Photothermal studies of single molecules and gold nanoparticles: vapor nanobubbles and conjugated polymers
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[88] The triisopropylbenzene is the main component of oil, sound velocities in some related compounds is about 1350 m/s, data from a commercial website (https://www.flexim.com).


Appendices
A

Thermodynamic and optical data of some common substances
Table A.1: Thermodynamic and optical data of some common substances at ambient temperature and pressure

<table>
<thead>
<tr>
<th>Substance</th>
<th>$n$</th>
<th>$10^4 \times \frac{dn}{dT}$ (K$^{-1}$)</th>
<th>$\rho$ (g·cm$^{-3}$)</th>
<th>$\kappa$ (Wm$^{-1}$K$^{-1}$)</th>
<th>$10^{-3} \times C_p$ (Jkg$^{-1}$K$^{-1}$)</th>
<th>$10^3 \times \gamma$ (Pa·s)</th>
<th>$T_b(T_m)$ (C°)</th>
<th>$v_l$ (m·s$^{-1}$)</th>
<th>$v_s$ (m·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water(25 C°)</td>
<td>1.33</td>
<td>-0.91</td>
<td>0.997</td>
<td>0.61</td>
<td>4.18</td>
<td>71.99</td>
<td>0.89</td>
<td>100</td>
<td>1497</td>
</tr>
<tr>
<td>glycerol</td>
<td>1.47</td>
<td>-2.7</td>
<td>1.261</td>
<td>0.28</td>
<td>2.4</td>
<td>63</td>
<td>1495</td>
<td>290</td>
<td>1904</td>
</tr>
<tr>
<td>n-pentane</td>
<td>1.36</td>
<td>-5.5</td>
<td>0.626</td>
<td>0.11</td>
<td>2.31</td>
<td>15.49</td>
<td>0.22</td>
<td>36.1</td>
<td>1008</td>
</tr>
<tr>
<td>methanol</td>
<td>1.31</td>
<td>-3.94</td>
<td>0.792</td>
<td>0.202</td>
<td>2.46</td>
<td>22.07</td>
<td>0.59</td>
<td>64.6</td>
<td>1121</td>
</tr>
<tr>
<td>ethanol</td>
<td>1.36</td>
<td>-3.7</td>
<td>0.789</td>
<td>0.167</td>
<td>2.36</td>
<td>21.97</td>
<td>1.203</td>
<td>78.2</td>
<td>1162</td>
</tr>
<tr>
<td>toluene</td>
<td>1.50</td>
<td>-5.68</td>
<td>0.87</td>
<td>0.135</td>
<td>1.69</td>
<td>27.73</td>
<td>0.56</td>
<td>110.6</td>
<td>1304</td>
</tr>
<tr>
<td>acetone</td>
<td>1.36</td>
<td>-5.42</td>
<td>0.8</td>
<td>0.19</td>
<td>2.18</td>
<td>22.72</td>
<td>0.295</td>
<td>56</td>
<td>1203</td>
</tr>
<tr>
<td>BK7 glass</td>
<td>1.52</td>
<td>-0.13</td>
<td>2.51</td>
<td>1.114</td>
<td>0.86</td>
<td>-</td>
<td>-</td>
<td>557</td>
<td>5100</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.46</td>
<td>-0.12</td>
<td>2.2</td>
<td>1.38</td>
<td>0.703</td>
<td>-</td>
<td>-</td>
<td>1600</td>
<td>5968</td>
</tr>
<tr>
<td>gold</td>
<td>0.27+2.95i</td>
<td>unknown</td>
<td>19.3</td>
<td>318</td>
<td>0.129</td>
<td>-</td>
<td>-</td>
<td>1064</td>
<td>3240</td>
</tr>
<tr>
<td>PMMA</td>
<td>1.49</td>
<td>-1.2</td>
<td>1.19</td>
<td>0.17-0.19</td>
<td>1.4-1.5</td>
<td>-</td>
<td>-</td>
<td>160</td>
<td>unknown</td>
</tr>
<tr>
<td>air</td>
<td>1</td>
<td>-0.01</td>
<td>0.001</td>
<td>0.026</td>
<td>1.01</td>
<td>-</td>
<td>0.018</td>
<td>-</td>
<td>346</td>
</tr>
<tr>
<td>water steam(100 C°)</td>
<td>1</td>
<td>unknown</td>
<td>0.001</td>
<td>0.025</td>
<td>2.08</td>
<td>-</td>
<td>0.012</td>
<td>-</td>
<td>472</td>
</tr>
</tbody>
</table>

