

Microfluidics: The Effects of Surface Tension

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1 Abstract

The behavior of liquids at a microscopic scale is quite distinct from that for fluids at a macroscopic level. At a macroscopic scale, pressures well above or below atmospheric pressure and gravity dominate fluid dynamics, while surface tension and capillary forces are generally negligible. At a microscopic scale, with volumes in the microliter range, this behavior is reversed. The pressure range in microfluidic system is generally well below a tenth of an atmosphere, and gravitational effects are minimal due to the exceedingly small volumes employed. As volume decreases, the surface-to-volume ratio increases, hence it is not surprising that surface tension and capillary effect—closely related to surface tension—dominate the fluid mechanics of microdroplets. Controlling or overcoming these forces is a basic goal of microfluidic systems.

2 Microfluidics

The study of microfluidics began with the inkjet printer before rapidly expanding into a powerful tool in a wide variety of disciplines. The design and control of microfluidics is predominantly a physics and engineering game, but it is biology and chemistry that have amassed the greatest array of potential applications. Biological reactions tend to be especially difficult to control, but microfluidic systems offer a means of improving control and efficiency for even the most complicated biological assays [5].

Microfluidic does not imply small devices but rather small volumes of liquid in the devices. The first goal of microfluidics is to take advantage of the benefits of scaling down: better control, lower cost, faster results, and more. Scaling down the entire system is almost always preferable, but it plays no role in defining the field of microfluidics. Lasers, high voltages power supplies, pumps, and other sizable equipment is often necessary for control of the microfluidic system. Developing these active controls is a large part of current research in microfluidics. At the same time, passive microfluidic systems are also earning a lot of interest. If a task can be carried out by simply designing a series of channel in a chip and letting the capillary effect and other microfluidic effects work without direct control, then that task becomes a cheap, portable, and disposable package that can be used anywhere without a need for expensive lab equipment. In both cases, microfluidics provides a promising avenue for technological growth. This paper only scratches the surface of microfluidics, describing the fundamentals of surface tension and its resulting effects before briefly describing a few examples of microfluidic systems [2, 5].

3 Surface Tension

Before defining surface tension, it is critical to establish the notion of an interface. An ideal interface is a smooth surface delimiting two disjoint regions (say two fluids, and fluid and a gas, etc.). In reality the molecules or atoms of the two media do not form a smooth and well-defined interface, and though this has an impact on relative motion of the two media at the interface we can ignore this mixing for the discussion of surface tension [2].

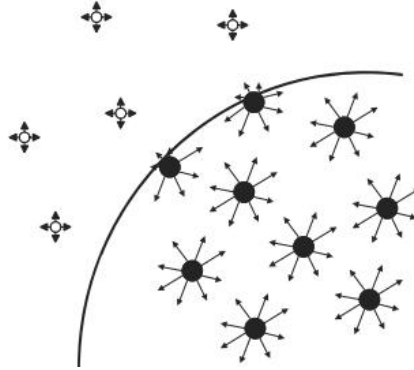


Figure 1: A simplified diagram of the origin of surface tension. Molecules of the liquid at a gas-liquid interface experience a net force inward, while the net force on bulk molecules is nearly zero [2].

Molecules or atoms in a bulk medium attract one another through van der Waals forces or dipole interactions for polar molecules (i.e. hydrogen bonding in water). At an interface, molecules experience an uneven force since the attractive force of the second medium will likely be different than that of the first. The difference in the cohesive energy pulling a molecule into and out from the bulk medium is represented by surface tension, and hence it takes units of J/m^2 , which can also be written as N/m , suggesting the behavior of surface tension as a force. If the difference in cohesive energy is very small, then the two liquid media will mix and are said to be miscible [2, 5].

