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Controlled Shrinkage and Re-expansion of a Single Aqueous Droplet Inside an Optical Vortex Trap

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Abstract

This paper describes the shrinkage and re-expansion of individual femtoliter-volume aqueous droplets that were suspended in an organic medium and held in an optical vortex trap. To elucidate the mechanism behind this phenomenon, we constructed a heat and mass transfer model and carried out experimental verifications of our model. From these studies, we conclude that an evaporation mechanism sufficiently describes the shrinkage of aqueous droplets held in a vortex trap, while a mechanism based on the supersaturation of the organic phase by water that surrounds the droplet adequately explains the re-expansion of the shrunk droplet. The proposed mechanisms correlate well with experimental observations using different organic media, when H₂O was replaced with D₂O, and when an optical tweezer was used to induce droplet shrinkage rather than an optical vortex trap. For H₂O droplets, the temperature rise within the droplet during shrinkage was on the order of 1K or less, owing to the rapid thermal conduction of heat away from the droplet at the microscale and the sharp increase in solubility for water by the organic phase with slight elevations in temperature. Because most chemical species confined to droplets can be made impenetrable to the aqueous/organic interface, a change in the volume of aqueous droplets translates into a change in concentration of the dissolved species within the droplets. Therefore, this phenomenon should find use in the study of fundamental chemical processes that are sensitive to concentration, such as macromolecular crowding and protein nucleation and crystallization.

INTRODUCTION

The ability to manipulate the motion accurately and control the volume of a single aqueous droplet is crucial in controlling nano-scale reactions often encountered in lab-on-a-chip technologies. Conventional optical tweezer methods, which employ Gaussian laser-beam profile, can be used to translate femtoliter-volume aqueous containers only when the container is made of materials such as biological membranes or polymer, which has a higher refractive index than the surrounding medium.^{1,2} In contrast, an aqueous droplet suspended in an organic medium cannot be trapped using a conventional Gaussian trap (optical tweezer): the intensity gradients in radial and axial directions induce dipole forces on the particle that favor the trapping and aggregation of materials of higher index of refraction, which is typically the organic phase rather than the aqueous phase, and would consequently tend to repel aqueous droplets away from the trap. With recent advances in optical vortex traps, which employ Laguerre-Gaussian (LG) beam profile, trapping low-index particles becomes possible.³⁻⁷ An LG profile is characterized by a dark focus in the center of the laser beam, which resembles a donut, and has found particular utility in trapping single femtoliter-volume aqueous droplets.

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Aqueous droplets, when present in an immiscible phase that has a slight solubility for water, will shrink and concentrate their contents via *passive* diffusion and dissolution of water into the immiscible phase.⁸ This phenomenon does not occur if the immiscible phase was pre-saturated with water. In this situation, however, we found we could still actively cause the droplet to shrink if it were held in an optical vortex trap at sufficiently high powers (~ 50 mW after the objective).⁷ Furthermore, we observed the droplet to expand towards its original size when the laser power was turned down or off.⁷ We believe the cause of this shrinkage to be localized energy transfer from the laser to the interface where the laser beam and droplet overlapped, which resulted in a localized increase in the solubility of the immiscible phase for water. Upon turning off the laser, the water in the surrounding supersaturated medium returned to the droplet, thereby resulting in droplet expansion.⁷

In investigating the shrinkage and expansion mechanism, this paper explored several experimental parameters to pinpoint the correct phenomenon and to correlate quantitatively our experimental data with theoretical calculations. Although in the following sections we only discuss in detail one mechanism – that of enhanced mass transfer due to localized laser-heating – we have also considered other emulsion destabilization mechanisms such as Ostwald-Ripening,⁹ microemulsion theories,^{10,11} and critical phase separation;¹² however, only the mechanism we describe in detail below provided quantitative agreement with our experimental observations.

As we seek to expand the applications of optical vortex trap to manipulate aqueous droplets, the mechanism of shrinkage must be understood and controlled. Controlled shrinkage of the droplet volume can provide additional ways to actively control the droplet composition and thus the interior reactions. The potential applications for such ability include increased experimental precision in measuring enzyme kinetics, investigating macro-molecular crowding effects, and controlling crystallization conditions of proteins at the nanoscale.

EXPERIMENTAL

Figure 1 shows a schematic of the experimental setup. The TEM_{00} output from a Nd:YAG laser (Millenia IR, Spectra Physics) was directed through a microfabricated diffraction phase hologram. After a short propagation distance, the first order mode LG_0^1 was isolated and spatially filtered, then sent to the back aperture of the objective ($100\times$ N.A. 1.3) placed in the inverted microscope (TE2000, Nikon). Laser power was measured at ~ 44 mW after the objective. The hologram was made from a transparent photopolymer (SU8, Microchem) patterned on a glass substrate. The hologram was fabricated using lithographic techniques, and blazed to maximize the intensity in the first diffraction order.

