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Plasmonic Marangoni forces

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Localized surface-tension-driven forces (microscale Marangoni effect) caused by a temperature inhomogeneity from the decay of optically excited surface plasmons into phonons have been engaged in the actuation of adsorbed and applied liquid on a thin metal film. Microfluidic operations of transport, separation, mixing, and sorting have been experimentally and theoretically demonstrated using this all-optical modulation scheme. [DOI: 10.2971/jeos.2006.06030]

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1 Introduction

Thin films have played an important role in microfluidics, where the management of micro- and nanoliter amounts of fluids support the development of fast, inexpensive and miniaturized processes, such as laboratories on a chip. Due to the tremendous potential of such studies for fluid manipulations at the microscale, several new works have been emerging, see Ref. [1]. Microfluidic systems can vary greatly with their architecture and flow actuation schemes. One classification of small volume systems is an open-surface configuration that allows immediate access to the fluids under study.

It is known that droplets are the results of a stretched (due to gravity force) mass of liquid, that undergoes strong surface tensions in order to reach the smallest surface area for a constant volume. This explains the spherical geometry adopted by the droplets. Moreover, the outside molecules of the droplet, that compose the interface with the surrounding, are subjected to an attraction force that is compensated by the resistance of the liquid to compression, and justify the minimization of the surface area. Furthemore, Marangoni [2] recognized that, when a droplet experiences a temperature gradient along its surface, it attempts to minimize its surface energy by moving in the direction of the gradient away from the higher temperature. Indeed, the surface energy S for a fluid may be defined as such,

$$S = \gamma - T \left(\frac{\partial \gamma}{\partial T} \right)_P , \tag{1}$$

where T is the temperature of the fluid studied, γ the surface tension and P the surrounding pressure. In our case, the pressure is kept constant as we work in atmosphere. Equation 1 shows that when a positive thermal gradient of magnitude ΔT is applied to the droplet, its surface energy decreases, and a surface tension gradient $\Delta\gamma$ is created. The relation between temperature and surface tension is only given by semi-empirical equations, however, it is common to say that the highest the T the lowest the γ. The γ can also be accessed by contact angle measurements.

Convective flows due to surface tension gradients have been utilized in microfluidic systems by employing various heat sources. Different approaches currently being investigated utilize resistive current sources [3] and references therein, light sources [4], and optical excitation of surface plasmons [5]–[8]. We introduce a new concept of surface plasmon (SP) excitation [9] to optically establish a temperature gradient at the bounded interface of a microdroplet [6]–[8]. Surface plasmons, the collective motion of conduction band electrons on metals, have rich spectral qualities that can be exploited for sensing, and exhibit quantum behavior that may be used to shape the thermal signature. We present in Section 2 experimental evidence of microdroplet Marangoni manipulations and offer comparison with a computational model, in Section 3, based on the Navier-Stokes equation. A conclusion is given in Section 4.

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2 PLASMONIC MICRODROPLETS ACTUATION

In order to investigate our concept of SP-based microfluidics, we devised an experimental setup that integrates a quartz prism-thin gold (Au) film assembly in the Kretschmann configuration and a scanning optical probing system, as illustrated in Figure 1a. A probe laser, of wavelength 635 nm and output power P=1 mW, and a corresponding position sensitive detector (PSD) are aligned in the z direction and navigated systematically in xy directions to scan a region of the Au film. For maximum resonance conditions, the Au film [$\epsilon(\omega)$] was optimized at 34 nm thick for the 514 nm excitation laser line of an Ar^+ ion laser beam (output power P=50 mW). A mechanical chopper intensity-modulated the excitation beam at a frequency of 100 Hz for the objective of generating a satisfactory signal-to-noise ratio, and provided a reference signal for a lock-in amplifier, which monitored the output of the PSD. The SP dispersion relation for quartz-Au-air formulated an incidence angle θ_{sp} of 52° for resonance excitation. The prism and probe assemblies were each supported on precision x-y-z stages to permit independent motion, allowing the position of the heat source, i.e. the SP excitation region, with regard to the droplet, without modifying the resonance conditions, see Figure 1b, and allowing the study of the onset of Marangoni actuation.

