Soft Matter

How a "pinch of salt" can tune chaotic mixing of colloidal suspensions†

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Efficient mixing of colloids, particles or molecules is a central issue in many processes. It results from the complex interplay between flow deformations and molecular diffusion, which is generally assumed to control the homogenization processes. In this work we demonstrate on the contrary that despite fixed flow and self-diffusion conditions, the chaotic mixing of colloidal suspensions can be either boosted or inhibited by the sole addition of a trace amount of salt as a co-mixing species. Indeed, this shows that local saline gradients can trigger a chemically driven transport phenomenon, diffusiophoresis, which controls the rate and direction of molecular transport far more efficiently than the usual Brownian diffusion. A simple model combining the elementary ingredients of chaotic mixing with diffusiophoretic transport of the colloids allows rationalization of our observations and highlights how small-scale out-of-equilibrium transport bridges to mixing at much larger scales in a very effective way. Considering chaotic mixing as a prototypal building block for turbulent mixing suggests that these phenomena, occurring whenever the chemical environment is inhomogeneous, might bring interesting perspectives from micro-systems to large-scale situations, with examples ranging from ecosystems to industrial contexts.

Transport and mixing of molecules or particles play a central role in many processes, from large scale phenomena such as industrial chemical reactors, dispersion of pollutants or deposition of sediments involved in biochemical cycles,[1,2] to the rapidly developing lab-on-a-chip micro-systems. In this field, strong limitation to mixing due to small-scale viscous flows has

triggered research for specific strategies[3,4] to optimize and facilitate (bio-)chemical analysis[5] or synthesis[6] operations in microsystems. The generic route for efficient mixing proceeds through the stretch and fold mechanism that generates ever-thinner structures of the substances to mix. This is achieved either from turbulent flow properties[7,8] in large-scale situations, or through laminar chaotic flows in viscous regimes[9–11] and, accordingly, mixing has been mostly approached from the "large" hydrodynamic scale perspective, focusing on flow characteristics. In all such processes however, mixing or homogenization involves a continuous interplay of global deformation within the flow, and local molecular transport – generically assumed to occur through Brownian diffusion.[8,10,12,13]

In this communication, we start from this molecular-scale perspective and ask if we can trigger a different molecular transport phenomenon, in place of the canonical diffusion, and impact in this way the global mixing properties. To explore this bottom-up approach to mixing, we consider an overlooked phenomenon – colloidal diffusiophoresis – recently studied in the context of surface-driven flow and non-equilibrium transport.[14–18] Local gradients of small chemicals – such as a salt – induce migration of particles with transport properties that can be orders of magnitude higher than bare particle diffusion.[19,20] We demonstrate here how this non-equilibrium phenomenon can be harnessed to take control of the molecular-scale transport involved in mixing and thus modify the overall mixing properties of suspended particles. Indeed we show for the first time that creating an inhomogeneous chemical environment by adding only traces of salt deeply alters the mixing dynamics of the colloidal suspension, which can be either boosted or inhibited. Moreover, we present a simple model which allows bridging between the onset of non-equilibrium nano-scale transport and the large-scale mixing properties.

Experimentally, the mixing of a suspension made of fluorescent colloids (200 nm diameter polystyrene, 0.02% w/v) with an aqueous buffer solution (1 mM Tris, pH = 9) is studied under laminar chaotic flows. This is done thanks to a Y-shaped

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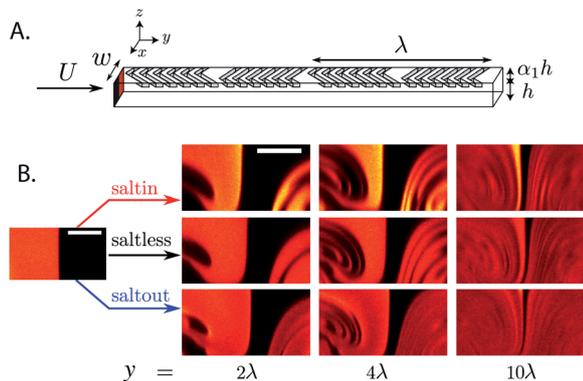
Fig. 1 Salt effect on chaotic mixing of suspended particles. (A) Sketch of a chaotic mixing experimental setup: a suspension of fluorescent colloids (orange) and a raw buffer solution (black) are injected at a constant flow rate into separate feeding channels (not shown) which merge into the main channel of a Staggered Herringbone Micromixer[10] ($w = 200$ μm, $h = 115$ μm, $\lambda = 2$ mm, $\alpha_1 = 0.35$) where chaotic mixing of the two solutions takes place. (B) Evolution of the suspension mixing process in the presence of salt: cross-section images of the central portion of the mixing channel at different locations l after merging of the solutions (white scale bar: 50 μm; mean flow velocity $U = 8.6$ mm s^{-1}). Central row: reference mixing process without salt (saltless configuration); upper and lower rows: effects of additional salt solute (20 mM LiCl) either into the colloidal suspension (salt-in configuration) or into the co-flowing buffer solution (salt-out configuration).

