Diffusion enhancement in a levitated droplet by a periodic deformation

Yuki Koyano, Hiroyuki Kitahata, Koji Hasegawa, Satoshi Matsumoto, Katsuhiro Nishinari, Tadashi Watanabe, Akiko Kaneko, and Yutaka Abe

1Department of Physics, Graduate School of Science, Tohoku University, Sendai, Miyagi 980-8578, Japan
2Department of Physics, Graduate School of Science, Chiba University, Chiba 263-8522, Japan
3Faculty of Engineering, Kogakuin University, Shinjuku-ku, Tokyo 163-8677, Japan
4Human Space Flight Technology Directorate, Japan Space Exploration Agency, Tsukuba, Ibaraki 305-8505, Japan
5Research Center for Advanced Science and Technology, The University of Tokyo, Meguro-ku, Tokyo 153-8904, Japan
6Research Institute of Nuclear Engineering, University of Fukui, Tsuruga, Fukui 914-0055, Japan
7Graduate School of System and Information Engineering, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

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The two mixing processes of a fluid, the agitation and diffusion, are often considered separately since they are dominant in different spatial scales. However, the recent experimental results indicate that the diffusion is enhanced by a time-reversible flow induced inside a levitated droplet [Watanabe et al. Sci. Rep. 8, 10221 (2018)]. In the present paper, we focus on the diffusion process coupled with the oscillatory flow, which cannot convect the solutes in time average. We theoretically derived that the diffusion process can be enhanced by the oscillatory flow, and the results are confirmed by numerical calculation of the over-damped Langevin equation with an oscillating flow.

I. INTRODUCTION

A levitated-droplet system has been intensively developed to realize contactless manipulation. For instance, it is advantageous for the measurement of physical or chemical quantities with avoiding the pollution and the significant disturbance from chamber walls [1]. Thus levitated-droplet systems are studied not only under microgravity conditions in a spacecraft or during a parabolic flight but also in various manners, i.e., electrostatic levitation [2,3], magnetic levitation [4,5], acoustic levitation [6-11], aero-dynamic levitation [12], and optical levitation [13]. For each levitation method, we have to design the droplet system for the stabilization of the levitating state, and thus it is somewhat challenging to apply additional manipulations. Related to the levitation techniques, the dynamics of a droplet has also been studied intensively [2,14-17].

Here we focus on the acoustic levitation, where a droplet can be levitated at the valleys of the standing wave in the three-dimensional sound pressure field [6-9]. Using the arrays of the sound sources and controlling the phases of the irradiated sound, multiple droplets can be levitated simultaneously and their positions can be controlled. This enables us to merge two or more levitated droplets with contactless operations, which will be of great importance for syntheses of materials without any contact with the apparatuses.

Recently, a contactless mixing technique in an acoustic levitation system is reported [18,19]. By applying the frequency modulation to the sound pressure field, the levitated droplet can exhibit a periodical deformation. Then, the flow inside the droplet is induced by the deformation. The flow field looks oscillatory and time-reversible. Owing to the scallop theorem [20], the time-reversible flow field is not capable of agitating. Nevertheless, the experimental results indicated that the mixing becomes faster than the case without the oscillatory deformation [18]. Since the diffusion enhancement by oscillatory flow was found heuristically, the clarification of the mechanism is awaited, which may contribute to develop the technique and to design more efficient systems.

The diffusion process affected by the oscillatory flow field is a nontrivial dynamics. So far, the dynamics of agitation by flow and that of diffusion originating from thermal fluctuation have been separately considered. This is because they have different time scales and spatial scales. The mixing by agitation proceeds faster on a larger spatial scale, while the diffusion proceeds faster on a smaller spatial scale. Moreover, in the convection-diffusion equation, the terms describing the convection and diffusion are separately described.

In the present paper, we study the effect of the oscillatory flow field on the diffusion process. In Section II, we construct a solution for the oscillatory flow field. Then, we formulate a diffusion equation per every period of the oscillatory deformation in Section III. We found that the diffusion coefficient includes not only the classical diffusion coefficient but also a combination term of diffusion and flow field. The latter term indicates the diffusion enhancement. The theoretical result is confirmed by the numerical calculations in Section IV. In Section V, the validity of the adopted assumptions is checked. Finally, we discuss the physical meaning of the diffusion coupled with the oscillatory flow as the summary.
II. FLOW FIELD IN A DROPLET

First, the model equations are introduced. The flow in the droplet, \( \mathbf{v}(r, t) \), is described by the Navier-Stokes equation [24, 25]:

\[
\rho \left( \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) = -\nabla p + \eta \nabla^2 \mathbf{v}
\]  

(1)

with incompressibility:

\[
\nabla \cdot \mathbf{v} = 0,
\]

(2)

where \( \rho \) and \( \eta \) are the density and viscosity of the fluid, respectively. \( p(r, t) \) denotes the pressure inside the droplet. In the experiments, the droplet periodically changes its shape with keeping the amplitude, and thus the viscous term \( \eta \nabla^2 \mathbf{v} \) should balance with the driving force originating from the acoustic pressure. Thus, we neglect the viscous term for simplicity:

\[
\rho \left( \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) = -\nabla p.
\]

(3)

By assuming that the flow has no rotation, the flow field can be represented by the stream function \( \Phi(r, t) \) as

\[
\mathbf{v} = \nabla \Phi.
\]

(4)

Then, Eq. (3) is represented as

\[
\rho \left( \frac{\partial \Phi}{\partial t} + \frac{1}{2} |\nabla \Phi|^2 \right) = -p.
\]

(5)

Equations (2) and (4) lead

\[
\nabla^2 \Phi = 0,
\]

(6)

which indicates that \( \Phi \) is a harmonic function.