The droplets were generated by means of sample emulsification, using a 10:1 ratio of organic to aqueous phase. The organic phase we used was pre-saturated with water, by periodically agitating the phase segregated oil and aqueous solutions over the course of three days. The continuous phases used were either decanol or acetophenone, the dispersed phases used were either H_2O or D_2O . The emulsion was stabilized using 0.1% wt of Span 80, a non-ionic surfactant (sorbital monooleate, Aldrich chemicals). The droplets were generated by agitating a 2-ml solution with manual shaking. This agitated solution was allowed to sit and to phase-separate, after which a region of the sample that contained droplets of radii 2–5 μm were removed and placed in a sample well made from polydimethyl siloxane (PDMS) bonded to a coverslip. This well had a volume capacity of ~ 0.2 ml and the coverslip was #1, which denotes a thickness that ranged from 130–160 μm . Once the well was filled, it was capped with a second coverslip to minimize evaporation.

THEORETICAL CALCULATIONS

Laser-On

The rapid shrinkage of a low-refractive-index droplet inside an optical vortex trap can be explained by the localized laser heating of the droplet and the subsequent increase in interfacial solubility. The theoretical treatment that follows is analogous to laser-evaporation of aerosol droplets or ice in air,¹³⁻¹⁷ with the exception that the external phase is now an immiscible organic liquid rather than air, which has different mass and heat transfer properties as well as solubility characteristics. Indeed, because of the much slower rates of mass transfer, the external organic phase is more susceptible to supersaturation, which leads to droplet re-growth once the laser is turned off.

For simplicity, we shall consider a spherically symmetric droplet consisting of only pure water (55 M) and with spatially uniform distribution of temperature T inside the droplet. At the boundary of the droplet, one can write a mass-conservation equation relating the change of the volume of the droplet to the mass flux leaving the droplet:

$$\frac{\partial}{\partial t}(\rho V) = 4\pi a^2 D \frac{\partial C}{\partial r} \Big|_{r=a} \cdot M_w \quad (1)$$

where V is the droplet volume, ρ is the density of the droplet (pure water), a is the radius of the droplet, D is the mass diffusion coefficient of water in the external organic phase, C is the external concentration (solubility) of water, and M_w is the molecular weight of water.

When the laser is on, radiation is absorbed by water, which leads to an internal enthalpy increase; however, enthalpy can be removed from the droplet via Fourier conduction into the organic phase as well as the mass flux leaving the droplet. Therefore, we can write an enthalpy conservation equation around the droplet boundary:

$$\rho V C_p \frac{\partial T}{\partial t} = 4\pi a^2 k \frac{\partial T}{\partial r} \Big|_{r=a} + \alpha I_0 V + \Delta H_{mix} \frac{\partial}{\partial t}(\rho V) \quad (2)$$

where the first term on the right side refers to the conductive heat flux at the interface of the droplet and the surrounding organic phase; the second term refers to the laser energy absorbed by the droplet; the third term refers to the mass flux leaving the droplet, carrying with it the enthalpy of mixing, which accounts for the energy of phase change to disperse water from pure phase into the organic phase. Were the droplet surrounded by ambient air, as in typical aerosol experiments, the energy of phase change would refer to the latent heat of vaporization. The nomenclature used in this equation is as follows: T is the temperature field; C_p is the heat capacity of the droplet; k is the thermal conductivity of the organic medium, I_0 is the laser power density at the focal plane, ΔH_{mix} is the enthalpy of mixing and α is the “average” radiation absorbance of the droplet. In our model we use a diffraction limited laser spot size of 0.75 μm at a power of 44 $\pm$ 8 mW.

The average absorption coefficient, α , consists of three contributing factors: (1) the intrinsic absorption of radiation at 1064 nm by water, (2) geometry of the laser incidence in relation with the droplet, and (3) refractive and scattering phenomena at the interface of the droplet and the medium. As the 1064 nm laser beam is focused to a $\sim 1 \mu\text{m}$ diameter focal spot to trap the droplet, the radiation first travels from a high refractive index organic medium to a low index aqueous phase, which results in $\sim 30\%$ loss of power. The radiation is then absorbed at a focal area of the particle section in a plane perpendicular to the axis of the laser beam. Thus one can write, for a spherical particle:^{16,17}