Though surface tension across various interfaces (surface tension depends on both media at an interface: the surface tension of water surrounded by air is different than that of water surrounded by oil) is generally found by various measurement techniques, we can estimate the surface tension of a liquid at a liquid-gas interface in the following way: say the total cohesive energy of a molecule in the bulk medium is U , then the cohesive energy of a molecule at the interface is approximately $U/2$ since the low density of gas ensures a minimal cohesive energy from the outside. Let δ represent a characteristic molecular dimension such that δ^2 represents the approximate surface area of a molecule, then the surface tension γ is approximately

$$\gamma \approx \frac{U}{2\delta^2}. \quad (1)$$

This estimate helps describe the very high surface tension of mercury and low surface tensions of oils and organic compounds just by comparing the relative size of these particles. For a homogeneous interface, the energy stored by the surface tension is

$$E = \gamma S \quad (2)$$

where S is the total surface area. This simple formula is the exact reason why liquids form minimal surfaces in the absence of other forces: it minimizes energy stored in surface tension. Some representative values of surface tension are recorded in table 1 [2, 5].

To understand surface tension physically, consider the units of surface tension in the form N/m . This can be interpreted as a tangential force, as illustrated by the following simple example. Consider a rectangular frame

Table 1: Surface tension and thermal coefficient for liquids in contact with air at 20° C

Liquid	γ ($\frac{\text{mN}}{\text{m}}$)	α ($\frac{\text{mN}}{\text{m}\cdot\text{K}}$)
Acetone	25.2	-0.112
Benzene	28.9	-0.129
Ethanol	22.1	-0.0832
Glycerol	64.0	-0.060
Mercury	425.4	-0.205
Water	72.8	-0.1514

of width W . Rest a tube on the frame at a distance x from one end of the frame (the distance x is parallel to the length dimension of the frame, the length of the frame doesn't matter, so long as it is larger than x) and let a film of liquid connect the x by W rectangle formed by the frame and tube (see figure 2). Ignore gravity, then the surface tension of the film is the only force acting on the tube. Suppose we move the tube by a very small amount in the x direction, then the work done on the tube is

$$dW = F dx = 2\gamma W dx.$$

The factor of 2 is necessary to account for the surface tension on both sides of the film [2].

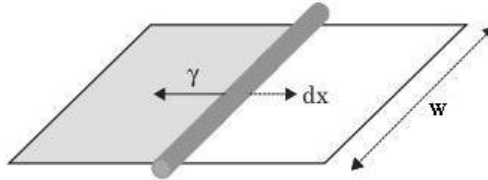


Figure 2: A tube placed on a rigid frame of width W with a liquid film occupying the left side. The film applies a force due to surface tension, so work is required to move the tube in the x direction [2].

4 Temperature and Surface Tension

In general, increasing the temperature of a liquid will decrease its surface tension, eventually reaching some critical temperature at which the surface tension goes to zero. The general formula for this relationship is empirical (from the observations of Katayama and later, Guggenheim), and is given by

$$\gamma = \gamma * \left(1 - \frac{T}{T_C}\right)^n, \quad (3)$$

where $\gamma*$ is a constant, T_C is the critical temperature, and n is an empirical factor ($n = 11/9$ yields good results for organic liquids). If the temperature variation is small, then we use the fact that $n \approx 1$ for the linear estimate

$$\gamma = \gamma * (1 + \alpha T). \quad (4)$$

It is generally easier to find a reference value (γ_0, T_0) and the critical temperature T_C and rewrite equation 4 as

$$\gamma = \gamma_0(1 + \beta(T - T_0)). \quad (5)$$

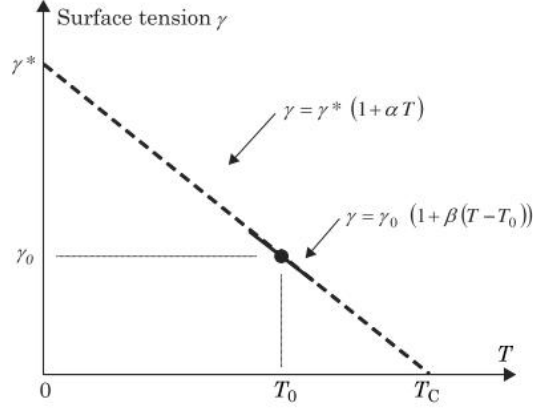


Figure 3: Standard relation between temperature and surface tension, showing equivalent equations 4 and 5 [2].