To describe the droplet, the following two boundary conditions are imposed. One is the balance of pressure at the droplet surface:

\[
p|_{r=r_b} = p_{\text{air}} - 2\gamma H|_{r=r_b},
\]

(7)

where \( p_{\text{air}} (= \text{const.}) \) is the atmospheric pressure and \( H \) is the mean curvature of the droplet surface. The vector \( \mathbf{r}_b = f(\theta, \varphi, t) \mathbf{e}_r \) represents a point on the droplet surface in polar coordinates. Here, \( \mathbf{e}_r \) is the unit vector in \( r \)-direction. Equation (7) indicates that the deformation of the droplet affects the flow through the Laplace pressure.

The other one is the boundary condition for the flow field. That is to say, the normal component of the flow \( \mathbf{v} \) should be equal to that of the velocity of the droplet boundary:

\[
\mathbf{v}|_{r=r_b} \cdot \mathbf{n}|_{r=r_b} = \frac{dr_b}{dt} \cdot \mathbf{n}|_{r=r_b},
\]

(8)

where \( \mathbf{n} \) is the outward normal unit vector at the droplet surface.

In order to obtain the solution for Eqs. (5), (6), (7), and (8), we used the perturbation method; the solution is expanded with respect to an infinitesimally small parameter \( \varepsilon \) up to the second order as

\[
f = f^{(0)} + \varepsilon f^{(1)} + \varepsilon^2 f^{(2)} + \mathcal{O}(\varepsilon^3),
\]

(9)

\[
\Phi = \Phi^{(0)} + \varepsilon \Phi^{(1)} + \varepsilon^2 \Phi^{(2)} + \mathcal{O}(\varepsilon^3),
\]

(10)

\[
p = p^{(0)} + \varepsilon p^{(1)} + \varepsilon^2 p^{(2)} + \mathcal{O}(\varepsilon^3).
\]

(11)

By substituting the above expressions, we obtain the order-separated equations with respect to \( \varepsilon \), which are shown in Appendix A. It is noted that the pressure \( p \) can be easily eliminated from the equation and boundary conditions, and thus the deformation \( f \) and the stream function \( \Phi \) are calculated.

As a trivial solution for the equation, we have

\[
\mathbf{r}_b = f^{(0)} \mathbf{e}_r = R \mathbf{e}_r,
\]

(12)

\[
\Phi = \Phi^{(0)} = 0,
\]

(13)

which correspond to the solution for the static state of a droplet with a radius of \( R \). The corresponding pressure and flow field are described as:

\[
p = p^{(0)} = p_{\text{air}} + \frac{2\gamma}{R},
\]

(14)

\[
\mathbf{v} = \mathbf{v}_0 = 0.
\]

(15)

When the droplet is deformed from the sphere, the droplet tends to return to the sphere because of the surface tension. Since the surface tension works as a restoring force, the droplet shows a harmonic oscillation in the order of \( \varepsilon \). The generic solution \( f_{\text{gen}}^{(1)} \) and \( \Phi_{\text{gen}}^{(1)} \) for the flow and deformation is explicitly described as:

\[
f_{\text{gen}}^{(1)} = R \left[ \sum_{\ell=2}^{\infty} \sum_{m=0}^{\ell} \beta_{\ell,m}^{(1c)} P_{\ell}^m(\cos \theta) \cos m\varphi \sin(\omega_t t + \delta_t) \right. \\
+ \left. \sum_{\ell=2}^{\infty} \sum_{m=1}^{\ell} \beta_{\ell,m}^{(1s)} P_{\ell}^m(\cos \theta) \sin m\varphi \sin(\omega_t t + \delta_t) \right],
\]

(16)

\[
\Phi_{\text{gen}}^{(1)} = R^2 \times \\
\left[ \sum_{\ell=2}^{\infty} \sum_{m=0}^{\ell} \beta_{\ell,m}^{(1c)} \frac{\omega_t}{\ell} \left( \frac{R}{r} \right)^\ell P_{\ell}^m(\cos \theta) \cos m\varphi \cos(\omega_t t + \delta_t) \right. \\
+ \left. \sum_{\ell=2}^{\infty} \sum_{m=1}^{\ell} \beta_{\ell,m}^{(1s)} \frac{\omega_t}{\ell} \left( \frac{R}{r} \right)^\ell P_{\ell}^m(\cos \theta) \sin m\varphi \cos(\omega_t t + \delta_t) \right],
\]

(17)

where \( P_{\ell}^m \) is an associated Legendre polynomial of the degree \( \ell \) and order \( m \). The amplitudes of the oscillation modes \( \beta_{\ell,m}^{(1c)} \) and \( \beta_{\ell,m}^{(1s)} \) are constants chosen arbitrarily. Here, the characteristic frequency \( \omega_t \) is described as

\[
\omega_t = \sqrt{\frac{\gamma (\ell - 1)(\ell + 2)}{\rho R^3}}.
\]

(18)
The result in the order of $\varepsilon$ is consistent with the results by Rayleigh. It is noted that $\omega_n = 0$ for the modes of $n = 0$ and $1$. This is because the mode of $n = 0$ corresponds to an expansion (or a contraction), and the mode of $n = 1$ corresponds to a translation. Therefore, we only need to consider the modes for $n \geq 2$.