$$\alpha = Q_{abs} \frac{G}{V} = \frac{3}{4a} Q_{abs} \quad (3)$$

Where $G = \pi a^2$, the area of particle perpendicular to the axis of beam propagation, V is the volume of the particle, and Q_{abs} is a factor of absorption that accounts for the intrinsic absorption of the droplet and the interface refraction; given by: 16-18

$$Q_{abs} = 4x \operatorname{Im} \left\{ \frac{N^2 - 1}{N^2 + 2} \right\} \quad (4)$$

where $N = (n_2 + ik_2)/(n_1 + ik_1)$, a complex index of refraction of the particle (subscript 2) with respect to the surrounding (subscript 1); and $x = 2\pi a / \lambda$, sometimes known as a wave or diffraction parameter. Defining the intrinsic absorption of the droplet as $\alpha_2 = 4\pi k_2 / \lambda$, one can re-write:

$$\alpha = f(n_1, k_1, n_2, k_2) \alpha_2 \quad (5)$$

where f is a correction factor to the intrinsic absorption coefficient given by:

$$f = \frac{3}{k_2} \frac{\{(n_2 k_2 - n_1 k_1) [(n_2^2 + 2n_1^2) - (k_2^2 + 2k_1^2)] - [(n_2^2 - n_1^2) - (k_2^2 - k_1^2)] (n_2 k_2 + 2n_1 k_1)\}}{\{(n_2^2 + 2n_1^2) - (k_2^2 + 2k_1^2)\}^2 + 4(n_2 k_2 + 2n_1 k_1)^2} \quad (6)$$

Using the physical parameters listed in Table I, we computed that for water droplet surrounded by acetophenone, $f = 0.67$. For water droplet surrounded by decanol, $f = 0.72$, which agrees with the fact that because decanol's refractive index (1.437) is closer to the refractive index of water (1.33) than is for acetophenone (1.537), less power loss due to refraction is expected for a trapped water droplet in decanol.

To evaluate the concentration and temperature fluxes at the interface, one must determine the external concentration and temperature profiles. In the organic phase, the Fickian diffusion of water molecule from the droplet leads to an external concentration profile, which can be written as:

$$\frac{\partial C}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) \quad (7)$$

Similarly, the Fourier conduction of heat in the organic phase leads to an external temperature profile:

$$\frac{\partial T}{\partial t} = \alpha_T \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) \quad (8)$$

where $\alpha_T = k / \rho C_p$, the thermal diffusivity of the organic phase. Note that equation (8) refers strictly to the organic phase. Equations (1), (2), (7) & (8) must be solved simultaneously, subject to the proper boundary conditions at the interface and far-away from the droplet. At the interface, we shall require that (1) the temperature inside the droplet matches the temperature profile from external conduction, and (2) the concentration of water at the interface, C_i , is governed by temperature-corrected equilibrium solubility:

$$C_i = C_0 e^{-\frac{\Delta H_{mix}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)} \quad (9)$$

where C_0 is the solubility of water in external phase at the reference temperature T_0 . For simplification, we shall use 293 K as the reference temperature, which also is the ambient temperature, or the far-away condition of the temperature profile.

Because a , the droplet radius, changes as a function of time, this problem falls under a class of difficult mathematical problems commonly referred to as Stefan (or moving-boundary) problems, of which only few select cases are known to be solvable exactly. However, strategies to obtain approximate solutions have been developed, and has been discussed succinctly in the

literature.¹³ Typical approaches involve solving Equations (7) and (8) independently first, assuming that the radius is stationary and the transient response of diffusion is instantaneous such that the steady-state solutions to Equations (7) and (8) can be used to evaluate the mass and temperature flux for Equations (1) and (2). This approach is sometimes referred to as “quasi-stationary”. Indeed, under our typical experimental conditions, since the droplet size ($\sim 5 \mu\text{m}$ in radius) is small comparing to the characteristic diffusional distance (i.e., $r / \sqrt{4Dt} \approx 0$ or $r / \sqrt{4a_T t} \approx 0$), the transient time correction in Equations (7) and (8) is very small and the steady-state solutions may be used.¹⁴ In essence, this approach assumes that the time-scales of mass and thermal diffusion are so much faster than the time-scale associated with the change in droplet size that the transient responses may be de-coupled, and from the perspective of change in droplet size, the external concentration and temperature profiles are established instantaneously.