Since γ goes to zero for $T = T_C$, we see that

$$\beta = -\frac{1}{T_C - T_0} \quad (6)$$

and hence we can recover γ^* and α by comparing the offset and slope of equations 4 and 5. Solving for γ^* and α yields

$$\gamma^* = \gamma_0(1 - \beta T_0), \quad \alpha = \beta \frac{\gamma^*}{\gamma_0} \quad (7)$$

See table 1 for representative values for α at 20° C [2].

5 Capillary Effect

The capillary effect is a combination of several effects that all stem from surface tension. In this paper, we will discuss several basic contributions to the capillary effect: the contact angle, a balance of surface energy at interface intersections; the minimization of energy stored in the surface area; and the Young-Laplace equation, an equation describing a pressure imbalance caused by the curvature of an interface.

5.1 Young's Law

Many microfluidic systems work with droplets of liquid on a solid plane or enclosed between two planes, surrounded by a gas or an immiscible liquid. Thus there is a triple point where the interfaces between each pair of media meet. At this point we define the contact angle θ as the angle of the solid-liquid interface. A solid is hydrophilic if the contact angle of that solid with water satisfies $\theta < 90^\circ$, and hydrophobic if $\theta > 90^\circ$. At this triple point, there are three tangential forces that arise from the surface tensions of the three interfaces, and it is the balance of these three forces that decide the contact angle. From figure ... we can see that the necessary balance between forces due to surface tension for the system to be in equilibrium is

$$\gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL} \quad (8)$$

and hence

$$\theta = \arccos \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}. \quad (9)$$

When an outside force is applied to droplet in equilibrium, it will push the contact angle out of equilibrium and thus the droplet will resist the applied force [2, 5].

5.2 Minimization of Surface Energy

Minimization of surface energy is the most conceptually simple components of the capillary effect. Since the energy stored in surface tension is equal to the surface tension times surface area, any system will naturally move to minimize energy by minimizing surface area, subject to other forces like gravity. This explains why soap films on wire frames take the shape of a minimal surface (gravity pulls the films out of the minimal surface, but small soap films will approximate the minimal surface closely). This effect is also observable in vertical capillary tubes—justifying the name of the effect—in which a liquid rises from the base of the tube above the water level around the tube. The simple explanation of this effect is that the interface between the liquid and solid tube stores less energy than the interface between the tube and glass, hence water rises in the tube until the increase in gravitational potential energy balances with the decrease in surface energy. Note that some materials store more energy for an interface between liquid and solid, and hence we see the reverse behavior: the liquid is pushed out of the tube until the surface energy and potential due to pressure balance. Solids that have lower surface energy when in contact with a liquid are called wetting surfaces, the opposite is non-wetting [2, 5].

We can explicitly calculate the capillary action using Young’s Law and minimization of free energy due to energy of an interface and gravitational potential energy. First, define

$$I = \gamma_{SG} - \gamma_{SL}, \quad (10)$$

then if $I > 0$ the liquid in the capillary tube will rise in the capillary. If $I < 0$ the liquid will be pushed out. Using Young’s Law, equation 10 can be rewritten

$$I = \gamma \cos \theta \quad (11)$$

where γ is the surface tension at the liquid-gas interface. The surface tension for liquid-gas interfaces is easier to calculate than surface tensions involving solids and the contact angle can be measured through direct observation, hence equation 11 is preferable to equation 10.