Hereafter, we consider the deformation with a single mode. Especially, we only consider the mode of $\ell = m = n$ ($n \in \mathbb{N}, n \geq 2$), corresponding to the deformation in the $xy$-plane. Moreover, only the cosine mode is considered for simplicity. As for the time evolution, we can arbitrarily choose $\delta_n$ owing to the time translational symmetry. Following the above assumptions, we have

$$ f^{(1)} = R \sin^2 \theta \cos n \varphi \sin \omega_n t, \quad \Phi^{(1)} = \frac{\omega_n R^2}{n} \left( \frac{r}{R} \right)^n \sin^2 \theta \cos n \varphi \cos \omega_n t. $$

Here we use

$$ P_n^0(\cos \theta) = [(-1)^n(n2n - 1)!!] \sin^n \theta, $$

and we set

$$ \beta^{(1c)}_{1,n} = \frac{1}{(-1)^n(n2n - 1)!!}, $$

so that the small parameter $\varepsilon$ represents the amplitude of the oscillatory deformation.

Then, we consider the flow field in the order of $\varepsilon^2$ in the case that the flow field in the order of $\varepsilon$ is expressed in Eqs. (19) and (20). From the equations for the order of $\varepsilon^2$ in Eqs. (A4), (A5), and (A6) in Appendix A, we obtain

$$ f^{(2)} = f_{2n,2n}^{(2,n)} \sin 2 \theta \cos 2n \varphi \cos 2\omega_n t + f_{2n,2n}^{(2,n)} \sin 2 \theta \cos 2n \varphi $$

$$ + \sum_{k=0}^{n} f_{2k,0}^{(2,n)} P_{2k}(\cos \theta) \cos 2\omega_n t $$

$$ + \sum_{k=0}^{n} f_{2k,0}^{(2,n)} P_{2k}(\cos \theta), $$

and

$$ \Phi^{(2)} = \Phi_{2n,2n}^{(2,n)} \left( \frac{r}{R} \right)^2 \sin^2 \theta \cos 2n \varphi \sin \omega_n t $$

$$ + \sum_{k=0}^{n} \Phi_{2k,0}^{(2,n)} \left( \frac{r}{R} \right)^2 P_{2k}(\cos \theta) \sin 2\omega_n t. $$

Here, we introduce the constants $j_{2n,2n}^{(2,n)}$, $j_{2n,2n}^{(2,n)}$, $j_{2k,0}^{(2,n)}$, $j_{2k,0}^{(2,n)}$, $\Phi_{2n,2n}^{(2,n)}$, and $\Phi_{2k,0}^{(2,n)}$, whose explicit forms are shown in Appendix B.

### III. DIFFUSION WITH THE OSCILLATORY FLOW

To describe the dynamics of the tracer particle inside an oscillatory deformed droplet, the over-damped Langevin equation suffering from the thermal noise and advection due to the oscillatory flow is adopted:

$$ \frac{dx}{dt} = v(x, t) + \xi(t), $$

where $x$ is the position of the tracer particle and $v(x, t)$ is a flow field obtained in the last section. The flow field can be expressed as

$$ v = \varepsilon \nabla \Psi^{(1)} \cos \omega_n t + \varepsilon^2 \nabla \Psi^{(2)} \sin 2\omega_n t + O(\varepsilon^3). $$

Here, we define $\Psi^{(1)}$ and $\Psi^{(2)}$ so that

$$ \Phi^{(1)}(x,t) = \Psi^{(1)}(x) \cos \omega_n t, $$

$$ \Phi^{(2)}(x,t) = \Psi^{(2)}(x) \sin 2\omega_n t, $$

where $\Phi^{(1)}$ and $\Phi^{(2)}$ are explicitly given in Eqs. (21) and (22), respectively. The function $\xi(t)$ corresponds to the thermal noise, which satisfies the following relations:

$$ \langle \xi_a(t) \rangle = 0, $$

$$ \langle \xi_a(t) \xi_b(s) \rangle = 2D \delta_{ab} \delta(t - s). $$

Here, $\delta_{ab}$ is the Kronecker delta and $\delta(\cdot)$ is the Dirac’s delta function, and $D$ is the diffusion coefficient originating from the thermal noise.

