steady state, we can see from Fig.2.4 that the liquid temperature outside the vapor bubble is always below the equilibrium temperature $T_{eq}(r)$. That means that the liquid temperature decreases steeply enough with radius to remove the heat from the vapor bubble, so that

the hot water layers outside the bubble remain stable, as shown by the crossing curves in Fig.2.4. On the other hand, when a very thin vapor shell forms quickly before the steady state is established, it can push the hot liquid outside the vapor. Then the equilibrium temperature will drop below the temperature of the liquid surrounding the vapor. As a consequence, the liquid will become superheated, and explosive boiling can set in. In this situation, the excess heat in the liquid cannot be removed sufficiently quickly and will raise the temperature of the vapor bubble. Thus the vapor bubble becomes unstable and grows to a bigger size. These effects will be seen in Chapter 3 since we could not pass continuously from liquid phase to stable vapor bubbles in the measurements. The vapor nanobubble's formation seems to be explosive even though the heating remains constant.

2.4. Linear variation analysis of bubble radius as a function of heating power

Because we are increasing the laser power only by a small amount above the critical power for the formation of a nanobubble, it may be useful to linearize the relationship between the steady state bubble radius and the absorbed power.

By making a small variation in the power P_{abs} , we change the bubble radius by an amount δr_b . For small enough variations Eq.2.3 leads to:

$$\begin{cases} \frac{d\gamma}{dT} \frac{2\delta T_b}{r_b} - \frac{2\gamma(T_b)}{r_b^2} \delta r_b = \frac{dp_{vap}}{dT} \delta T_b \\ \delta T_b = \frac{\delta P_{abs}}{4\pi\kappa_l r_b} - \frac{P_{abs}}{4\pi\kappa_l r_b^2} \delta r_b \end{cases} \quad (2.5)$$

Then we get the bubble radius change δr_b :

$$\frac{\delta r_b}{r_b} = \frac{\delta P_{abs}}{P_{abs}} \left[\frac{8\pi\gamma(T_b)}{P_{abs}} \left(\frac{2}{r_b} \frac{d\gamma}{dT} - \frac{dp_{vap}}{dT} \right)^{-1} + 1 \right]^{-1} \quad (2.6)$$

The required values at threshold for a gold nanoparticle in water are given in Table 2.2. The slope at the threshold is 0.8 nm/ μ W for water. We note that the bracket in the denominator may in principle change sign, which would make it impossible to have a stable bubble. However, we checked that this cannot happen in the parameter region corresponding to our experiments.

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Table 2.2: Numbers required for a linear variation analysis for the formation of a vapor bubble around a particle in water (first line) and pentane (second line). T_b is boiling temperature at the surface of a 40 nm radius particle.

| liquid | r_p (nm) | r_b (nm) | P_{abs} (μW) | T_b (K) | $\gamma(T_b)$ (Nm^{-1}) | $d\gamma/dT$ ($Nm^{-1}K^{-1}$) | p_{vap} (MPa) | dp_{vap}/dT ($MPaK^{-1}$) |
|--------------------------------|---------------|---------------|--------------------------|--------------|--------------------------------|-------------------------------------|--------------------|----------------------------------|
| H ₂ O | 40 | 40 | 62.13 | 483.2 | 3.571×10^{-2} | -2.28×10^{-4} | 1.889 | 3.768×10^{-2} |
| C ₅ H ₁₂ | 40 | 40 | 4.0 | 366.9 | 8.269×10^{-3} | -9.9×10^{-5} | 0.514 | 1.198×10^{-2} |

2.5. Photothermal signals with and without nanobubbles

In principle, the photothermal signal is proportional to the integrated change of refractive index surrounding the absorber over the volume of heat diffusion.

$$S \sim \int \Delta n dV \quad (2.7)$$

We now consider the photothermal signal in two cases.

I. Gold nanoparticle surrounded by liquid:

Under steady state, we have

$$\Delta n = \frac{dn}{dT} \Delta T = \frac{dn}{dT} \cdot \frac{P_{abs}}{4\pi\kappa r} \quad (2.8)$$

P_{abs} is the power absorbed by the absorber; n , κ are the refractive index and thermal conductivity of the surrounding medium; dn/dT is determined by the properties of the medium; r is the radius as measured from the center of the absorber. Substituting Eq.2.8 into Eq.2.7, we get the photothermal signal of a gold nanoparticle in liquid as follows:

$$S_1 \sim \int \Delta n \cdot \exp\left(-\frac{r^2}{a^2}\right) dV = \frac{P_{abs}}{4\pi\kappa} \frac{dn}{dT} \cdot 2\pi a^2 \quad (2.9)$$

where $a^2 = \int e^{-\frac{r^2}{a^2}} dr^2 = 2\kappa/\omega C_p$, a is the heat diffusion length related to the heating modulation frequency; κ is the thermal conductivity of liquid; ω is the modulation frequency and C_p is the heat capacity per unit volume. The slope of the signal with respect to the absorbed power is:

$$\frac{d|S_1|}{dP_{abs}} = \frac{1}{4\pi\kappa_L} \left| \frac{dn}{dT} \right| 2\pi a^2 \quad (2.10)$$

II. Gold nanoparticle surrounded by a thin vapor shell in liquid:

In this case, heat diffuses through both the thin vapor shell and the outside liquid. So the integration in Eq.2.7 should have two photothermal contributions

corresponding to the steam and the liquid:

$$S_2 = S_V + S_L \quad (2.11)$$

for a thin vapor shell, S_V is approximately $(n_v - n_L) \cdot 4\pi R^2 d$, where n_v and n_L are the refractive index of vapor steam and liquid ($n_v \approx 1, n_L = 1.3$), R is the particle radius and d is the thickness of the vapor shell. The derivative of S_V over absorbed power can be calculated from the analysis in Section 2.4:

$$\frac{d|S_V|}{dP_{abs}} = (n_L - n_V) \cdot 4\pi R^2 \frac{dh}{dP_{abs}} = (n_L - n_V) \cdot 4\pi R^2 \frac{\delta r_b}{\delta P_{abs}} \quad (2.12)$$

Then the slope ratio between vapor shell and liquid is:

$$\frac{d|S_V|}{dP_{abs}} \Big/ \frac{d|S_L|}{dP_{abs}} = 8\pi\kappa_L \frac{\delta r_b}{\delta P_{abs}} \frac{R^2}{a^2} (n_L - n_V) \cdot \left| \frac{dn}{dT} \right|^{-1} \quad (2.13)$$

Consider $n_L - n_V = 0.3$, $\left| \frac{dn}{dT} \right| \approx 10^{-4} \text{K}^{-1}$, $R = 40 \text{ nm}$, $a \approx 100 \text{ nm}$, $\frac{\delta r_b}{\delta P_{abs}} \approx 1 \text{ nm}/\mu\text{W}$ at the threshold, the slope ratio is about 8. In chapter 3, we will see that this number is close to the data measured with photothermal microscopy.

2.6. Conclusions

In this chapter, we provide a simple thermodynamic model of vapor nanobubbles assuming steady state. Based on the standard physical data from NIST, we calculated the minimum/critical boiling temperature and pressure of a vapor nanobubble around a CW laser-heated gold nanoparticle. We also consider the temperature distribution with and without vapor nanobubbles under various absorbed powers, and the optical signal change due to the presence of vapor bubbles. Even though this model is very simple, it provides insight into the thermodynamic properties of vapor bubbles as well as into the experimental conditions for vapor nanobubble studies.