As a liquid climbs up the walls of the tube, it gains gravitational potential energy but the system loses capillary energy. Let ρ be the density of the liquid, g be acceleration due to gravity, h be the height of the water above the outer water level, V be the volume of the liquid in the tube, S be the surface area of the water-tube interface above the outer water level, and R be the radius of the tube, then

$$\begin{aligned} E &= \frac{1}{2}\rho ghV - SI \\ &= \frac{1}{2}\rho gh(\pi R^2 h) - 2\pi RhI \\ &= \frac{1}{2}\rho g\pi R^2 h^2 - 2\pi Rh\gamma \cos \theta \end{aligned} \quad (12)$$

This does not take into account the contribution of the shape of the meniscus which can contribute an additional force, as we shall see in the following section. In this case, that force is small and can be ignored. The condition we must satisfy for this equation to be balanced is

$$\frac{\partial E}{\partial h} = 0. \quad (13)$$

Solving for h yields

$$h = \frac{2\gamma \cos \theta}{\rho g R}. \quad (14)$$

Equation 14 is called Jurin’s law, and shows that capillary rise is inversely proportional to the radius of the tube. Current microfluidic systems employ capillary tubes of approximately 100 μm in diameter. Suppose we use water ($\gamma \approx 72 \text{ mN/m}$) and a tube satisfying $\cos \theta = 1/2$, then equation 14 predicts a capillary rise of 14 cm, which is very large relative to the scale of microfluidic systems [2, 5].

To relate this example back to surface tension, consider the capillary force at equilibrium. Since the capillary force balances the force due to gravity at equilibrium, we have

$$F = \rho g \pi R^2 h. \quad (15)$$

Using equation 14 to replace h yields

$$F = 2\pi r \gamma \cos \theta. \quad (16)$$

From this form, we see that the capillary force is just length ($2\pi R$) times surface tension (with a $\cos \theta$ to account for the non-zero contact angle), similar to the wire frame and tube example in section 3 [2].

5.3 Young-Laplace Equation

The Young-Laplace equation relates a difference of pressure across an interface to the curvature of the interface. This force is yet another direct result of surface tension, since a greater curvature leads directly to a greater imbalance between the internal and external cohesive energy of surface molecules. A basic form of the Young-Laplace equation is

$$\Delta P = \gamma \nabla \cdot \hat{n} = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right). \quad (17)$$

where γ is still the surface tension, \hat{n} is the unit normal to the surface, and R_1, R_2 are the principle curvatures of some point on the surface. To understand this effect, consider two spherical droplets of water connect by a small channel. The principle curvatures of a sphere are both equal to $1/R$, where R is the radius of the sphere. According to the Young-Laplace equation, the difference in the ambient pressure and the pressure inside a droplet is larger for a smaller radius (greater curvature), hence the fluid in the smaller droplet will flow through the channel into the larger droplet [2, 5].

For a more mathematical example, consider a liquid plug between two non-parallel plates (see figure 4). If the planes consist of a wetting solid, then the contact angle (the angle formed by the solid and liquid) will be less than 90° , as in the figure. Consider the situation in 2D, then the Young-Laplace equation yields

$$P_0 - P_1 = \frac{\gamma}{R_1}, \quad P_0 - P_2 = \frac{\gamma}{R_2} \quad (18)$$

for the left and right interfaces respectively. Combining these equations yields

$$P_1 - P_2 = \gamma \left(\frac{1}{R_2} - \frac{1}{R_1} \right). \quad (19)$$

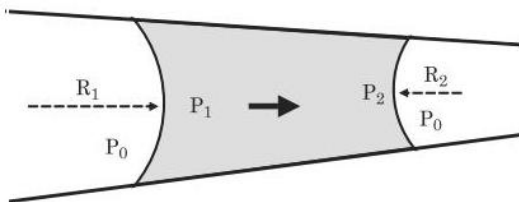


Figure 4: Cross section view of a liquid plug between two non-parallel planes [2].