The Fokker-Planck equation for Eq. (25) is derived as:

$$ \frac{\partial q(r,t)}{\partial t} = -\nabla \cdot (D(r,t)q(r,t)) + D^2 q(r,t), $$

where $q(r,t)$ is the probability density of the tracer particle. In this Fokker-Planck equation, the effects of the convection and the diffusion separately appear. Here, we consider the map of the probability density $q(r,t)$ per the period of the oscillation of flow field $T = 2\pi/\omega_n$, instead of the Fokker-Planck equation. The first and second moments for the time interval $T$ are defined as the alternatives of the Kramers-Moyal coefficients:

$$ M^{(1)}(r) = \frac{1}{T} \langle \Delta x_\alpha \rangle, $$

$$ M^{(2)}(r) = \frac{1}{T} \langle \Delta x_\alpha \Delta x_\beta \rangle, $$

where $\Delta x_\alpha = x_\alpha(T) - x_\alpha(0)$. Then the map for the probability density $q(r,mT)$ is described as

$$ q(r, (m+1)T) - q(r, mT) = -\frac{\partial}{\partial x_\alpha} \left( M^{(1)}(r) q(r, mT) \right) $$

$$ + \frac{1}{2} \frac{\partial^2}{\partial x_\alpha \partial x_\beta} \left( M^{(2)}(r) q(r, mT) \right), $$

where $m \in \mathbb{N}$. Equation (34) is considered to be a discrete Fokker-Planck equation. The higher-order spatial derivatives of $q$ are neglected. The moments $M^{(1)}$ and $M^{(2)}$ are calculated as

$$ M^{(1)}(r) = \frac{D \varepsilon^2}{2\omega^2} \frac{\partial^3 \Psi^{(1)}(r)}{\partial x_\alpha \partial x_\alpha \partial x_\alpha} + O(\varepsilon^3, D^2), $$

$$ M^{(2)}(r) = \frac{D \varepsilon^4}{8\omega^4} \frac{\partial^5 \Psi^{(1)}(r)}{\partial x_\alpha \partial x_\alpha \partial x_\alpha \partial x_\alpha \partial x_\alpha} + O(\varepsilon^5, D^2). $$
Here, the terms with the order of $\varepsilon^3$ and $D^2$ or higher are neglected. By substituting Eqs. 33 and 30 into Eq. (31), we have

$$
\frac{q(r, (m+1)T) - q(r, mT)}{T} = \frac{\partial}{\partial x_\alpha} \left( D_{\alpha\beta}(r, t) \frac{\partial q(r, t)}{\partial x_\beta} \right),
$$

where $D_{\alpha\beta}(r, t)$ is defined as

$$
D_{\alpha\beta} = \frac{1}{2} M^{(2)}_{\alpha\beta}. 
$$

As seen in Eq. (37), only the diffusion term remains. The convection term does not appear reflecting that the flow field is oscillatory, and the net convection in a period should be zero. The remarkable point is that the diffusion tensor $D_{\alpha\beta}$ depends on not only the thermal diffusion coefficient $D$ but also the flow field, and thus it has the spatial dependence $D_{\alpha\beta} = D_{\alpha\beta}(r)$. Here we consider the diffusion on the $xy$-plane at $z = 0$, where the deformation is largest. Reflecting the system symmetry, the diffusion tensor in the cylindrical coordinates $(\rho, \varphi, z)$ is considered, which is defined in Eqs. (C1) to (C5) in Appendix C. The effective diffusion coefficient $\bar{D}$ is defined as

$$
\bar{D} = \frac{1}{3} \left( D_{\rho\rho} + 2D_{\varphi\varphi} + D_{zz} \right). \quad (39)
$$

From the theoretical calculation, it is obtained as

$$
\frac{\bar{D}}{D} = 1 + \varepsilon^2 \sum_{k=1}^{n} \frac{\rho}{R} \cos(2n\varphi),
$$

where

$$
a_n = \frac{2}{3} (n - 1)^2. \quad (41)
$$

Since $a_n$ is positive for $n \geq 2$, the diffusion is enhanced for all modes of the deformation. In the case of $n = 2$, the effective diffusion coefficient $\bar{D}$ does not have a spatial dependence, reflecting that the averaged shear strain is the same at any point in the droplet. On the other hand, in the case of $n \geq 3$, the effective diffusion coefficient $\bar{D}$ is larger near the surface of the droplet. This result is reasonable since the deformation of the fluid element is large near the surface of the droplet.

Below, each component in the diffusion tensor is given:

$$
\frac{\bar{D}_{\rho\rho}}{D} = 1 + \varepsilon^2 \left[ b_n + \sum_{k=2}^{n} c_{nk} \left( \frac{\rho}{R} \right)^{2(k-1)} + d_n \left( \frac{\rho}{R} \right)^{2(n-1)} \cos(2n\varphi) \right],
$$

IV. NUMERICAL SIMULATION

The numerical calculations were performed to confirm the theoretical results. The over-damped Langevin equation in Eq. (25) for a tracer particle is adopted. In the calculation, we set the parameters to be $\omega_n = 1$, $R = 1$ and $D = 10^{-5}$. The calculation is executed with the second-order Runge-Kutta method (explicit midpoint method), and the Gaussian white noise is generated with the Box-Muller method [26]. The time step is set to be $\Delta t = T/400$.

In Fig. 1, the trajectories of the tracer particles on the $xy$- and $xz$-planes during one period are shown for $n = 2, 3,$ and 4 to illustrate the particle motion and flow field. Here we set the oscillation amplitude $\varepsilon = 0.1$. The particles are confined in the droplet by recalculating the noise till the next particle position is located inside the droplet.