(*The tabulated constants for each material are the refractive index $n$ at 589.3 nm, the derivative of refractive index with respect to temperature $\frac{dn}{dT}$, the density $\rho$, the thermal conductivity $\kappa$, the heat capacity $C_p$, the surface tension (of liquid) $\gamma$, the viscosity $\mu$, the boiling point $T_b$ for liquids, the melting point $T_m$ for solids, the velocity of longitudinal sound waves $v_l$, and the velocity of shear waves $v_s$. The data are from the CRC Handbook of Chemistry and Physics (90th), National Institute of Standards and Technology (NIST), and Photothermal Spectroscopy Methods for Chemical Analysis [40]. The "unknown" means the data are not found in the above resources.)
Scheme of the pressure system
Figure B.1: Scheme of the pressure system used for the measurements in near-critical xenon. V1, V2, V3 and V4 are the gas valves; P1, P2 and P3 are the valves on the compression cylinder. Pressure chamber is labeled as "Cell"; "R" is the pressure regulator.
Comparison of calculated boiling temperature with experiments

We compare the theoretical value of the critical powers for the boiling as found in Fig.2.3 in Chapter 2 to the experimental critical powers found in Fig.3.2 of Chapter 3 and in Chapter 4. In Chapter 3, we find that the critical absorbed power for a particle with 40 nm radius (80 nm diameter) in water is 62.1 $\mu$W from Fig.2.3. This is calculated for a particle in water, but in our experiments we have particles in water on a silica substrate. To correct for this we use the average value of the thermal conductivity of water (0.65 Wm$^{-1}$K$^{-1}$) and silica (1.38 Wm$^{-1}$K$^{-1}$). Then we find:

$$P_{crit. abs.} = \frac{1}{2}(0.65 + 1.38) \times 62.1(\mu W) = 97(\mu W)$$  \hspace{1cm} (C.1)

Based on the diffraction-limited microscope's point spread function we estimate the size/diameter of the focus of the heating beam to be:

$$d = 1.22 \times \frac{\lambda}{N.A.} = 1.22 \times \frac{532}{1.45} (nm) = 448(nm)$$  \hspace{1cm} (C.2)

Taking the refractive index of the medium surrounding a gold nanosphere to be the average of the refractive index of water and glass, we can use Mie theory to estimate the absorption cross section of the particle. We find $\sigma_{abs} = 1.7 \times 10^4$ nm$^2$ at 532 nm. We can now relate the critical absorbed power for the formation of a nanobubble to the critical power in the focus:

$$p_{focus \; crit.}^{80nm} = \left( \frac{A_{focus}}{\sigma_{abs}} \right) \times P_{crit. abs.} = \left[ \frac{\pi(448/2)^2}{1.7 \times 10^4} \right] \times 97(\mu W) = 0.9(\mu W)$$  \hspace{1cm} (C.3)
This should be compared to critical powers measured in experiments, which depended on the conditions. For water on a BK7 glass substrate (Fig.3.6 in Chapter 3), the critical power was about 1.0 mW, in good agreement with the above estimate. On a fused silica substrate, because of the aberrations introduced by the poor index matching with the objective, the critical power rose to about 3 mW (see Fig.3.2, where the power is not corrected for objective transmission). A similar reduction of local intensity was found by Ruijgrok et al. [83] in the calculated and measured values of the intensity at the focus of a high numerical-aperture objective and attributed to spherical aberrations. For pentane on BK7 glass, the critical power was much lower, about 100 µW (Fig.3.5 in Chapter 3, insert).

In Chapter 4, we use a 50 nm diameter gold sphere in water and BK7 glass substrate. The critical absorbed power for the boiling in water around a 50 nm gold sphere is about 42.3 µW from Fig.2.3 in Chapter 2. If we consider the substrate, the critical absorbed power becomes:

\[ P_{\text{crit. abs.}}|_{50\text{nm}} = \frac{\pi}{0.65} \left(0.65 + 1.11\right) \times 42.3(\mu W) = 57.3(\mu W) \]  

(C.4)

The N.A. of the objective used in Chapter 4 is 1.4, so the diffraction-limited diameter of the focus of the CW heating beam (532 nm) is:

\[ d = 1.22 \times \frac{\lambda}{\text{N.A.}} = 1.22 \times \frac{532}{1.4} (nm) = 464(nm) \]  

(C.5)