Now all that remains is to compare R_1 and R_2 . From figure 5 we see that

$$d_2 = R_2 \sin \beta = R_2 \sin \left(\frac{\pi}{2} + \alpha - \theta \right) = R_2 \cos(\alpha - \theta) \quad (20)$$

and so

$$R_2 = \frac{d_2}{\cos(\alpha - \theta)}. \quad (21)$$

Flipping the orientation of the meniscus and applying the same reasoning yields

$$R_1 = \frac{d_1}{\cos(\alpha + \theta)}. \quad (22)$$

Since $d_2 < d_1$ and $\cos(\alpha - \theta) > \cos(\alpha + \theta)$, equations 21 and 22 show that $R_2 < R_1$ and hence $P_1 > P_2$ from equation 19. Thus, this system is not in equilibrium and the plug moves from high pressure to low pressure: the plug moves toward the narrower region, and will continue to do so until it reaches the point (unless air pressure builds up and stops it) or an open end of the wedge [2].

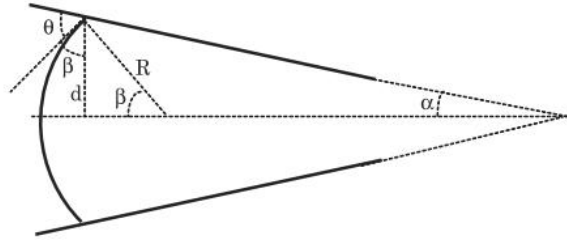


Figure 5: Curvature at the liquid-gas interface [2].

6 Marangoni Effect

The preceding sections described the behavior of homogeneous interfaces, so the next step is to consider the effects of an inhomogeneous interface. When there exists a gradient across an interface, the tangential force due to the surface tension pulls liquid along the surface from regions of low tension to regions of high tension. This motion is known as the Marangoni effect. Many influences can create a surface tension gradient on a droplet, including heat (recall section 4), surfactants, and concentrations. Since the Marangoni effect stems from surface tension, and surface tension is the dominant force on the microfluidic scale, making use of the Marangoni effect is among the most effective means of actively controlling microfluidic systems.

Unfortunately, the Marangoni effect is rarely described theoretically. Since the overall motion depends strongly on not only the surface tension gradient, but also the properties of the liquid (e.g. viscosity), the interfaces of the liquid, the viscosity and density of the surrounding environment, and other factors it is difficult to describe the effect with a single set of elegant formulas. In general, the Marangoni effect is studied experimentally [2].

Optical microfluidics is a rapidly growing method of active control of microfluidic systems making use of the Marangoni effect. Looking at the figure, we expect that focusing a laser on one side of a droplet will heat the droplet unevenly and induce motion along the surface of the droplet. This will push against the surrounding media and push the droplet towards the laser. However, most droplets in microfluidic systems carry surfactants, molecules with hydrophilic and hydrophobic ends that collect at interfaces and lower surface tension. In these cases, focusing a laser on the droplet can actually push the droplet away from the laser (or stop it from flowing down a certain channel in a microfluidic chip). Heat tends to scatter surfactants and can actually allow the surface tension to rise at the laser dot and thus push the droplet away. Using this method, droplets of volume 10 pL to 1 μ L can be pushed through a fluid at around 3 mm/s [4].

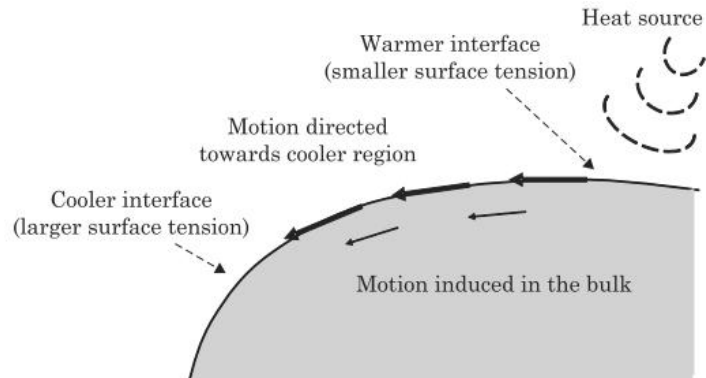


Figure 6: A simple illustration of the Marangoni effect: a heat source heats the surface on one side of a droplet, causing a thermal and hence surface tension gradient. The region of high surface tension pulls liquid along the surface of the droplet from the region of low surface tension [2].