The steady-state solutions to Equations (7) and (8), subject to the interfacial conditions ($C|_{r=a} = C_i$ and $T|_{r=a} = T_2$) and far-away conditions ($C|_{r=\infty} = C_0$ and $T|_{r=\infty} = T_0$) are:

$$C - C_0 = \frac{a}{r} (C_i - C_0) \quad (10)$$

$$T - T_0 = \frac{a}{r} (T_2 - T_0) \quad (11)$$

From Equation (10) and (11), the interfacial fluxes $(\partial C / \partial r)|_{r=a}$ and $(\partial T / \partial r)|_{r=a}$ may be computed and inserted into Equations (1) and (2). Upon re-arranging, we arrive at the following coupled nonlinear differential equations:

$$\frac{da}{dt} = - \frac{D_{2-1} \cdot M_{w2} \cdot C_0}{\rho_2 \cdot a} \left(e^{-\frac{\Delta H_{mix}}{R} \left(\frac{1}{T_2} - \frac{1}{T_0} \right)} - 1 \right) \quad (12)$$

$$\frac{dT_2}{dt} = - \frac{3}{a^2} \frac{k_1}{\rho_2 C_{p2}} (T_2 - T_0) + \frac{\alpha}{\rho_2 C_{p2}} I_0 + \frac{3}{a} \frac{\Delta H_{mix}}{C_{p2}} \cdot \frac{da}{dt} \quad (13)$$

For clarification, we have introduced subscript 1 to indicate the external organic phase, and subscript 2 still refers to the dispersed aqueous phase. Equations (12) and (13) may be integrated numerically; we used the RKADAPT solver routine in MathCad (Mathsoft Corporation, Cambridge, MA), which uses fourth order Runge-Kutta algorithm with adaptive step size to ensure convergence, to integrate these two equations subject to the initial conditions of droplet radius and temperature (293 K).

Laser-Off

After the laser is turned off, the decrease in temperature leads to supersaturation of water in the organic phase, which causes a reversal of mass flux that leads to the re-growth or expansion of the volume of the droplet. To model this growth behavior after laser is turned off, we can estimate the supersaturation concentration by summing the amount of water that left the droplet and the initial water content (excluding the droplet) in the organic phase:

$$C_s V_{ext} = \eta \cdot \Delta M + C_0 V_{ext} \quad (14)$$

where C_s is the effective supersaturation concentration; V_{ext} is the external volume of the organic phase; $\Delta M = \rho \Delta V$ is the mass of water lost by the droplet earlier when the laser was on; η is an empirical “recovery factor” whose value is typically ~ 0.2 , to account for the experimental observation that after the laser is turned off, the droplet usually does not grow fully back to its initial volume in an open volume and in the presence of other droplets, which suggests that water molecules that left the droplet are not completely recoverable in such cases. One can rationalize this observation by considering that, as water molecules leave the droplet,

they have the possibility of remaining in the organic phase, or they can join into other droplets in the suspension. Thus other droplets in the suspension become material sinks that grow at the expense of the droplet being held by the laser. Indeed, using this mechanism we were able to expand the volume of a “target” droplet by shrinking a nearby “donor” droplet.⁷

It is also important to note that V_{ext} , the external volume of the organic phase, is not the same as the entire sample volume. Because the suspension consists of many droplets, each in local equilibrium with the bulk organic phase, any local alteration of a single droplet will not affect droplet environment that is too far away. Thus V_{ext} more accurately should, in some way, reflect the droplet-to-droplet distance. This concept is akin to the “cell” approach to model saturation: ^{19,20} one can envision that a suspension of many small droplets may be subdivided into cells around each droplet, and the volume of each cell contains the local equilibrium around each droplet. Empirically by fitting the experimental data, we found that $V_{ext} \sim 10^5$ times the smallest droplet volume, which is equivalent to a sphere with radius 90 times the droplet radius. The recovery factor and external volume used in each data fitting are listed in Table III.

As time progresses after the laser is turned off, the droplet reaches an equilibrium size as the growth rate tapers off. This observation suggests that the correct modeling must reflect the fact that the concentration of water in the surrounding organic phase must decrease with time from supersaturation to eventually saturation as water is again consumed by the droplet. Thus we can write the following differential material balance for C_s :

$$\frac{d(C_s V_{ext})}{dt} = -\rho \frac{dV}{dt} \cdot Mw = -\rho \cdot 4\pi a^2 \frac{da}{dt} \cdot Mw \quad (15)$$

where ρ , V , and Mw again refer to, as in Equation (1), the density of pure water, volume of the droplet, and molecular weight of water, respectively. Using C_s as the far-away concentration in Equation (10) and Equation (14) to compute the initial value of C_s , one can integrate Equations (12), (13) and (15) simultaneously with respect to time to determine the droplet radius, temperature, and the supersaturation concentration.

