ABSTRACT

The use of microscopic discrete fluid volumes (i.e., droplets) as microreactors for digital microfluidic applications often requires mixing enhancement and control within droplets. In this work, we consider a translating spherical liquid droplet to which we impose a time periodic rigid-body rotation which we model using the superposition of a Hill vortex and an unsteady rigid body rotation. This perturbation in the form of a rotation not only creates a three-dimensional chaotic mixing region, which operates through the stretching and folding of material lines, but also offers the possibility of controlling both the size and the location of the mixing. Such a control is achieved by judiciously adjusting the three parameters that characterize the rotation, i.e., the rotation amplitude, frequency and orientation of the rotation. As the size of the mixing region is increased, complete mixing within the drop is obtained.

INTRODUCTION

Although most microfluidics have been using fluid streams as the main means to carry fluids, devices based on individual droplets have been proposed as well. In the latter, also called “digital microfluidic” systems, “discrete” fluid volumes (droplets) rather than continuous streams are used, with the potential to utilize individual droplets as microreactors [1]. Whether fluids are encapsulated within droplets or flow along channels, reactions can occur efficiently only in presence of rapid mixing. Such mixing conditions are not easy to fulfill due to the low Reynolds number of the flow involved, which prevents turbulence from taking place. Stirring, in addition to molecular diffusion, is needed to stretch and fold fluid elements, thus significantly increasing interfacial areas. Whereas some strategies are based on complex channel geometry for flows in microchannels, active methods (via external forcing) (see, e.g., [2,3,4,5,6]) have also resulted in efficient mixing, especially at very low Reynolds numbers [7]. The combination of both geometry alteration and forcing has been explored as well [7,8,9,10,11]. Chaotic advection inside a liquid droplet subjected to a forcing
has been studied extensively [12][13][14][15][16][17][18] and obtained experimentally by means of oscillatory flows [19][20]. In this paper as in [21], we concentrate on controlling both the size and the location of the mixing. Indeed, we are interested in the ability to control the quantity of fluid mixed, from almost zero mixing to complete mixing, as well as in the localization of the mixing. On the one hand, researchers have mostly concentrated so far on complete mixing as it is often desired for reactions to occur uniformly since variations in the mixing could result in unacceptable variability in the properties and performance of the end-product. On the other hand, incomplete and localized mixing - when well controlled - could be useful for the synthesis of inhomogeneous particles (see, e.g., Janus particles) made of two (or more) components whose properties differ. For instance, such particles could have a part of their surface hydrophobic and some other parts hydrophilic. Such a variation within the same particle could result in superior particle properties useful in applications such as nanotechnology (self-assembly), biomedicine and advanced sensors.

In this article, we extend the work of [21] that focuses on unsteady - yet periodic - forcing on a translating droplet and its influence on the chaotic regions within the droplet. The existence of chaotic behavior in three-dimensional bounded steady flows has been shown (e.g. [12][13][22][23]). Our work is distinct from the latter contributions through the addition of unsteadiness, which is crucial to control the chaotic mixing behavior through resonance effects [24][25][18]. The physical system under consideration in this work is described in the first section, and numerical results are exposed in the fourth section. We study the chaotic mixing zone by monitoring its location and its size. Specifically, the creation and control of the chaotic mixing regions’ location and size are studied qualitatively via Liouvillian sections. A quantification of the size as a function of the various parameters involved is also performed, thus leading to mixing optimization in parameter space. From this quantification of the size, an optimization of the quantity of internal mixing is performed.