By changing the initial distance from the center, we calculated the normalized total effective diffusion coefficient, $\bar{D}/D$. We prepared the particles at a distance $r$ from the center on the $xy$-plane with 100 different initial angles, i.e., $\varphi = 2\pi k/100$ for $k = 0, \ldots, 99$. To obtain the effective diffusion coefficient, we calculate each component of the second moment $M^{(2)}(r)$ in Eq. (33), by averaging the displacements of $10^7$ particles for each initial locations. Then it was translated into the cylindrical coordinates using the relations in Eqs. (C1) to (C5) in Appendix C. The calculated $\bar{D}/D$ is shown in the left
FIG. 1. Trajectories of 400 tracer particles for 1 cycle (from $t = 0$ to $T$) on $xy$- (top) and $xz$- (bottom) planes. They basically go and back with the oscillatory flow, but off from the streamlines due to the thermal noise. The particles are randomly located on each plane as the initial condition. The oscillation amplitude $\varepsilon$ is set to be 0.1. The gray regions indicate the area of the droplet, where the time-dependent shapes are all superimposed.

(a) $n = 2$ 
(b) $n = 3$ 
(c) $n = 4$

$xy$-plane 
$xz$-plane

FIG. 2. Numerical results on the normalized effective diffusion coefficient $D_{\text{eff}}/D$ depending on the initial distance $\rho$ from the center (left) and the oscillation amplitude $\varepsilon$ (right) on the $xy$-plane for $n = 2, 3,$ and 4. The effective diffusion coefficient was estimated from the mean square displacement of the particles. For the left panel, $\varepsilon$ is fixed as $\varepsilon = 0.1$, and for the right panel, the initial radius is fixed as $\rho/R = 0.5$ (red) and $\rho/R = 0.9$ (cyan). The black thin curves show the results of theoretical analysis.

(a) $n = 2$ 
(b) $n = 3$ 
(c) $n = 4$

$D_{\text{eff}}/D$ $D_{\text{eff}}/D$

FIG. 3. Numerical results on the components of the normalized effective diffusion coefficient depending on $\varphi$ for $n = 2, 3,$ and 4. $D_{\rho\rho}^{\text{eff}}$ (red), $D_{\varphi\varphi}^{\text{eff}}$ (cyan), $D_{zz}^{\text{eff}}$ (green) are shown in the left panel, while $D_{\rho\varphi}^{\text{eff}}$ is plotted on the right panel. The black thin curves show the results by the theoretical analysis. The initial distance from the center is $\rho/R = 0.5$, and $\varepsilon = 0.1$.

panels of Fig. 2. The numerical results well correspond to the values obtained by the theoretical analysis.

The dependence of the normalized diffusion coefficient $\bar{D}^{\text{eff}}/D$ on the oscillation amplitude $\varepsilon$ is also calculated for the initial distance from the center $\rho/R = 0.5$ and 0.9. The averaging procedure is the same as the one for the radial dependence. The results are shown in the right panels of Fig. 2. The effective diffusion increases with an increase in $\varepsilon$ both for $n = 2, 3,$ and 4. The numerical results well meet the results by the theoretical analysis.

In order to obtain the $\varphi$-dependence of the components of the normalized effective diffusion coefficient, $D_{\rho\rho}^{\text{eff}}/D$, $D_{\varphi\varphi}^{\text{eff}}/D$, $D_{zz}^{\text{eff}}/D$, and $D_{\rho\varphi}^{\text{eff}}/D$, the numerical calculations were performed from the initial condition $\rho/R = 0.5$ and $\varphi = 2\pi k/100$ for $k = 0, \ldots, 99$. The averaging was done for $10^5$ particles from each initial position. The results are also shown in Fig. 3 for $n = 2, 3,$ and 4. From the figure, $D_{\varphi\varphi}^{\text{eff}}$ and $D_{zz}^{\text{eff}}$ are greater than the thermal equilibrium diffusion coefficient, and they depend on $\varphi$ with a wave number of $2n$. On the while, $D_{\rho\rho}^{\text{eff}}$ is smaller than it and is independent of $\varphi$. The normalized effective cross diffusion coefficient $D_{\rho\varphi}^{\text{eff}}$ is also periodic with a wavenumber of $2n$. Every plot obtained by the numerical calculation well corresponds to the theoretical results.
V. DISCUSSION

In our model, the viscous term $\eta \nabla^2 v$ is omitted from Eq. (11), and Eq. (13) is adopted. The nonlinear term, $\varrho (v \cdot \nabla) v$, is assumed to be smaller than the other terms in Eq. (5) in the theoretical calculation. Here the validity of these assumptions is checked. In the experiments in Ref. [18], the characteristic time scale was 6.5 ms, which indicates that the adopted assumptions are valid.