RESULTS AND DISCUSSION

A. H₂O vs. D₂O

To validate that the observed droplet shrinkage is a result of radiation absorption, we compared the behaviors of H₂O and D₂O droplets in a vortex trap, because H₂O and D₂O have different absorption cross-sections at 1064nm. Figure 2a shows the change in volume over time of vortex-trapped aqueous droplets surrounded by acetophenone. The volumes have been normalized with respect to the initial droplet volumes, because the sizes of the droplets in suspension were not monodisperse. From our calculations, we have verified that normalized rates are indeed independent of the initial droplet sizes.

The shrinkage rate was slower for D₂O than H₂O droplets as anticipated, because of the difference in the near IR absorption of H₂O and D₂O. The Lambert absorption coefficient ranges from 0.36 cm⁻¹ to 0.15 cm⁻¹ in the near IR region for H₂O;²¹ however, for D₂O, as determined using a NIR spectrophotometer (Cary 500, Varian), the absorption coefficient was only ~15% that of H₂O at 1064nm. Figure 2a shows our theoretical model quantitatively accounts for the difference in the behaviors of H₂O and D₂O. Three key physical parameters were changed in adapting the calculations for D₂O: (1) absorption coefficient (0.06 cm⁻¹ for D₂O vs. 0.36 cm⁻¹ for H₂O), (2) density (1.1 g/cc for D₂O vs. 1.0 g/cc for H₂O), and (3) molecular weight (20 g/mole for D₂O vs. 18 g/mole for H₂O). The latter two parameters contributed only to a very small correction in our simulations, mostly in conversion from mass to molar units. Because chemically D₂O and H₂O are indistinguishable, all other physical properties can be considered identical within reasonable limit of accuracy.

At the onset of laser illumination, the temperature of the droplet is increased rapidly. As the droplet shrinks, the temperature decreases and leads to a decline in interfacial solubility and the outward mass flux. Figure 2b shows the calculated temperature history of H₂O droplets in acetophenone with initial radii ranging from 2.5–5.0 μm . The temperature rise, which ranges from ~ 0.3 K for the smallest droplet to ~ 1.3 K for the largest droplet (Fig. 2c), is consistent with the typical literature values of temperature rise caused by heating from optical traps.^{22–25} The normalized rates of decay are independent of droplet size (radii calculated within the range 2.5–5.0 μm), but the temperature rise of the larger droplet is higher than that of the smaller droplet. The dependence of the rate of temperature rise on droplet size is due to the surface-to-volume (S/V) ratio of the droplet, which determines the rate of heat transfer away from the droplet to the surrounding immiscible medium via Fourier conduction. This dependence can be readily seen in Equation (2), once both sides of the equation are divided by the droplet volume. Although larger droplets do have larger thermal mass to counter temperature rise, the dominant term in governing the temperature profile is the thermal conduction. As droplet shrinks, the S/V ratio increases and thus improves the heat conduction away from the droplet, thereby resulting in lower droplet temperature. With lower droplet temperature, however, the interfacial solubility of water in organic phase is decreased and the mass flux is thus reduced, resulting in the tapering of the shrinkage rate. This self-balancing between temperature and mass flux is the reason that the decay rate diminishes as droplet shrinks, and why complete dissolution of the droplet is very hard to achieve.

Although the initial temperature rise is only on the order of 1 K and that the temperature continues to decline as time progresses, the mass transport via this mechanism is significant enough to cause a H₂O droplet in acetophenone to lose more than 99% of its original volume within 42 seconds. The mass flux due to changes in interfacial solubility is more sensitive to temperature than in most other macro-emulsion transformation mechanisms. For example, the temperature effect on Ostwald-Ripening, which expresses interfacial concentration in terms of the differential in Laplace pressure,^{9,10} is at least one order of magnitude too small to induce the shrinkage effect that we observed, especially considering that the suspension is stabilized with small amount of surfactant Span 80. Microemulsion theory, which describes droplets with diameters in the nanometers range, provides increased temperature sensitivity near the emulsion inversion temperature by introducing temperature dependence on the bending of the surfactant film and hence the interfacial tension,¹¹ but it is of questionable applicability in our experimental context because the droplets in our system are on the order of microns in radius.