**PHYSICAL SYSTEM**

Let us assume a Newtonian liquid droplet of spherical shape suspended in an incompressible Newtonian fluid whose motion consists of a translation and a slow rigid body rotation (see [13]). As in the previous reference, we assume that the interfacial tension is sufficiently large for the drop to remain spherical through its motion and that the Reynolds number is very small compared to 1. Thus, a reasonable approximation is to consider that both the internal and external flows are Stokes flows. The boundary conditions at the droplet surface can be derived from the continuity of velocity and tangential stress conditions. The resulting internal flow is a superimposition of a steady base flow (non-mixing flow) and an unsteady rigid-body rotation. Consider a Cartesian coordinate system translating with the center-of-mass velocity of the droplet with the orientation of the axes such that the unit vector $\mathbf{e}_1$ points in the direction of the translation and the unit vector $\mathbf{e}_2$ lies in the $\mathbf{e}_3 = \mathbf{e}_1 \times \mathbf{e}_2$ plane. We then obtain the following unsteady internal flow:

\[
\begin{align*}
    u &= \dot{x} = z \varepsilon a_\omega(t) \sin \beta y, \\
    v &= \dot{y} = y + \varepsilon a_\omega(t) (\sin \beta x - \cos \beta z), \\
    w &= \dot{z} = 1 - 2 \dot{x}^2 - 2 \dot{y}^2 - \dot{z}^2 + \varepsilon a_\omega(t) \cos \beta y,
\end{align*}
\]

In Eqs. (1-3), all the lengths and velocities were made dimensionless by using the droplet radius and the magnitude of the translational velocity as the length and velocity scales, respectively. The rotation is characterized by a maximum amplitude $\varepsilon \ll 1$, a fixed orientation vector with angle $\beta$ and a form $a_\omega(t)$ given by

\[
a_\omega(t) = \frac{1}{2} (1 + \cos \omega t),
\]

Note that the equations above, together with their derivation, are identical to those of [13], except that the vorticity vector is now time dependent. The time dependency is introduced either via the external boundary conditions or through a time dependent body force in the momentum equation.

In practice, this could be realized for instance by creating a time-dependent swirl motion in the external flow or by applying an electric field that exerts a torque on the drop (see, e.g., work on traveling wave dielectrophoresis [26] or on electrorotation [27]). A possible design based on the latter phenomenon is proposed in Fig. 1. Electrorotation stands for the spinning of an electrically polarized particle (or droplet in our case) while the latter is subjected to a “rotating” electric field, that is an ac electric field generated by voltages which are out of phase of one another. The proposed device would thus consist of a square column/channel with electrodes embedded within its four walls creating a rotating electric field due to the phase difference between the voltages of adjacent electrodes. It is known that such a four-pole electrode setting would generate a controlled spinning motion, or rigid body rotation, of a drop trapped in the middle of the channel. The drop steady translating motion, on another hand, could simply be produced by a constant pressure gradient along the channel or simply buoyancy in the case of a vertical column. In order to vary the orientation of the axis of rotation compared to the direction of translation, we propose a series of electrodes lying within inclined planes along the length of the channel (see Fig. 1). The angle of the inclined planes with the vertical could be adjusted. The periodicity in the angular velocity is then obtained by imposing a phase difference to the voltages applied to the electrodes of adjacent planes, thus generating
acceleration and deceleration phases in the imposed rigid body rotation.

NON-MIXING CASE

The non-mixing (unperturbed) case or base flow, i.e., \( \varepsilon = 0 \), is characterized by streamlines that are joint lines of constant streamfunction \( \psi \) and azimuthal angle \( \phi \), denoted by \( \Gamma_{\psi,\phi} \).

\[
\psi = \frac{1}{2} \left( x^2 + y^2 \right) \left( 1 - x^2 - y^2 - z^2 \right), \quad \phi = \arctan \left( \frac{y}{x} \right), \quad (5)
\]

where \( \psi \in [0, 1/8] \) and \( \phi \in [0, 2\pi] \). Besides the heteroclinic orbits connecting the two hyperbolic fixed points located at the poles of the sphere, all other streamlines are closed curves that converge toward a circle of degenerate elliptic fixed point \( (x^2 + y^2 = 1/2, z = 0) \) as \( \psi \) is increased toward the value 1/8. The frequency of motion on the streamline \( \Gamma_{\psi,\phi} \) is independent of \( \phi \) and given by

\[
\frac{2\pi}{\Omega(\psi)} = \frac{2\sqrt{2}}{\sqrt{1 + \gamma}} K \left( \sqrt{\frac{2\gamma}{1 + \gamma}} \right), \quad (6)
\]

with \( \gamma(\psi) = \sqrt{1 - 8\psi} \) and \( K \) is the complete elliptic function of the first kind. The trajectories of the system (1-3) are periodic orbits (with period \( 2\pi/\Omega(\psi) \)) which come in families (labeled as \( \psi \)). No chaotic mixing occurs since there is no exponential divergence in the bulk of the droplet. However, due to the difference in frequency a very small mixing occurs in \( \psi \) (but not in \( \phi \) due to the degeneracy).