The change in the pressure is estimated as

$$\Delta H = \left( \frac{1}{R + \Delta R} - \frac{1}{R - \Delta R} \right) = \frac{2\Delta R}{R^2}. \quad (46)$$

From these values, the orders of the terms in Eq. (1) are estimated as

$$|\varrho \frac{\partial v}{\partial t}| \sim 4.5 \times 10^3 \text{ kg/}(m^2s^2), \quad (47)$$

$$|\varrho v \cdot \nabla v| \sim 9.0 \times 10^2 \text{ kg/}(m^2s^2), \quad (48)$$

$$|\eta \nabla^2 v| \sim 30 \text{ kg/}(m^2s^2), \quad (49)$$

$$|\nabla p| \sim 3.0 \times 10^3 \text{ kg/}(m^2s^2). \quad (50)$$

Here the symbol “∼” represents that the terms connected with the symbol are in the same order. Thus we have

$$|\eta \nabla^2 v| \ll |\varrho v \cdot \nabla v| \ll |\varrho \frac{\partial v}{\partial t}| \sim |\nabla p|, \quad (51)$$

which indicates that the adopted assumptions are valid.

It should be noted that our approach is not applicable for $n = 5$ and $n = 10$, since $c_{nk}$, $g_{nk}$, and $h_{nk}$ in Eqs. (12), (13), and (14) diverge for $(n, k) = (5, 4)$ and (10,8). This is because of the resonance, in which the second harmonic of the considered mode is the same as the other characteristic mode. Actually, $2\omega_5 = \omega_8$ and $2\omega_{10} = \omega_{16}$. We confirmed that pairs of positive integers $(n, k)$ that satisfy $2\omega_n = \omega_{2k}$ are $(5, 4)$ and $(10, 8)$ in the range of $2 \leq n \leq 100$.

In actual systems, such a divergence of oscillation amplitude will not occur due to the following reasons. First, if the amplitude of the deformation oscillation becomes larger, the perturbative treatment does not work, and the present approach cannot be adopted. Second, the energy dissipation would play an essential role in the case of the larger deformation. As we discussed, the energy dissipation is relatively smaller than the other effect, such as inertia or pressure. In our model, we neglected the energy dissipation, but it cannot be neglected when the amplitude becomes large. It is known that when the energy dissipation and injection balance, the amplitude of the oscillation mode becomes finite. Thus our model can be adopted if we extend our model to include energy dissipation and injection. Third, the droplet deforms to an ellipsoidal shape due to the gravity effect and anisotropy of the acoustic field in experiments. In such a case, the characteristic frequency should be shifted [27], and then such resonance should not occur.

VI. SUMMARY

Dynamics of mixing where flow and diffusion processes take place is usually described by the convection-diffusion equation [31]. The one way to investigate the cooperative dynamics of flow and diffusion is to track the time evolution of the convection-diffusion equation. However, it is difficult to determine the position-dependent diffusion coefficient from the dynamics of the concentration field. In the present study, on the whole, we derive the discrete time evolution equation per the period of the oscillatory flow shown in Eq. (34). Since the oscillatory flow does not induce net convection in a period, the convection term disappears, as shown in Eq. (37). Instead, we can directly see the effective diffusion coefficient per the period and have succeeded in showing that the oscillatory flow, which cannot agitate a fluid, affects the diffusion.

The Brownian motion causes the transition of a tracer particle between fluid elements. The probability of the single transition is equal to that for the inverted process, which results in the normal diffusion. When a flow is stimulated, the fluid elements deform and change their conformation in time. Thus a sequent transition process due to thermal fluctuation becomes irreversible, which realizes an anisotropic Brownian motion. The diffusion enhancement is induced by such anisotropic Brownian motion.

The representation of the effective diffusion tensor indicates that the diffusion process can be affected by any oscillatory flow. In the present system with a levitated droplet, the diffusion is enhanced by the oscillatory flow, but it is not clear whether any oscillatory flow always enhances the diffusion. It remains as future work.

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Appendix A: Equation and boundary conditions with respect to $\varepsilon$

Here, we show the equations and boundary conditions with respect to an infinitesimally small parameter $\varepsilon$. By substituting Eqs. (9), (10), and (11) to Eq. (5) and the boundary conditions (7) and (8), we obtain the equations for the order of $\varepsilon$ as

\[
\frac{\partial \Phi^{(1)}}{\partial t} = -p^{(1)}, \quad (A1)
\]

\[
p^{(1)}(r = R) = -\frac{2\varepsilon}{R^2} \left[ f^{(1)}(\theta, \varphi, t) + \frac{1}{2} \frac{\partial^2 f^{(1)}}{\partial \theta^2} \right.
\]
\[
+ \cos \theta \frac{\partial f^{(1)}}{\partial \theta} + \frac{1}{2} \frac{\partial^2 f^{(1)}}{\partial \varphi^2} \bigg] \bigg|_{r = R}, \quad (A2)
\]

\[
\nabla \Phi^{(1)} \bigg|_{r = R} \cdot \mathbf{e}_r = \frac{\partial f^{(1)}}{\partial t}. \quad (A3)
\]