Experimentally, we observed that the shrunk droplet began to grow back after the laser was turned off. As mentioned in the Theoretical Calculation section, we attribute this phenomenon to the localized supersaturation of water in the organic phase. This phenomenon has not been reported in the case of aerosol evaporation in air, but has been discussed in atmospheric condensation theories.^{26,27} Initially, the temperature surrounding the droplet increases with the droplet temperature. When the laser is turned off, the temperature of the surrounding medium decreases and returns to its initial ambient temperature. This creates a supersaturation condition in the surrounding organic phase, as the solubility is temperature dependent. Also, because the mass diffusivity in liquid is much less than that in air, the material that left the droplet is still largely localized. We note, however, the droplet does not grow back to its original size under our experimental conditions, even after 200 seconds. This is due to the fact that the solution does not consist of only one single droplet, but many droplets. The nearby droplets may serve as sinks to absorb the material that left the heated droplet. Unfortunately, once the laser is turned off, there is no mechanism for the nearby droplets to discharge the materials it accumulated except possibly via the Ostwald Ripening process, which is a much slower process, commonly on the order of days.

To fit the experimental data, two empirical parameters were used: η , the recovery fraction, and V_{ext} , the volume of the external organic phase. The values of these parameters are listed in Table III. Although these *ad hoc* parameters offer a way to quantify the droplet re-growth, critically speaking, the underlying theory is not an exact reflection of the situation. When the laser was on, the concentration and temperature profiles in the external organic phase decays as $1/r$, as described in Equations (10) and (11), which implies that the concentration of water is the highest near the droplet, and therefore supersaturation concentration should be the highest close to the droplet once the laser is turned off. However, in our mathematical formulation, we retained the $1/r$ concentration profile, but instead of using the supersaturation concentration condition closest to the droplet, we used it as the far-away condition, because we are obliged to use the interfacial equilibrium condition at the surface of the droplet. This subtle discrepancy between our model and reality should serve as a reminder that approximate solutions to moving-boundary problems can not always take into account all of the physical phenomenon.

B. Acetophenone vs. Decanol

To further validate the model, we also studied the effect of changing the surrounding medium on droplet shrinkage. Figure 3a compares the shrinkage of a H_2O droplet in acetophenone to that in decanol. Table I lists the differences in physical property between acetophenone and decanol. Experimentally we observed that droplets shrink faster in acetophenone than in decanol, which can be accounted for with the differences in the mass diffusion coefficients of water in each medium and in the index of refraction.

According to the inverse relationship between diffusion coefficient and viscosity as described in the Wilke-Chang correlation,²⁸ water should have a slower mass diffusion coefficient in decanol ($\mu=12$ cps) than in acetophenone ($\mu=1.6$ cps). The values of the diffusion coefficients are listed in Table II, with the diffusion coefficient of water molecules in decanol to be $\sim 1/6$ of that of water in acetophenone. Thus the mass flux leaving the droplet should be slower in decanol.

Countering the reduction in mass flux is a slight difference in the refractive indices of the external media. Because decanol's refractive index is closer to that of water (1.437 for decanol and 1.537 for acetophenone), the refractive loss of the laser beam entering from decanol into the water droplet should be less. Thus for the same power input, about 5% more power is absorbed by the droplet when the external phase is decanol rather than acetophenone, resulting in slightly higher droplet temperature. However, this slight change in droplet temperature does not exert as much influence on the shrinkage process as the large difference in diffusion coefficients. As thermal conductive media, decanol and acetophenone are fairly comparable and their thermal diffusivities (as listed in Table I) are within 5% difference.

Figure 3 shows the difference in the rate of droplet shrinkage for H_2O and D_2O droplets in decanol and acetophenone. Overall, our model explains well the experimental data. Except for H_2O droplets (Fig. 3a) near 240 seconds, where the theoretical calculation is quite a bit below the decanol data point. Indeed, experimentally H_2O droplet in decanol does not shrink to such a low volume as predicted by our model. This discrepancy may be attributed to the fact that the decay model does not factor in the possibility of external supersaturation (growth model does, however). When the laser is on, with thermal diffusivity usually much larger than mass diffusivity, the local solubility usually increases with increasing temperature, and therefore supersaturation is typically not expected when the laser is on. However, with the mass diffusion coefficient so much slower in decanol, it is possible that the concentration build-up is so localized that it becomes difficult to deplete the droplet.

Figure 3b shows the comparison between acetophenone and decanol, except this time D_2O was used as the aqueous phase. Again, changing the dispersed phase to D_2O merely changes

the amount of laser radiation absorbed ($\sim 15\%$ relative to H_2O), the density of the droplet (1.1 g/cc vs 1.0 g/cc) and molecular weight. Theoretical prediction accounts for these differences very well, and the experimental data is in good agreement with our model. Because diffusion coefficient of water is still higher in acetophenone than in decanol regardless of the isotope form, the rate of droplet shrinkage is faster in acetophenone as expected. The D_2O data in decanol matches the model better than for H_2O in decanol, because of the much lower rates of shrinkage of D_2O droplets, which made it more difficult to rapidly build up the local concentration of D_2O around the droplet.