7 Applications

7.1 Lab-on-a-Chip

The Lab-on-a-Chip (LOC) is the most common and well-developed result of the field of microfluidics. The idea of a LOC is to construct a small chip of microfluidic channels, valves, mixers, sorters, reaction chambers, etc. that can perform tasks that previously required a large collection of bench-top lab equipment. Microfluidic chips can be produced using well-known photo lithography and soft lithography techniques and are etched into relatively inexpensive substrates (Often PDMS, a silicone). They can be manufactured very precisely and quickly, an ideal replacement for bulky, expensive laboratory equipment. LOC technology is already being applied in labs, and has consistently produced excellent results. Some standard LOC applications are chemical control and analysis (gas detectors), medical testing (DNA testing or bacterial culturing), and occasional miscellaneous devices (implantable drug pumps) [5].

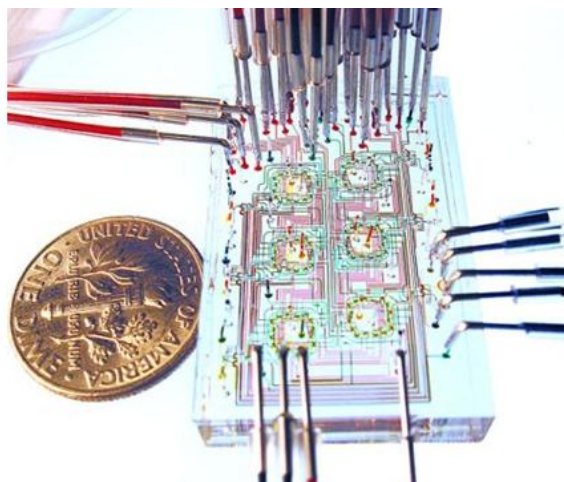


Figure 7: A LOC used to study the growth of microbial populations. The colors are dyes used to trace the channels. This chip can maintain six parallel reactions [6].

7.2 Lab-on-a-Robot

One way to take advantage of the portability of LOC technology is to build a LOC into a robot, lovingly named lab-on-a-robot (LOR). This example incorporates an electrochemical detection unit that can identify trace contaminants in the air. Using a LabVIEW based user interface, the research team sends a GPS location to the robot, which autonomously travels to the location using an onboard GPS system. Once on-site, a microelectromechanical system (MEMS) diffuses a gas sample into 50 μL of buffer solution. A small sample of the buffer solution is injected into a microfluidic chip that electrophoretically separates the components of the gas and sends it to a detector. The information from the detector is sent back to the computer running the control program where it can be analyzed. Now, the robot is ready to receive a new location, repeating the cycle until it runs out of power or testing reagents. This allows researchers to take and test air samples in potentially hazardous environments without risking the safety of their student assistants [1].

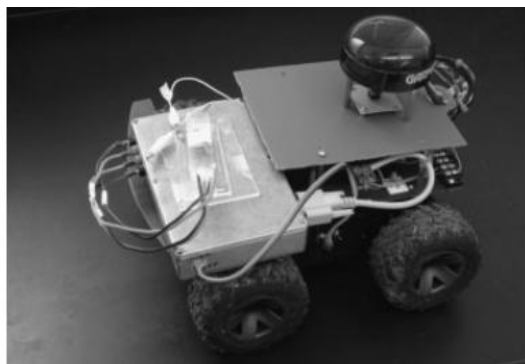


Figure 8: The lab-on-a-robot, able to navigate to prescribed locations, test a gas sample, and communicate wirelessly with a base computer [1].

7.3 Fast PCR

The polymerase chain reaction (PCR), a DNA amplification reaction, is one of the most common biological assays used in modern molecular biology. Standard PCR reactions are highly parallel and tend towards small reaction volumes (from about 20 to 200 μL) and hence it is a prime candidate for microfluidic techniques. However, the PCR reaction requires temperature cycling, ranging from about 55°C to 95°C. This is not a simple feat for standard microfluidic circuits, but can be accomplished by incorporating heaters into the substrate of the chip. This method yields the standard benefits of microfluidic circuits: small volumes (less cost), fast heating and cooling, and quicker overall reaction time. However, the limitations due to placement of heaters in the substrate is not flexible enough to be suitable for highly parallel reactions and cross-contamination can result from the direct contact between sample and heater. To address these difficulties, a new method has been introduced that dispenses of the need for microfluidic circuitry while still taking advantage of microfluidic properties [3].