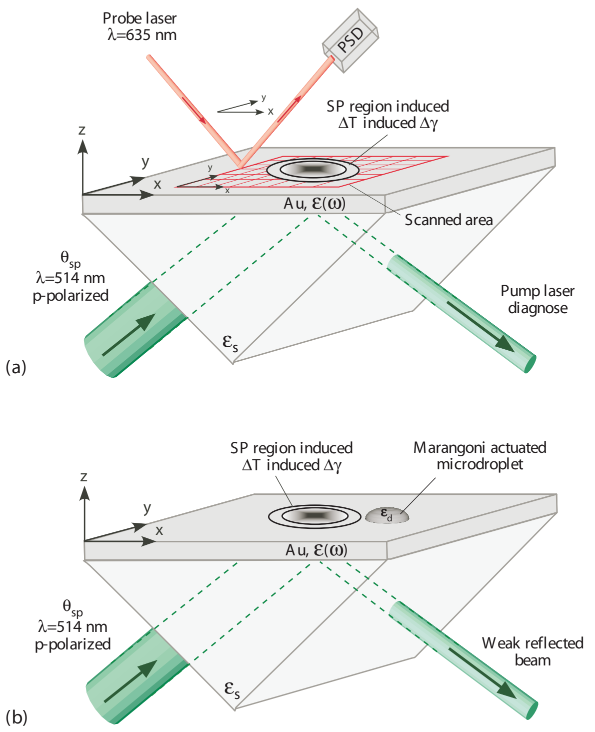

FIG. 1 Experimental schemes based on the Kretschmann configuration. In (a), an additional probe beam associated with a position sensitive detector (PSD) scans the excitation region to highlight the existence of the plasmonic thermal gradient. The PSD signal is collected via a lock-in amplifier locked on the modulation frequency of the pump beam. In (b), a microdroplet is deposited in the vicinity of the thermal gradient, creating a surface tension gradient at the microdroplet interface, that will then undergo Marangoni forces.

Prior to introducing the fluids in our setup, we investigated the plasmonic thermal gradient ΔT installed in the Au film to justify the use of the surface plasmon decay as a thermal source. By measuring the deflection of the probe beam linked to a PSD above the SP excitation region, as depicted in Figure 1a, plasmonic thermal gradient are observed, as shown in Figure 2, and bring to light the existence of a thermal gradient, even for low excitation laser powers. A larger deflection is measured at the edges of the excitation region, that may be referable to the thermal expansion of the thin film. In fact, the variations of the film expansion are expected to be more pronounced at the edges of the excitation region where the thermal gradient is created. This latter belongs to the microscale realm as it is linked to the decay length of the SP, that depends strongly on the material used and the working wavelength. As an example, tenths of micrometers can be achieved in the visible range for gold thin films. These considerations allow us to confirm the presence of the plasmonic thermal gradient necessary for Marangoni manipulation at the microscale.

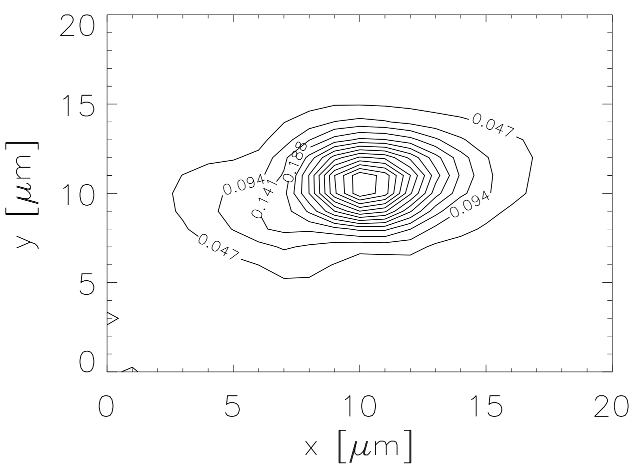

FIG. 2 A typical scan of the surface plasmons excitation region of a 34 nm gold film. The contours clearly demonstrate the formation of a temperature gradient emanating from the center of the excitation region. The profile was obtained by measuring the deflection of the probe beam, locked on the modulation frequency of the Ar^+ excitation laser beam. See Figure 1a.