C. Laguerre-Gaussian Beam vs. Gaussian Beam

If radiation absorption is indeed responsible for the droplet shrinkage in a vortex trap, then one would expect to also observe droplet shrinkage in a Gaussian beam. The latter has never been reported in the literature, however, because it has not been possible to trap an aqueous droplet in organic medium using a conventional Gaussian trap. We compensated for the trap-repelling effect of low-index particles by selecting for droplets that have been settled and attached onto a surface. To generate a surface that a water droplet would settle onto but would not wet, a thin-layer of PDMS is spun-coated and cured onto a #1 glass coverslip. PDMS is highly hydrophobic and thus an aqueous droplet would not spontaneously wet and flatten across the surface of PDMS. On top of the coverslip, the water-in-oil suspension is deposited and the Gaussian beam is focused from below the coverslip.

Figure 4 compares the behavior of H_2O droplet in acetophenone in an optical vortex trap with that on a surface and heated using a Gaussian beam under comparable laser powers. The normalized decay rate is faster in a vortex trap than on a surface. The important point to note here, however, is that Gaussian beam heating can generate similar shrinkage behavior. The potential mechanisms for the slower decay rate on a surface include (1) we no longer have a 3-dimensional spherical diffusional space for H_2O to diffuse outward and thus one would expect the diffusion rate to reduce, and (2) potentially the surface of the glass coverslip can act as a heat-sink and can conduct away some heat. The simulation shown for the on-surface droplet shrinkage was done by using the same spherically symmetric model described before, but used the diffusion coefficient as an adjustable parameter for comparison. With the reduced outward mass transfer, the rate of decay on surface is equivalent to that in the vortex trap, had the diffusion coefficient been reduced by 3.5 times.

CONCLUSIONS

Gaining a better understanding of the mechanism behind droplet shrinkage and re-growth allows one to tune this process. For example, to minimize heating of the droplet contents, an external medium with high thermal diffusivity and high viscosity (i.e. low mass diffusion coefficient) will allow rapid heat conduction away from the droplet while reducing the mass flux and loss of water from the surrounding organic phase. The organic phase also plays an important part in determining the rate and degree to which droplet shrinkage and re-expansion occurs. The behavior that underlies droplet re-growth is indicative of relaxation of a system from a supersaturated state to equilibrium. Because typically the droplet does not grow fully back to its original size prior to shrinkage, the mass flux leaving the droplet must be consumed elsewhere, most likely by other droplets in the suspension. As a result, isolation of the droplet in a confined volume (e.g. in a microfluidic chamber or within another droplet) would allow for much greater recovery of the lost water and thus greater levels of tunability. This mechanism also points to the ability to expand a droplet beyond its original size if the droplet is placed adjacent to another droplet undergoing shrinkage. Dynamic control over the concentrations of dissolved species, without inducing significant increase in temperature, provides a degree of control that was previously difficult to achieve in a macroscopic chemical

system. We believe the use of the phenomenon described here will aid in the study of chemical processes that are sensitive to changes in concentration, ranging from protein nucleation and crystallization to the effects of macromolecular crowding.

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Figure 1.

(a) Schematic of the optical setup. The 1064 nm output of the Nd:YAG laser was focused through a microfabricated glass hologram to form the Laguerre-Gaussian (LG) beam, after which the first order LG mode was selected and spatially filtered. This was then directed into the microscope to generate an optical vortex trap. Imaging was performed using bright-field illumination and a CCD camera. DC = Dichroic filter, TS = Telescope, BS = Beam splitter, WP = Waveplate, PH = Pinhole, and HG = Hologram. (b-f) A sequence of images that show the shrinkage and re-expansion of a droplet that contained $\sim 100 \mu\text{M}$ Alexa 488; inset at the upper-right corner of each panel shows the corresponding fluorescence image of the trapped droplet. The scale bar in (b) represents $3 \mu\text{m}$ and applies to panels (b) to (f).

Figure 2.