As for the equations for the order of $\varepsilon^2$, we have

\[
\frac{\varepsilon}{R} \frac{\partial \Phi^{(2)}}{\partial t} + \frac{\varepsilon}{2} \left| \nabla \Phi^{(1)} \right|^2 = -p^{(2)}, \quad (A4)
\]

\[
p^{(2)}(r = R) + \frac{\partial p^{(1)}}{\partial r} \bigg|_{r = R} \left[ f^{(1)}(\theta, \varphi, t) \right.
\]
\[
+ \frac{2\varepsilon}{R^3} f^{(1)}(\theta, \varphi, t) \left[ f^{(1)}(\theta, \varphi, t) + \frac{1}{2} \frac{\partial^2 f^{(1)}}{\partial \theta^2} \right.
\]
\[
+ \cos \theta \frac{\partial f^{(1)}}{\partial \theta} + \frac{1}{2} \frac{\partial^2 f^{(1)}}{\partial \varphi^2} \bigg]
\]
\[
\left. + \cos \theta \frac{\partial f^{(2)}}{\partial \theta} + \frac{1}{2} \frac{\partial^2 f^{(2)}}{\partial \varphi^2} \bigg] \bigg|_{r = R}, \quad (A5)
\]

\[
\nabla \Phi^{(2)} \bigg|_{r = R} \cdot \mathbf{e}_r + \frac{\partial}{\partial r} \left( \nabla \Phi^{(1)} \right) \bigg|_{r = R} \cdot \mathbf{e}_r f^{(1)}(\theta, \varphi, t)
\]
\[- \nabla \Phi^{(1)} \bigg|_{r = R} \cdot \frac{1}{R} \left( \frac{\partial f^{(1)}}{\partial \theta} \mathbf{e}_\theta + \frac{1}{\sin \theta} \frac{\partial f^{(1)}}{\partial \varphi} \mathbf{e}_\varphi \right)
\]
\[= \frac{\partial f^{(2)}}{\partial t}. \quad (A6)
\]

It should be noted that $p^{(1)}$ and $p^{(2)}$ are not unique but any constant value can be added.
Appendix B: Explicit forms of the coefficients in Eqs. (23) and (24)

The explicit forms of the coefficients in Eqs. (23) and (24) are shown as follows:

\[ j_{2k,0}^{(2,n)} = \frac{Y(n,k)}{[(2n - 1)!!]^2}, \quad (B3) \]

\[ j_{2k,0}^{(2,n)} = \frac{Z(n,k)}{[(2n - 1)!!]^2}, \quad (B4) \]

\[ \Phi_{2n,2n}^{(2,n)} = -\frac{3\omega_n(n+1)(n-1)^2}{8n(n^2+1)} R^2, \quad (B5) \]

\[ \Phi_{2k,0}^{(2,n)} = -\frac{\omega_n \Xi(n,k)}{[(2n - 1)!!]^2} R^2. \quad (B6) \]

Here, we set

\[ Y(n,k) = \frac{(-1)^k(4k + 1) [(2n)!!]^2 (2k - 1)!! \left[ (4n^2 - 4k^2 n + 4k n^2 - 2k^3 - k^2 - kn)(n-1)(n+2) + 4kn(n^2 + n-1) \right]}{2^{n+4} n(k-k^2 - 2k^3 - 2n + n^2 + n^3)(2n + 2k + 1)!!(n-k)!!}, \quad (B7) \]

\[ Z(n,k) = \frac{(-1)^k(4k + 1) [(2n)!!]^2 (2k - 1)!! \left[ k(2k^2 + k - n)(n-1)(n+2) + 4kn(n^2 + n-1) \right]}{2^{n+4} k(k-1)n(2n + 2k + 1)!!(n-k)!!(k+1)!}. \quad (B8) \]

\[ \Xi(n,k) = \frac{(-1)^{k-1}(4k + 1) [(2n)!!]^2 (2k - 1)!!}{2^{n+4} n(k-k^2 - 2k^3 - 2n + n^2 + n^3)(2n + 2k + 1)!!(n-k)!! k! \times [8k^3 + 8k^4 + k(n+1)(n-4) - n(n-1)(n+2)(4n+5) + 2k^2(n^2 - 3n - 3)]}, \quad (B9) \]

Appendix C: Explicit forms of the diffusion coefficient

The diffusion tensor in the cylindrical coordinates is obtained as:

\[ D_{\rho\rho}^{eff} = D_{xx}^{eff} \cos^2 \varphi + D_{yy}^{eff} \sin^2 \varphi + 2D_{xy}^{eff} \sin \varphi \cos \varphi, \quad (C1) \]

\[ D_{\varphi\varphi}^{eff} = D_{xy}^{eff} \sin^2 \varphi + D_{yy}^{eff} \cos^2 \varphi - 2D_{xy}^{eff} \sin \varphi \cos \varphi, \quad (C2) \]

\[ D_{\rho\varphi}^{eff} = (D_{xy}^{eff} - D_{xx}^{eff}) \sin \varphi \cos \varphi + 2D_{xy}^{eff} (\cos^2 \varphi - \sin^2 \varphi), \quad (C3) \]

\[ D_{\rho\varphi}^{eff} = (D_{xy}^{eff} \cos \varphi + D_{yy}^{eff} \sin \varphi), \quad (C4) \]

\[ D_{\varphi\varphi}^{eff} = (-D_{xx}^{eff} \sin \varphi + D_{yy}^{eff} \cos \varphi). \quad (C5) \]