After confirming the existence of the plasmonic thermal gradient, droplets of silicone oil (SO) and glycerol (Gl), with index of refraction n_i, surface tension γ_i, viscosity ν_i, $i = 1, 2, ...$, were applied onto the Au film to be linked to the plasmonic thermal gradient of magnitude ΔT. The range in size of the droplets is recapitulated in Table 1.

-	Thickness (μm)	Length (μm)	Width (μm)
Minimum	20	30	30
Maximum	50	250	150

TABLE 1 Range in size of the deposited microdroplets

By controlling the location of the SP excitation region, we were able to manipulate the microdroplets, as demonstrated in Figure 3 and Figure 4 for SO and Gl droplets respectively. In both figures, the scattered light from SP excitation region (delimited bright spot) allows us to localize the plasmonic thermal gradient ΔT with respect to the droplets. Due to surface tension and viscosity, energy requirements for affecting SO is less than for Gl, allowing the discrimination of fluid types by tuning laser intensity as reported in Refs. [7, 8] (data not shown). An optimized ΔT is thus scanned toward the droplets to install the Marangoni-based convective flow inside the droplets inducing motions of the fluids as illustrated in Figure 3 and Figure 4. In the case of SO in Figure 3, the actions of splitting [Figure 3b] and transport [Figure 3c] are achieved, where the two parts of the deposited droplet (D_1 and D_2) are separated by more than 200 μm, with a speed of the droplet around 100 μm/s, as previously reported [8].

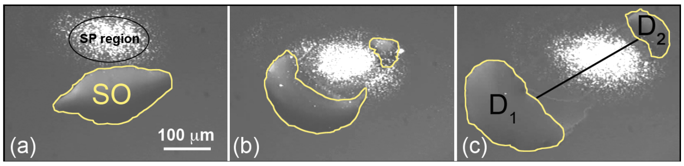

FIG. 3 Silicone oil droplet division and transport. By precisely locating the SP excitation region (marked with the black oval) near the microdroplet (yellow marked regions), the liquid is divided into two and one sub-microdroplet (D_2) is driven away from the stationary part (D_1). The droplet used is 240 μm $\times$ 90 μm with a contact angle θ_c of 10°.

In the case of Gl in Figure 4, the mechanism of mixing is also performed [Figure 4c$_1$–c$_3$], together with the splitting [Figure 4a$_1$–a$_3$] and transport [Figure 4b$_1$–b$_3$] processes. Indeed, one droplet is transported and approached to a motionless second one, see Figure 4c$_1$, until they coalesce to form only one droplet in Figure 4c$_3$.

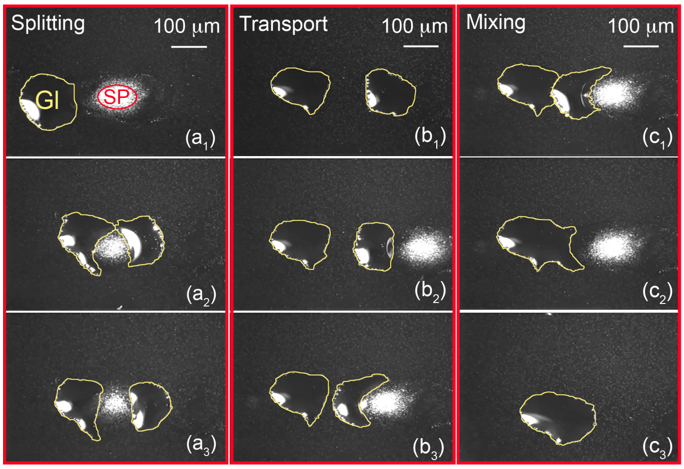

FIG. 4 Division, transport and merge of a Glycerol droplet. The plasmonic gradient is scanned independently over the Au thin film without modifying the resonance conditions, creating Marangoni forces in different zones of the microdroplet. Depending on the position of the thermal gradient, we carried out droplet division (a_1-a_3), transport (b_1-b_3), and merging (c_1-c_3). The used droplet is 120 μm $\times$ 110 μm with a contact angle θ_c of 50°.

