Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Materials

1 Dynamics of particle motion

The motion of finite-sized particles in fluids is a common phenomenon encountered in nature and engineering. It is well known that the dynamics of finite-sized particles can differ remarkably from the infinitesimal particle dynamics. When the carrier flow is turbulent, a striking feature is the tendency of heavy particles to inhomogeneously distribute in space, forming spatial clusters, that is called *preferential concentration*.[25] The phenomenon of preferential concentration of heavy particles in turbulent flows has been extensively researched theoretically and experimentally, and ascribed to the mechanism of heavy particles being centrifuged out of turbulent vortices.[29]

The recent studies concluded that in high *Re* regime, preferential concentration of *heavy* particles is in the regions of *high* strain rate and *low* vorticity.[30-32] However, most of the studies have been restricted to turbulent flows and not many studies have been conducted to study the dynamics of almost neutrally buoyant particles ($\rho_p \approx \rho_f$**)**. In particular, the dynamics of neutrally buoyant particles in the laminar (chaotic) flow is much less understood.

The pioneering theoretical work conducted by Babiano et al. (2000)[16] showed that a large finite-sized particle will preferentially move into a region with a negative value of Okubo-Weiss number, Q, which is defined as:

$$Q = \frac{(s^2 - w^2)}{4} \tag{4}$$

where s is the strain rate, s^2 is the sum of the squared normal and shear components of the strain reate tensor, w is the vorticity, and Q gives an indication on the flow that is either dominated by vorticity, or by strain rate.[33] It is obvious that when $Q > 0$, the flow is strain dominated, while when $Q < 0$, it is vorticity dominated. The prediction conducted by Babiano et al. (2000) thus showed that the finite-sized particles tend to scatter from the strain-dominated region(s) and settle in the vorticity-dominated region(s).[16] However, Sapsis and Haller made further prediction and suggested that the tendency of particle motion is only dependent only on strain rate, not on vorticity.[18] The only quantitative experimental study on dynamics of inertial particle, as far as we are aware, is the work conducted by Ouellette et al. (2008). The main conclusions from their studies are that large inertial particles tend to deviate from the underlying flow field and the effects of small amount of inertia are still vital in a long-time statistical data.[14]

In general, no universal agreement has been made on the tendency of inertial-particle motion in laminar fluid flow. Our work firstly provides the experimental evidence that large inertial particles tend to concentrate, or cluster in the regions of *low* strain in stirred laminar flows (**Fig. 10**), just the opposite of what have been reported in turbulent flows where particles cluster in *high* strain regions.[29,30]