MIXING CASE

In this work we follow the approach of [21] that enables the generation of a three-dimensional chaotic mixing region, for which we are able to control both the location and the size. The method consists in bringing a specific family of the unperturbed tori \( \{ \Gamma_{\psi_0} \} \) (composed by a family of periodic orbits along the azimuthal angle) into resonance with the periodic perturbation \( a_0(t) \) by selecting the frequency \( \omega \) so that it satisfies the resonance condition:

\[
n\Omega(\psi_n) - \omega = 0, \quad \text{for} \quad n \in \mathbb{N}. \quad (7)
\]

The control is realized by adjusting the three parameters that characterize the periodic rigid body rotation, specifically its the maximum amplitude \( \varepsilon \), its frequency \( \omega \) and the orientation of the axis of rotation \( \beta \) (see Eqs. [1-3]). The amplitude satisfies \( 0 \leq \varepsilon << 1 \), where the lower and upper limits correspond to the absence of mixing and complete mixing, respectively.
NUMERICAL RESULTS

The numerical results presented below have been obtained by using a standard explicit fourth order Runge-Kutta scheme [29].

Controlling the location of the chaotic mixing region

Figures 3, 4 display the Liouvillian sections of the mixing system, which consist of two-dimensional projections of time-periodic three-dimensional flows by a combination of a stroboscopic map and a plane section (here, the y = 0 plane). In other words, the points on the Liouvillian sections are the intersections of the trajectories with the plane y = 0 at every period 2π/ω.

The perturbation $a_0(t)$ generates two non-negligible three-dimensional chaotic mixing regions (see Fig. 3): one around the pole-to-pole axis and near the droplet surface labeled $CMR_{n>1}$. In Fig. 3, we clearly see that the location of $CMR_1$ varies with the value of ω according to Eq. (7). It is important to note that $CMR_{n>1}$ stay anchored around the pole-to-pole axis and to the surface due to the flat part of $Ω(ψ)$ close to $ψ = 0$. This is due to the flat part of $Ω(ψ)$ (see Fig. 2).

For small values of ω, all resonances are located near the pole-to-pole heteroclinic connections (at $ψ = 0$, near the z axis and near the surface of the droplet, see Fig. 3). For larger ω values, $CMR_1$ separates from the chaotic mixing region close to the pole-to-pole axis and penetrates deeper into the droplet. In the interval $0 < ω < √2$, $CMR_1$ is the largest chaotic region, followed by $CMR_{n>1}$. As ω is increased further, $CMR_1$ moves toward the location of the elliptic fixed point of the unperturbed system by following the location of the resonant tori with the frequency ω.

Controlling and optimizing the size of the chaotic mixing region

In this section, we quantify the size of the main chaotic mixing region, i.e., $CMR_1$ as the three parameters ε, ω and β vary. This quantification is performed by computing the maximum variation $∆ψ$ of the stream function $ψ$ for one trajectory inside the $CMR_1$. Whereas the frequency ω of the rigid body rotation is mostly responsible for the location of $CMR_1$ (while $CMR_{n>1}$ is always anchored around the heteroclinic orbits), it is the amplitude ε and the orientation β that mostly determine the size of the $CMR_1$. Figure 4 shows qualitatively the size of the chaotic mixing regions created by the $n = 1$ and, $n > 1$ resonances, i.e., $CMR_1$ and $CMR_{n>1}$. In this figure, we see that the size of both the $CMR_1$ and $CMR_{n>1}$ increases with the amplitude of the perturbation. It is also interesting to note that around $ε = ε_{max} ≈ 0.20$, the $CMR_1$ and $CMR_{n>1}$ join together to cover the entire droplet volume. At that point, complete chaotic mixing is obtained. The size of $CMR_1$ as a function of the frequency $ω$ is depicted in Fig. 6 (lower panel). From this figure it is clear that for each value of $ε$ the size reaches a maximum for a certain value $ω_{max}$ of the forcing frequency.