microfluidic device (Fig. 1A) where the two solutions to mix merge into the main channel of a Staggered Herringbone Micromixer (SHM).[10,21–23] Cross-section images are captured with a confocal microscope at different channel locations y from the inlet (see Fig. 1A and ESI† for further details). This allows us to follow the evolution of the mixing process with elapsed time $t = y/U$ or with the number of stretch and fold cycles y/λ, with U being the mean downstream flow velocity and λ is the length of one SHM cycle. While the flow lies in the laminar regime, ensuring convenient reproducibility and stationarity conditions for experiments, this SHM was shown to generate a chaotic mixing process,[9,10] see Fig. 1B, middle.

Now, keeping the global hydrodynamics unchanged, we observe in Fig. 1B that adding a small amount of a passive molecular solute (20 mM LiCl salt) to one of the two solutions has a very noticeable impact on the mixing process. Indeed when the salt is added to the colloidal suspension (salt-in configuration, Fig. 1B, top), initial stages of mixing show an increased concentration of the colloidal suspension associated with thinner and brighter fluorescent filaments with sharper edges as compared to the saltless reference mixing. A "pinch of salt" in the particle phase thus counteracts the homogenization within the mixing process, usually provided by the coupling with local diffusion.

In contrast, when the salt is added to the buffer solution (salt-out configuration, Fig. 1B, bottom), mixing is again modified but with opposite consequences. Initial stages of mixing now show thicker and dimmer fluorescent filaments with blurred edges (see e.g. $y/\lambda = 4$ in Fig. 1B). There a trace concentration of salt has a clear enhanced mixing effect.

Indeed, compared to the previous salt-in experiment, the main central colloidal tongue appears 2–3 times wider, while the right-hand stack of colloidal filaments has fully homogenized. Importantly, we stress that with salt contrast from ∼1 mM in buffer solvent to 20 mM in salty solution, no density or viscosity mismatches nor any flocculation or interparticle interactions can be at stake here.

These observations are confirmed by a more quantitative analysis, using the normalized standard deviation of the colloid concentration field $\sigma = \sqrt{\langle c^2 \rangle - \langle c \rangle^2}/\langle c \rangle$ to quantify mixing (where the concentration in colloids c was checked to be proportional to the fluorescence intensity). As shown in Fig. 2, this analysis confirms the previous picture: the presence of salt in the outer solution results in a faster decrease of the concentration inhomogeneities as compared to the saltless case, while, on the opposite, the salt added to the colloidal suspension delays homogenization. In the following, we define a mixing length y_m using a threshold value as $\sigma(y_m) = \sigma_c = 0.3$.

With all flow parameters unchanged, our experiments clearly point to the importance of molecular effects in mixing processes. Such effects are known to occur in the homogenization step, where it is classically assumed that coupling with molecular diffusion allows for local cross-filament transport. The signature of molecular diffusivity has been reported so far in chaotic[10,21] or moderately turbulent[8,12] mixing flows. Qualitatively, mixing is achieved when the diffusional spreading length L_D compares with the typical width of the stretched filaments, say L_s. One readily expects $L_D \sim \sqrt{Dy_m/U}$, with D being the molecular diffusivity of the mixed species, while in a fully chaotic flow $L_s \sim (w/2)\exp(-y_m/\delta)$, with w being the channel width and δ the stretching length.[10] This predicts a weak signature of molecular effects on the mixing length y_m in the form $y_m \sim \log(Uw/D)$.