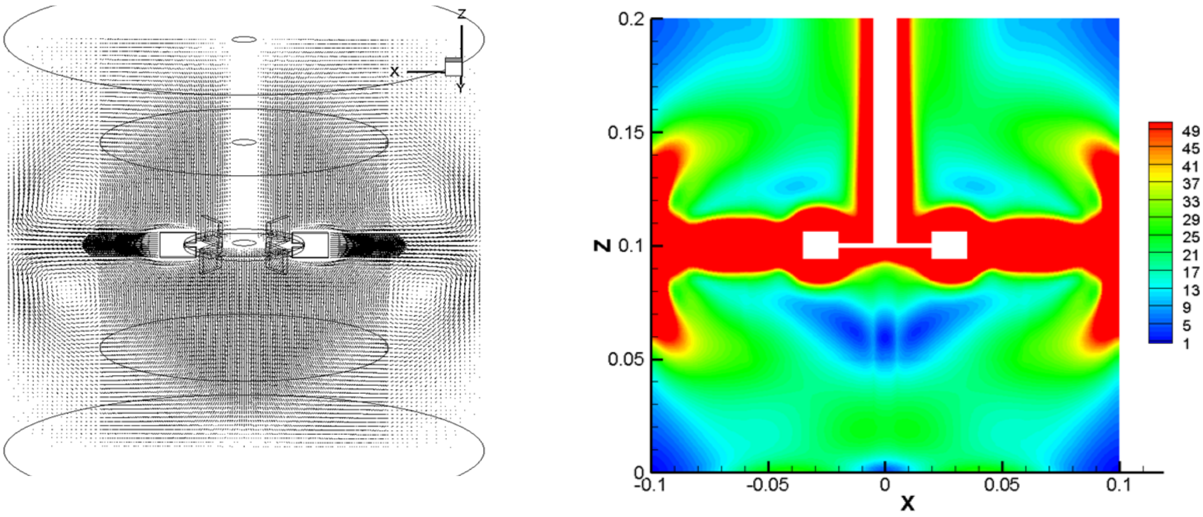

Figure 10 CFD prediction for velocity field and strain rate ($\dot{\gamma}$: 1/S) in the laminar mixing tank. In the strain-rate plot, red is the high-strain area; blue is the low-strain area. *Re*=120. Particles tend to scatter from the high strain regions and cluster in the regions of low strain in this case. (Cells number: 700,000, cell: hexahedron and pentahedron)

Repellers and attractors exist in the dynamical systems, and they are caused by common features of natural or engineering flows. In a dynamical system, a point set in phase space attracting all surrounding phase trajectories from some regions is an attractor. An attractor could be stochastic or chaotic, depending on the associated flow behaviour of the system. In contrast to attractor, particle trajectories are repelled from the current phase, and the regions repelling the particles are called repellers. It should be noted that attractors and repellers are only present in the dissipative systems.[13]

2 Passive particle motion

Flow in an unbaffled stirred tank is axisymmetric in a time-averaged sense, and it produces a dynamical system that is 2-dimensioinal and conserves phase space. **Fig. 11** illustrates the skeleton of the laminar stirred flow which has KAM tubes above and below the impeller. In our system, the six-evenly-spaced blades perturb the base flow periodically, resulting in chaotic flows due to the repeating formation of stretching and folding; as a consequence of this, the introduction of chaos is made to surround somewhat smaller KAM tubes. Recent studies show that the surface area of the KAM tubes admit *no* advective fluid flux across them; the dyed areas (decolourization results mentioned in Section 2) remained unchanged for scales of days, because only slow molecular diffusion occurs.[8,9]

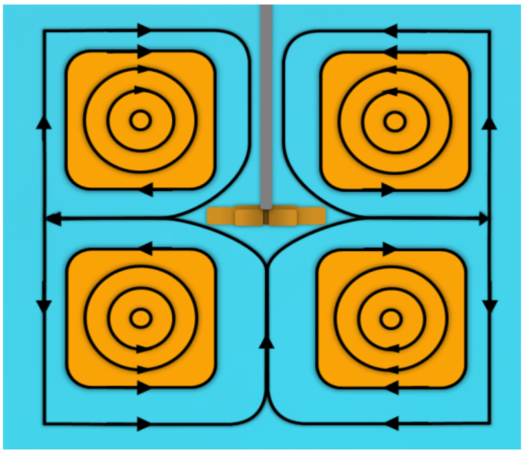

Figure 11 Fluid particle system for (laminar) stirred tank at low Re; two tori present above and below the impeller. Yellow area: KAM tubes (low strain area); the rest of the system: chaotic flow area (high strain area).

3 Inertial Particle motion

The critical parameter describing the particle motion in fluid flow is the particle Reynolds number:

$$Re_p = \frac{|V_p - u|L}{\nu} \tag{5}$$

where $\boldsymbol{V_p}$ is the velocity of a rigid spherical particle, $\boldsymbol{u}$ is the velocity of ambient fluid, L is the characteristic length scale of the flow. For passive particle, Re_p=0 as $|V_p - u|$ vanishes; for small-enough inertial particles, Re_p<<1 and it is usually assumed that when particle concentration is low, particle motion does not affect the ambient **u**.

Newton's law for the particle motion in fluid flow is:

$$m_p\frac{dV_p}{dt} = F_D + F_H + F_E + F_I \tag{6}$$

where m_p is the mass of the particle. The terms, or forces on the right hand side of the equation are, respectively, the hydrodynamic drag force, the other hydrodynamic forces, external forces and internal forces generated by the rigid particle.