Also noteworthy is that these various mechanisms are feasible if the ΔT is extended enough with respect to the droplets, rendering this method really suitable for micro- and nanoscale objects. Indeed if the droplet is much larger than the ΔT region then no flow is observable, the same if the ΔT is placed just underneath the fluids. Moreover, a measurement of the thermal gradient threshold showed that the onset of droplet actuation takes place when the ΔT is at 30 μm away from the droplet.

This method permits fluid manipulations by tailoring solely the threshold of the ΔT. Indeed, this may be adapted to one specie that can be moved while the other present ones remain stationary. However, a number of parameters of the optical excitation may be altered, in the point of view of the incident laser beam, by different incident polarization, wavelength and/or angle. Moreover, these modifications may come from the thin metallic film with distinct thicknesses/roughness and/or materials, from the material (different index of refraction) of the substrate supporting the coupling to SP, or from the index of refraction of the surrounding. Any variations of one of these parameters would allow the tuning of the thermal gradient to be adapted to each specie under consideration for Marangoni actuation. Nevertheless, although we have numerous degrees of freedom that may permit a great number of actions, the optimization of each remains a complex task that play an important role for the efficiency of the coupling. This latter is accessible through reflected spectrum measurement, as in SP resonance technique, introducing this microfluidic process in the field of sensing.

3 COMPUTATIONAL RESULTS

In order to ensure that the observed effect is directly linked to Marangoni convective flow, we studied the internal flow of a SO droplet of cross-section 220 μm $\times$ 220 μm, thickness 20 μm and contact angle, θ_c, of 10 degrees, numerically. As a first approximation, the shape of the droplet is assumed to be unchanged and the flow of an incompressible viscous fluid inside the section of the sphere is considered. Within the body of the droplet, the time independent Navier Stokes equation, convective heat transfer and the continuity equation were considered. These equations will be closed together with appropriate boundary conditions as follows.

On the surface of the gold film, the temperature was assumed to vary linearly with x with a gradient of 10 degrees per millimeter and all velocity components were set to zero. The interface between the droplet and the air was assumed to be adiabatic and the velocity component normal to it was set to zero. Otherwise, we assumed that the viscous forces acting from the liquid side balanced the effect of variations of the surface tension caused by temperature differences. As the position of the free surface is fixed, this set of conditions results in a closed and well-posed set of equations that can be solved numerically [10].

The complete set of nonlinear equations was discretized using second order elements in a finite element methodology, linearized and solved iteratively until convergence was obtained. It was found beneficial to solve first the conduction equation once with the velocity field kept constant and then solve the hydrodynamic equation once with the temperature field kept constant before the normal iterative procedure was applied. Exact equations and more details about the procedure can be found in [8]. Although the nonlinear terms were included in the Navier Stokes equation, numerical experiments indicate that they do not influence the results much and can be neglected. This is not a surprising observation but an important one if approximative analytical solutions are sought.

The computational numerical results for SO are presented in Figure 5.