The coefficients in Eqs. (12) to (15) are explicitly derived as follows:

\[ b_n = \frac{n(n-1)}{2}, \quad (C6) \]

\[ c_{nk} = \frac{(-1)^k(2k-1)(2k-1)!! \Xi(n,k)}{2^{2k-2}[(k-1)!!][(2n-1)!!]^2}, \quad (C7) \]

\[ d_n = \frac{3(n+1)(n-1)^2(2n-1)}{4(n^2+1)}, \quad (C8) \]

\[ g_{nk} = \frac{(-1)^k(2k-1)!! \Xi(n,k)}{2^{2k-2}[(k-1)!!][(2n-1)!!]^2}, \quad (C9) \]

\[ h_{nk} = \frac{(-1)^{k-1}(2k)!! \Xi(n,k)}{2^{2k-2}[(k-1)!!][(2n-1)!!]^2}. \quad (C10) \]

Here, the explicit forms of the effective diffusion coefficient \( \tilde{D}^{eff} \) and the components of the effective diffusion tensor in the \( xy \)-plane for modes \( n = 2, 3, \) and 4 are shown as follows: For \( n = 2 \), we have

\[ \frac{\tilde{D}^{eff}}{D} = 1 + \frac{2}{3} \varepsilon^2, \quad (C11) \]
\[
\frac{D_{\rho\rho}^{\text{eff}}}{D} = 1 + \varepsilon^2 \left[ \frac{89}{63} + \frac{81}{700} \left( \frac{\rho}{R} \right)^2 + \frac{27}{20} \left( \frac{\rho}{R} \right)^2 \cos(4\varphi) \right],
\tag{C12}
\]

\[
\frac{D_{\varphi\varphi}^{\text{eff}}}{D} = 1 + \varepsilon^2 \left[ \frac{89}{63} + \frac{27}{700} \left( \frac{\rho}{R} \right)^2 - \frac{27}{20} \left( \frac{\rho}{R} \right)^2 \cos(4\varphi) \right],
\tag{C13}
\]

\[
D_{zz}^{\text{eff}} = 1 + \varepsilon^2 \left[ -\frac{52}{63} - \frac{27}{179} \left( \frac{\rho}{R} \right)^2 \right], \tag{C14}
\]

\[
D_{\rho\varphi}^{\text{eff}} = \varepsilon^2 \left[ -\frac{27}{20} \left( \frac{\rho}{R} \right)^2 \sin(4\varphi) \right]. \tag{C15}
\]

For \( n = 3 \), we have

\[
\frac{D_{\rho\rho}^{\text{eff}}}{D} = 1 + \frac{8}{3} \varepsilon^2 \left( \frac{\rho}{R} \right)^2, \tag{C16}
\]

\[
\frac{D_{\varphi\varphi}^{\text{eff}}}{D} = 1 + \varepsilon^2 \left[ \frac{2}{7} + \frac{177}{44} \left( \frac{\rho}{R} \right)^2 + \frac{10}{11} \left( \frac{\rho}{R} \right)^4 + 6 \left( \frac{\rho}{R} \right)^4 \cos(6\varphi) \right], \tag{C17}
\]

\[
D_{zz}^{\text{eff}} = 1 + \varepsilon^2 \left[ \frac{2}{7} + \frac{235}{44} \left( \frac{\rho}{R} \right)^2 + \frac{2}{11} \left( \frac{\rho}{R} \right)^4 - 6 \left( \frac{\rho}{R} \right)^4 \cos(6\varphi) \right], \tag{C18}
\]

\[
D_{\rho\varphi}^{\text{eff}} = \varepsilon^2 \left[ -\frac{945}{68} \left( \frac{\rho}{R} \right)^6 \sin(8\varphi) \right]. \tag{C20}
\]

For \( n = 4 \), we have

\[
\frac{D_{\rho\rho}^{\text{eff}}}{D} = 1 + 6 \varepsilon^2 \left( \frac{\rho}{R} \right)^4, \tag{C21}
\]

\[
\frac{D_{\varphi\varphi}^{\text{eff}}}{D} = 1 + \varepsilon^2 \left[ \frac{664}{2695} - \frac{3936}{5005} \left( \frac{\rho}{R} \right)^2 + \frac{157}{22} \left( \frac{\rho}{R} \right)^4 + \frac{735}{9724} \left( \frac{\rho}{R} \right)^6 + \frac{945}{68} \left( \frac{\rho}{R} \right)^6 \cos(8\varphi) \right], \tag{C22}
\]

\[
\frac{D_{\rho\varphi}^{\text{eff}}}{D} = \varepsilon^2 \left[ -\frac{1328}{2695} - \frac{15248}{5005} \left( \frac{\rho}{R} \right)^2 - \frac{15}{11} \left( \frac{\rho}{R} \right)^4 - \frac{210}{2431} \left( \frac{\rho}{R} \right)^6 \cos(8\varphi) \right], \tag{C23}
\]

\[
\frac{D_{zz}^{\text{eff}}}{D} = 1 + \varepsilon^2 \left[ -\frac{1328}{2695} - \frac{15248}{5005} \left( \frac{\rho}{R} \right)^2 - \frac{15}{11} \left( \frac{\rho}{R} \right)^4 - \frac{210}{2431} \left( \frac{\rho}{R} \right)^6 \cos(8\varphi) \right], \tag{C24}
\]

\[
\frac{D_{\rho\varphi}^{\text{eff}}}{D} = \varepsilon^2 \left[ -\frac{945}{68} \left( \frac{\rho}{R} \right)^6 \sin(8\varphi) \right]. \tag{C25}
\]