Maxey and Riley[31] considered the motion of a small spherical particle in an unsteady non-uniform flow, and they proposed an equation based on the Newton's law that is

$$\rho_p\frac{dV_p}{dt} = \rho_f\frac{Du}{Dt} + (\rho_p - \rho_f)g - \frac{9\nu\rho_f}{2a^2}(V_p - u) - \frac{\rho_f}{2}(\frac{dV_p}{dt} - \frac{Du}{Dt}) \tag{7}$$

where g is the gradational acceleration (9.81 m/s^2), ρ_p is particle density, ρ_f is the fluid density and a is the particle radius. This equation is known as Maxey-Riley equation. The forces (on the right hand side of the equation) are, respectively, the forces exerted by the undistributed flow on the particle, the buoyancy force, Stokes drag and the added-mass from part of the fluid. D / Dt in this equation represents the time derivative following the flow. The assumptions of the MR equation are that impacts of the Faxén corrections and Basset history force are negligible.[13]

Inertial parameter σ is given by Eq. (1) in the main text. In the solid-particle systems we studied here, $St << 1$ because Re_f is small in laminar flows, $a/L << 1$, and $\rho_p / \rho_f \approx 1$. σ gives the ratio of the particle relaxation time and the typical timescale of the flow. Note that the larger the inertia parameter, the more important the effect of inertia; as $\sigma \rightarrow 0$, $Re_p=0$, indicating that the particle move passively with the fluid. We can substitute the inertia parameter into the Eq.(7):

$$\sigma\left(\frac{dV_p}{dt} - \frac{Du}{Dt}\right) = -(V_p - u) \tag{9}$$

This equation is valid in the following conditions: buoyancy is completely neglected by setting g = 0, the particle density is small, where the interaction among particles can be neglected, $Re_p << 1$ and particle motion does not affect the ambient fluid flow **u.**

4 Clustering criteria

Particle inertia adds additional degree of freedom into the dynamical system, where the 2-dimensional fluid dynamical system changes into 4-dimensional dynamical system, in which the inertial particle trajectories move. **Fig. 12** schematically shows the phase space and representative orbits of the inertial dynamical system. The fluid coordinates are the plane that is an attracting slice of the total particle-fluid system. The fluid plane is attracting, because of the hydrodynamic drag in laminar flows: a particle will always nearly move passively with the fluid motion until perturbed away. When perturbed, a particle can leave the fluid coordinates and move non-passively through the particle coordinates of the dynamical system. This simply means that when an inertia particles move non-passively, it requires four numbers, the particle location and its velocity, to describe its state. The boundaries of the KAM tubes (we termed *separated flow regions* here) are transport barriers in the fluid plane only, when particles leave the fluid plane and move through particle coordinate space, they can either reattract to any part of the fluid plane, either in the *separated flow region* (red orbit in **Fig. 12**), or outside of this region (blue orbit). Eventually all particles settle into the separated flow region.

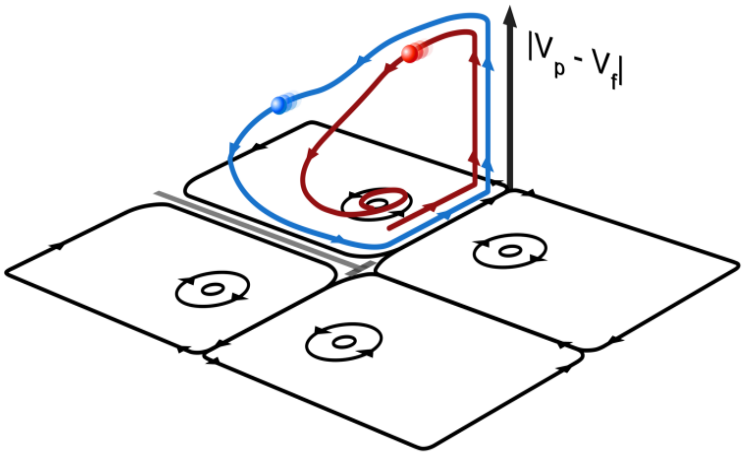

Figure 12 Phase space of augmented dynamical system for particle motion. 2-dimensional attracting plane of the fluid coordinates is perspective view of Fig. 8. Vertical coordinate is particle Reynolds number. Particle trajectories are repelled from the fluid coordinates to move in the particle coordinates. Some particles (blue) reattract outside tubes and can be repelled again; other particles (red) reattract inside tubes and do not encounter repellors again.