(a) Shrinkage of a H₂O droplet inside an optical vortex trap compared with the shrinkage of a D₂O droplet. The external phase was acetophenone. Arrow indicates when the laser was turned off. Initial droplet volumes: H₂O, 88 μm³; D₂O, 252 μm³. (b) Calculated temperatures for a H₂O droplet held in an optical vortex trap. Initially, absorption of laser power caused a sharp jump in droplet temperature. Owing to large thermal diffusivity, however, the rise in droplet temperature was only ~1 K. As time progressed, the droplet temperature decreased, because the larger surface-to-volume (S/V) ratio of the shrinking droplet led to more efficient thermal dissipation of heat from the droplet. The figure shows six traces, each depicting a different

initial droplet radius: 2.5 μm , 3.0 μm , 3.5 μm , 4.0 μm , 4.5 μm , and 5.0 μm . Although the initial rise in temperature is higher for a larger droplet due to the smaller S/V ratio, the normalized volumetric shrinkage rate is independent of the initial size of the droplet. (c) Modeled initial temperature increase inside the droplet at initial radii that ranged from 2.5–5.0 μm . The figure shows a trend line indicating that within this size range, the droplet temperature never spikes above 1.3 K.

Figure 3.

(a) Shrinkage and re-expansion of a H_2O droplet in a vortex trap in two different external phases: acetophenone and decanol. Decanol and acetophenone have similar thermal diffusivity, but the mass diffusion coefficient of water in decanol is only about 1/6 of that in acetophenone, thus resulting in slower rates of droplet shrinkage. Initial droplet volumes: H_2O in acetophenone, $88 \mu m^3$; H_2O in decanol, $49 \mu m^3$. (b) Shrinkage and re-expansion of a D_2O droplet in a vortex trap, surrounded by acetophenone (solid line) and decanol (dotted line). Initial droplet volumes: D_2O in acetophenone, $252 \mu m^3$; D_2O in decanol, $134 \mu m^3$.

Figure 4.

Shrinkage and re-expansion of a H₂O droplet held in a vortex trap compared with a surface-bound droplet that was heated with a Gaussian beam (optical tweezer). The external phase in both cases was acetophenone. Initial droplet volumes: H₂O in trap, 88 μm^3 ; H₂O on surface heated by Gaussian beam, 425 μm^3 .

Table I
Physical parameters of pure substances used in theoretical modeling.

	H ₂ O	D ₂ O	Acetophenone	Decanol	Unit
<i>M_w</i> , molecular weight	18	20	120	158	<i>g / mole</i>
<i>C_p</i> , heat capacity	4200	4200	1896 ²⁹	2325 ³⁰	<i>J / kg·K</i>
<i>ρ</i> , density	1.0	1.1	1.03	0.829	<i>g / cc</i>
<i>k</i> , thermal conductivity	0.6	0.6	0.175 ³¹	0.165 ³¹	<i>W / m·K</i>
<i>α_T</i> , thermal diffusivity	1.4×10^5	1.4×10^5	0.90×10^5	0.86×10^5	$\mu\text{m}^2 / \text{sec}$
Refractive index	$1.327 + 2.89 \times 10^{-6}i$, 21	$1.327 + 2.89 \times 10^{-6}i$, 21	1.537	1.437	
<i>μ</i> , viscosity	N/A	N/A	1.6	11.8 ³²	<i>centipoise</i>

The parameters are from CRC handbook or commercial sources unless otherwise indicated

Table II

Physical parameters of mixture or inter-phase properties used in theoretical modeling.

	B = Acetophenone	B = Decanol	Unit
D_{H_2O-B} , diffusion coefficient of H ₂ O in phase B [†]	2600	403	$\mu m^2 / sec$
D_{D_2O-B} , diffusion coefficient of D ₂ O in phase B [†]	2600	403	$\mu m^2 / sec$
C_∞ , solubility of H ₂ O (or D ₂ O) in Phase B at 293 K.	1.02 ³³	1.52 ³⁴	<i>mole / L</i>
ΔH_{mix} , heat of mixing of H ₂ O (or D ₂ O) in Phase B. [‡]	4200	8043	<i>J / mole H₂O</i>

[†] Computed using Wilke-Chang correlation for estimating mass diffusivity²⁸.[‡] Computed from thermodynamic data in³³ and³⁴.

Table III

Fitting parameters used in the calculation of droplet expansion.

	η	$V_{ext} (\times V_{droplet})$	Equiv. Drop. Radius in μm
Figure 2a			
H ₂ O/Acetophenone - Vortex	0.2	7×10^5	89
D ₂ O/Acetophenone - Vortex	0.2	7×10^5	89
Figure 3a			
H ₂ O/Acetophenone - Vortex	0.2	7×10^5	89
H ₂ O/Decanol - Vortex	0.6	7×10^5	89
Figure 3b			
D ₂ O/Acetophenone - Vortex	0.2	7×10^5	89
D ₂ O/Decanol - Vortex	0.35	1×10^5	46
Figure 4			
H ₂ O/Acetophenone - Vortex	0.2	7×10^5	89
H ₂ O/Acetophenone - Gaussian	0.2	7×10^5	89