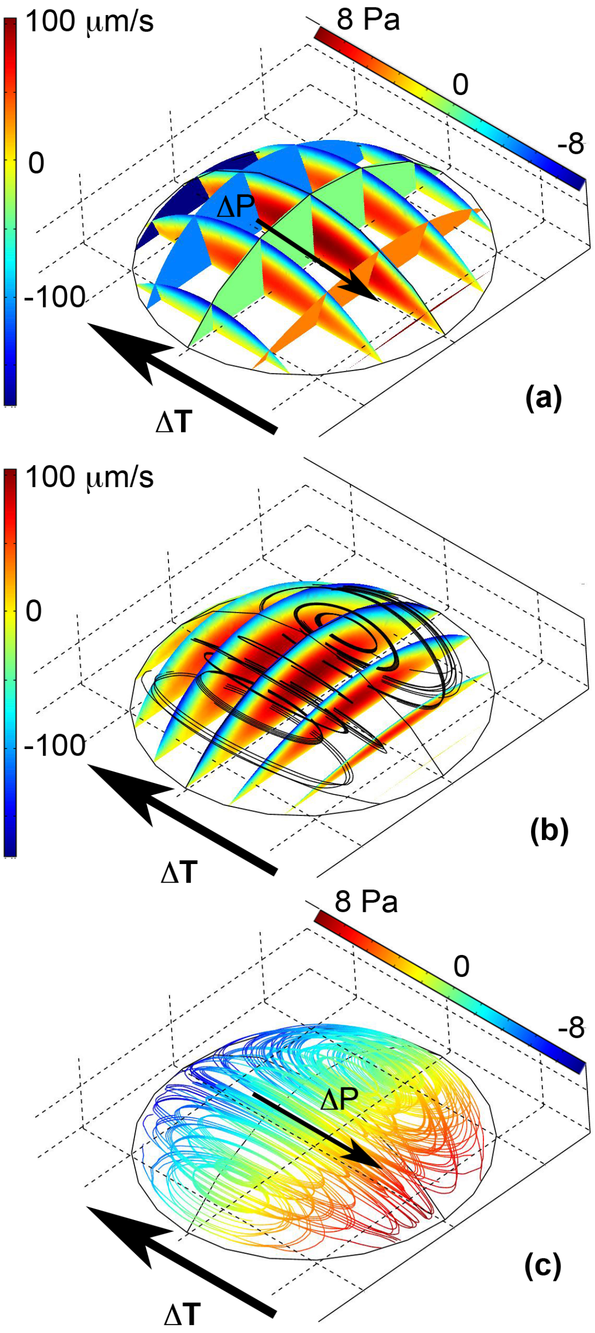

FIG. 5 Internal flow of a silicone oil droplet taken to be 220 μm × 220 μm. (a) Velocity component in the direction of the thermal gradient ΔT together with the pressure gradient sets in the opposite direction. A maximum speed of the droplet is found to be 100 μm/s. (b) and (c) illustrate the streamlines inside the droplet, related to the thermal gradient for (b) and to the pressure gradient for (c), linked to the internal flow of the microdroplet leading to its actuation.

The model of the internal flow inside a droplet predicts a maximum droplet flow velocity of 100 μm/s that is in a good agreement with our experimental observations. It is clearly shown that due to the positive thermal gradient ΔT, the droplet is disturbed and the flow field is set up. In the numerical simulations, due to the fixed shape of the droplet, this flow results in a pressure variation, ΔP, in the opposite direction. This would change the shape of the droplet and role it in the inverse direction of the temperature gradient, as observed experimentally. To conclude, this investigation demonstrates the Marangoni-based process experimentally observed, and justifies the use of SP as an energy source for convective flows.

4 CONCLUSION

We have uniquely applied the nonradiative decay of surface plasmons as the thermal vehicle for Marangoni-based fluid actuation. Fundamental studies in surface tension and interface phenomena can be explored with the microfluidic operations offered by this technique. Furthermore, the application of surface plasmons opens up possibilities in simultaneous fluid manipulation and sensing, currently under investigation [11]. For example, the numerous changes, monitored via the optical coupling efficiency, cited in Section 2, may direct to chemical reactions at the micro and nano scale as the mixing of several droplets of different chemical compositions is rendered achievable. We anticipate that future studies of surface plasmon assisted Marangoni forces in thin films will encourage plasmonic applications in the fields of micro and nanofluidics, opto-fluidics, and biological and chemical sensing.

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