Next, we need to derive a criterion to identify the repelling regions (condition (1)) in our stirred tank system. Sapsis and Haller proved that the fluid plane of Eq. (9) is overall attracting, but also that some parts in the fluid plane can repel particle whenever

$$\sigma_{min}\left[S + \mu^{-1} I\right] < 0. \qquad (10)$$

where $\boldsymbol{S}$ is the rate of strain tensor ($S = 1/2[\nabla u + (\nabla u)^T]$, **I** is the unit tensor and $\sigma_{min}[\cdot]$ denotes the minimum eigenvalue of the racketed tensor.[18-20] As our flow is axisymmetric, the required eigenvalue can be determined from the characteristic equation of 2 × 2 martix in Eq. (7) as $\sigma_{min} = \mu^{-1} - (-det(S))^{\frac{1}{2}}$. From a general result of matrix algerbra $-\det(s) = (1/2)trace(S^2) = (1/2)$ **S : S,** where it is based on the fact that $trace(S) = 0$, and the dyadic (double dot) product leads to the sum of the squared strain rates along the eigendirections of **S**. The invariant dyadic product of the rate of strain tensor is used as the definition of the total strain rate,[35,36] and the total strain rate at a point can be defined as $\dot{\gamma} = (1/2)(S:S)^{1/2}$. In these considerations, the repelling (or scattering) criterion becomes Eq. (2).

As σ contains a factor of *Re*, data for each particle plots along a diagonal line with a slope proportional to inerta. The thick line in **Fig. 13** is the equality of Eq. (3). To the right and above the line, the theory predicts clustering, which is confirmed by experiments. It should be noted that that **Fig. 13** had no adjustable parameters, indicating that it is also applicable to other mixing systems.

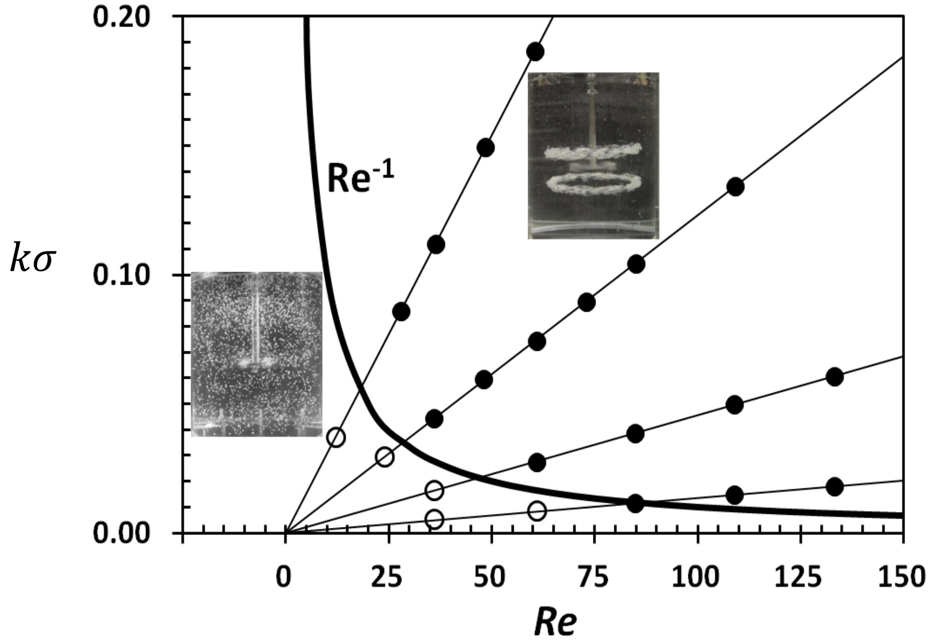

Figure 13 Instability boundary theory and data; open circles, no clustering; filled circles, clustering. Thick line is rearranged form of Eq. (3).

Supplementary References

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