The effects of the parameter β on the size of $CMR_1$ present two distinguishable behaviors one where the size is weakly dependent and another where the size is strongly dependent. Such behaviors are easily observed on the lower panel of Fig. 6 where the size of the $CMR_1$ as a function of β is displayed. On one hand, when β is well inside the two limit values, 0 and $π/2$, the size is practically constant. On the other hand, when β gets closer to the limits, the size decreases significantly. Such observation are qualitatively confirmed in the Liouvillian section in Fig. 5. In the first two panels, we see a very small change in size.
Figure 5. LIOUVILLIAN SECTIONS FOR THE FREQUENCY $\omega = 1.25$, THE AMPLITUDE $\epsilon = 0.05$ AND THE ORIENTATIONS $\alpha = \pi/8, \pi/4, 29\pi/80, 7\pi/16$ (a-d). THE (RED) LINE INSIDE THE CMR$_1$ IS THE TORUS $\Gamma_{\omega=1}(\alpha)$.

However, in the last two panels the size decreases drastically. Having such a relation between the size of the CMR$_1$ and the orientation of the rotation $\beta$ can be handy in practice to control the size of mixing. In some applications, where the experimenters are faced with the dilemma of precisely controlling the size of mixing with an imprecise fluctuation of $\beta$, setting $\beta$ well inside the limit value and controlling the size through the parameter $\epsilon$ could be the solution. Then, more restrictive, applications where increasing the amplitude of rotation may not be possible (e.g., biomedical ones where biological particles need to be handled with care), fixing $\epsilon$ and tuning the size of the mixing by varying $\beta$ around the limit value $\beta = \pi/2$ could be the solution. One should notice that at the critical orientation $\beta = \pi/2$ no three-dimensional chaotic mixing occurs since $\psi$ is conserved.

CONCLUSIONS

In this work we have shown that chaotic mixing within a translating droplet can be obtained by adding a perturbation in the form of an oscillatory rigid body rotation. The frequency of the latter was selected in order to create resonances with the natural frequencies of the system, namely the frequencies of the various tori embedded within the droplet. A particularly interesting feature of the perturbed system lies in the fact that both the size and the location of the mixing region can be varied. This was achieved by adjusting the control parameters of the perturbation, specifically the frequency, amplitude and orientation of the rigid body rotation. While the frequency is used to target a particular location, both the amplitude and the orientation influence the size. The latter property introduces additional flexibility in the system, particularly for applications which allow for the variation of one of these two parameters only.

Figure 6. UPPER PANEL: NORMALIZED SIZE $\Delta \psi$ VS. FREQUENCY $\omega$ FOR AMPLITUDES $\epsilon = 0.01, 0.05, 0.10, 0.20$ (a-d) WITH ORIENTATION $\beta = \pi/4$; MIDDLE PANEL: NORMALIZED SIZE $\Delta \psi$ VS. AMPLITUDE $\epsilon$ FOR FREQUENCIES $\omega = 0.55, 0.93, 1.28, 1.41$ (a-d) WITH THE ORIENTATION $\beta = \pi/4$; LOWER PANEL: NORMALIZED SIZE $\Delta \psi$ VS. ORIENTATION $\beta$ FOR AMPLITUDES $\epsilon = 0.01, 0.05, 0.10, 0.20$ (a-d) WITH FREQUENCY $\omega = 1.25$. TOP AND MIDDLE PANELS REPRINTED FROM [21] WITH PERMISSION FROM THE AMERICAN PHYSICAL SOCIETY.

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