A PCR reaction consists of nothing but temperature cycling, the reaction generally does not require any additional reagents to be mixed in and no samples will be taken until the PCR is complete. Using a few basic microfluidic properties and laser heating offers a solution that combines the desirable properties of microfluidic behavior and the possibility of highly parallel systems. Droplets of reagents can be suspended in a 20mm wide by 6mm deep mineral oil filled well via pipette in volumes of about 20 to 100 nL (PCR mixes are aqueous, hence they do not mix with the oil) and heated with a defocused infrared laser tuned to a vibrational state of water molecules. The tuned laser has little effect on the oil or plastic substrate containing the oil and droplets of PCR mix, and because it is defocused, it can heat an entire droplet uniformly. Furthermore, a silicon o-ring around the outside of the well forces a contact angle of 90° to keep the surface of the oil flat and avoid diffraction of the laser beam. The substrate is heated to the lowest temperature of the PCR cycle and the laser is used for higher

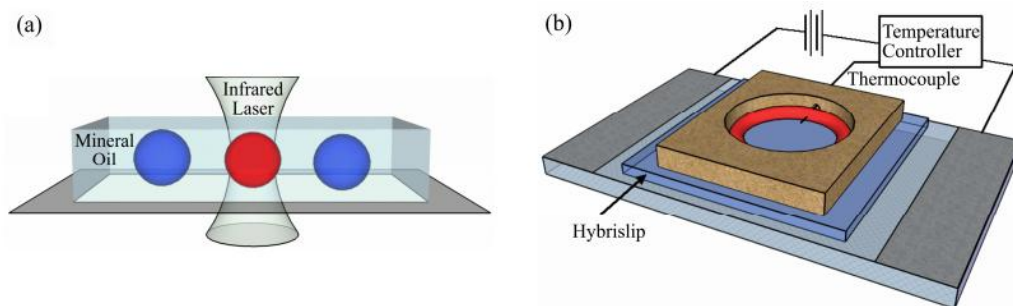


Figure 9: (a) Representation of the infrared laser heating a droplet immersed in mineral oil. (b) PCR chamber, 20mm wide and 6mm deep, with a silicon O-ring to keep the surface of the oil flat. A conductive glass slide underneath is held at a constant temperature and disposable Hybrislip serves as the floor of the chamber [3].

temperatures. Since the volume of the droplets is very small, heating (using the laser) and cooling (using the Peltier effect) are efficient. The temperature for each step in the cycle is maintained by adding a temperature sensitive dye to the reaction mix. To minimize contamination between runs, a disposable hybrislip is placed between the substrate and oil. To prevent droplet from sticking to the bottom of the well, the hybrislip is hydrophobic [3].

Using this laser heating method, a full 40 cycle PCR can be completed in just 370 seconds. Standard modern PCR machines, which generally use the Peltier effect to heat and cool blocks that can hold a fairly large number of samples (around 50 is standard), would take up to two hours to complete the same PCR. Due to precise tuning, the laser can be operated at approximately 30 mW, delivering little power beyond that necessary to heat the droplets. The Peltier effect is far from efficient, it is chosen for reliability (no moving parts) and ability to quickly produce or draw off heat rather than energy efficiency. Finally, the droplet and laser based system carries the standard added efficiency of microfluidic systems: smaller volumes will produce the same results. Considering the high cost of PCR reagents, minimizing the volume of samples is certainly a priority (as mentioned above, sample sizes are already down to 20 to 200 μL). Laser-based PCR systems are still in their infancy, but they provide a dramatic improvement on a very widely used process, and may very well be developed into a commercial bench-top system[3, 7].

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