The absorption cross section of a 50 nm diameter gold sphere on a BK7 substrate in water, taking into account the BK7 substrate, is calculated to be about 7650 nm² at 532 nm. Using the same equation as Eq.C.3, we find the critical power in the focus for the formation of a vapor nanobubble around a 50 nm gold sphere:

\[ P_{\text{crit. focus}}|_{50\text{nm}} = \left(\frac{A_{\text{focus}}}{\sigma_{\text{abs}}}\right) \times P_{\text{crit. abs.}}|_{50\text{nm}} = \left[\frac{\pi(464/2)^2}{7646}\right] \times 57.3(\mu W) = 1.3(mW) \]  

(C.6)

The critical power found in such calculations is close to, but a bit higher than the CW heating power found in our pump-probe experiments when the vapor bubble forms. Note that in the pump-probe experiments, both the pump and probe pulses contribute to the temperature rise of gold nanoparticle. More importantly, the acoustic vibration of the gold nanoparticle can behave as a trigger to tear the hot liquid molecules apart and initiate a vapor bubble.
Energies involved in the vapor bubble growth

To understand bubble growth and instability better, we have estimated the main energy contributions involved in the explosion. Although this process appears to follow an inertial regime, we neglected kinetic energy, which can be considered in a future dynamic model. The three main contributions mentioned in the main text of Chapter 3 were calculated as follows, assuming the non-evaporated overheated liquid is pushed mechanically by the created vapor, without heat conduction through the interfaces:

i) Surface energy: it is calculated for varying bubble radius from the surface tension which is temperature dependent. The temperature is assumed to be the equilibrium one, although this is certainly not true during the expansion.

ii) Latent heat and heat capacity: this energy is calculated from the internal energy of liquid and gas, as a function of bubble diameter.

iii) Overheated liquid thermal energy: this is the heat stored in the overheated layer, integrating all layers of liquid whose temperature exceeds the equilibrium curve between regimes I and II (dashed line in Figure D.1). The temperature profiles of the liquid immediately before the explosion (blue solid curve) and for two different bubble diameters (red curves) are presented in Fig.D.1. Liquid layers with temperature above the dashed curve are in principle able to give energy to the vapor shell and to feed the expansion.

The three energy contributions above are plotted as functions of the bubble radius in Fig.D.2. Only half of the overheated liquid energy has been used to heat the bubble, the other half was assumed to dissipate into the colder outer layers. The net energy contribution, plotted in Fig.D.3 against bubble radius, is
Figure D.1: Temperature profiles along the radial direction. The solid blue curve shows the initial temperature profile. The dashed black curve (phase diagram) gives the surface temperature of the vapor shell as found from the Laplace pressure. The solid blue curve crosses the dashed black curve at a radius of about 50 nm, corresponding to an overheated liquid between 40 nm and 50 nm. The solid red curves show the temperature of the liquid after it has been pushed out by the vapor shell. The part of the solid red curves above the black dashed curve at the vapor shell radius (i.e. the start of the red curves) represents excess energy partly available to feed the explosion.

negative for small radius, driving bubble expansion. Its slope, corresponding to the driving force, changes sign for 150 nm, creating an effective potential resisting expansion. In the absence of friction and heat diffusion, the maximum bubble diameter would be 230 nm. However, dissipation soon cools the surface bubble and suppresses overheating, entailing the collapse of the bubble until heating by the nanoparticle can start a new explosion.
Appendix D

Figure D.2: Variations in internal energy (blue curve), surface energy (black curve) between state I and state II, and excess overheating energy (red curve; only half this energy is available for the bubble heating, the rest is assumed to diffuse to the cold outside liquid layers).

Figure D.3: The energy difference between state I and state II as a function of vapor shell radius. In principle there is enough excess energy to expand the vapor shell up to about 240 nm radius, much beyond the steady state radius of about 50 nm.
Analysis of delay time between two successive explosions

In order to understand the details of the delay time between two successive explosions in Chapter 3, we plot the delay time as a function of event number (red dots) as well as a histogram of the delay times (green histogram) in Fig.E.1. We attribute the strong correlation between successive delay times observed in these plots to the slow drift of the laser power, during which bubbles appeared, maintained a high repetition rate, and eventually subsided (blue trace in insert). Indeed, upon selecting a part of the data from n=800 to 2600 where laser power drift appears negligible, the data shows essentially no correlation between successive delay times. We fit the histogram of the selected delay times from n=800 to 2600 with a Gaussian distribution function as follows:

\[
p(\tau) = \frac{A}{\omega \sqrt{\pi/2}} \exp \left[ -\frac{2(\tau - \tau_c)^2}{\omega^2} \right]
\]  

(E.1)

The fitted results are shown in Fig.3.3 (d) in Chapter 3.

To further illustrate the absence of correlation between successive delay times we simulated random delay times using the fitted Gaussian distribution. We created scatter plots of successive delay times for both the experimental data and simulation (in which correlation is absent), see Fig.E.2. By comparing the two scatter plots, we conclude that the delay time data in the central part of Fig.E.1, which we think is governed solely by the nanobubble system and not by drift of the laser power, is essentially uncorrelated.
Figure E.1: a) The delay time between two successive explosions as a function of the event number $n$. Insert: time trace of the intensity of the scattered probe light; b) Histogram of the delay time distribution. The red line is a fitted curve. Insert: the scatter plot of $\tau_{n+1}$ and $\tau_n$. 

$\tau_n$ (\mu s)
Appendix E

Figure E.2: a) A scatter plot of $\tau_{n+1}$ and $\tau_n$ using the experimental data; b) A scatter plot of simulation of a random succession of delay times drawn from the Gaussian distribution that is used to fit to the data from $n=800$ to 2600.
Hereafter, we briefly speculate about the mechanism of after-burst triggering by the echo. If enough energy is left in the hot liquid and in the gold nanoparticle after the first explosion, and if the returning cooled water has enough contact time with the nanoparticle to become overheated again, the system may be reloaded for a new explosion, although the temperature profile is much less extended than that before the main explosion. The heat diffusion length for a time of 150 ns, the time interval between the main bubble collapse and the arrival of the echo, is 100 nm ($D_{\text{pentane}} = 6 \times 10^{-8} \text{ m}^2/\text{s}$). For a 1 µs time it's about 2.5 times larger, 250 nm. For a long enough waiting time, a second explosion can take place, with a reduced amplitude as there is less energy stored in the overheated water to feed the expanding after-bubble. Sometimes, we even observe a third after-burst, which appears again 150 ns after the second one (see Figure F.1). This delay of 150 ns corresponds to twice the propagation time in the oil gap ($2 \times 100\mu\text{m} \text{ at } 1350 \text{ m/s}$). Indeed, the first echo from the far side of the coverslip arrives 60 ns after the explosion, while the bubble just contracted and not enough energy has been transferred to the liquid yet. The echo from the objective surface arrives 150 ns later still (see Fig.3.4.c in Chapter 3) and finds enough hot water to trigger a second explosion or after-burst. In some conditions two or more afterbursts can be observed (see Fig.F.1). In these events, the nanobubble performs as an amplifier fed back on itself, producing damped relaxation oscillations. A similar phenomenon observed in water is shown in Chapter 3. However, in this latter case, the oscillation period is about 30 ns and is too short to arise from an acoustic echo. We attribute this instability to bub-
Figure F.1: The time trace including a third after-burst (black arrow). The experimental conditions are the same as Fig.3.4 in Chapter 3. The gold nanoparticle is immersed in n-pentane.

These observations highlight the remarkable sensitivity of the nanobubble to extremely weak multiple acoustic reflections from interfaces more than 100 μm away.
In Fig.G.1, we present a single-shot time trace of the signal of a nanobubble formed by raising the heating power above the critical value. This event is a typical one taken out of the long time trace with hundreds of explosions, shown together with the heating intensity profile. The bubble starts with a small explosion clearly visible in Fig.G.1.a, and is followed by a persistent phase before disappearing about a microsecond later when the power is decreased again. The histogram of Fig.G.1 (c) shows the jitter delays $\Delta$ between the heating pulse and the time of the explosion, taken at the mid-rising edge of the explosion signal. These delays are all positive, confirming that the explosions are all caused by the heating increase. Moreover, we see that the histogram is almost $0.5 \mu s$ broad, comparable to the spread of inter-explosion delays in the time traces in Chapter 3 with constant heating.
Figure G.1: The non-averaged time trace showing the improvement of nanobubble stability. a) Probe signal; b) Heating power; The heating beam is modulated by AOM, using a block pulse profile with a frequency of 100 kHz, and a duty cycle of 10% (1 μs on-time in a 10 μs period); c) The histogram of the jitter delay between the probe rise edge and heating rise edge. The gold nanoparticle is immersed in n-pentane in these measurements.