As shown in Fig. 3, this crude argument captures the main effect of molecular diffusivity on mixing in saltless solutions. In this graph, the mixing length y_m is plotted – for a given flow velocity U – versus the molecular diffusivity of the suspended
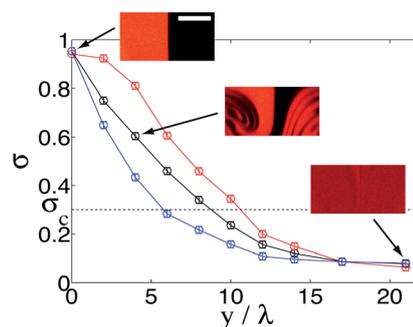

Fig. 2 Normalized standard deviation $\sigma = \sqrt{\langle c^2 \rangle - \langle c \rangle^2}/\langle c \rangle$ of the colloid concentration c in the channel cross-section as a function of the location y/λ for the three mixing configurations (mean flow velocity $U = 8.6$ mm s^{-1}): salt-in (red), saltless (black), salt-out (blue); with salt solutions incorporating 20 mM LiCl. Three corresponding cross-sections are shown for illustration (saltless case). Mixing length y_m (see text) is defined at a standard deviation threshold set to $\sigma_c = 0.3$.
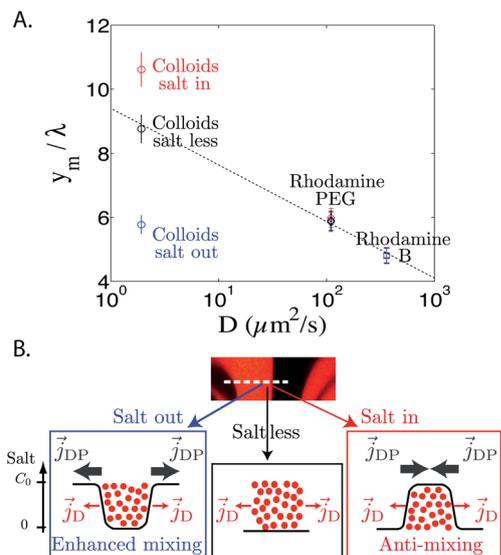
Fig. 3 (A) Reduced mixing length y_m/λ as a function of molecular diffusivity D (mean flow velocity $U = 8.6$ mm s^{-1}): ($\square$) Rhodamine B dye, ($\diamondsuit$) Rhodamine–PEG5000, ($\bigcirc$) 200 nm diameter colloids. Colors correspond to different salt configurations: black, saltless solutions; red, salt-in (20 mM LiCl salt with a colloidal suspension); blue, salt-out (20 mM LiCl salt with coflowing solution). Note that saltless, salt-in and salt-out results are almost undistinguishable for Rhodamine B and Rhodamine–PEG. B Diffusiophoretic transport in chaotic mixing: sketch of the underlying salt gradients at the edges of mixing filaments of the colloidal suspension. For salt-in and salt-out configurations, total cross-filament flux of colloids (red beads) reads $\vec{J}_c = \vec{J}_D + \vec{J}_{DP}$, with bare diffusive flux $\vec{J}_D$ dominated by orders of magnitude[17,19] by diffusiophoretic transport $\vec{J}_{DP}$. One thus expects boosted-mixing (salt-out, left) or anti-mixing (salt-in, right).

particles, from molecules to colloids (see ESI† for further details), with diffusivities spanning more than 2 orders of magnitude. The measured evolution is compatible with the log dependency expected for chaotic flows, as reported previously for this SHM geometry whereby the effect of changing flow velocity U was probed.[10]

Now, as is evident from Fig. 3, the salt effects as a co-mixing solute do not fit into this Brownian diffusion paradigm for molecular transport. While no change is observed for the molecular dye and the short PEG polymer, in line with the absence of variations in bulk properties, colloids show very different behavior. Indeed, with colloid diffusivity rigorously unchanged, salt-in and salt-out configurations delay or boost mixing as if the molecular transport was changed by about 3 orders of magnitude (as would be measured in the "diffusivity scale" Fig. 3A). As we show now, this is a striking manifestation of the onset and influence of an out-of-equilibrium local transport mechanism (here diffusiophoresis) overtaking classical diffusion.

Diffusiophoretic transport refers to the migration of particles (colloids or macromolecules) induced by gradients of the solute. This subtle phenomenon of osmotic origins was studied in pioneering studies by Anderson, Prieve, and co-workers[14,24] and recently received in-depth characterization of its effects on the migration, trapping or patterning of particles.[17–20,25] For salt

as a solute with a concentration field C_s, saline gradients induce a diffusiophoretic drift velocity of a particle as

$$V_{DP} = D_{DP}\nabla\log C_s, \qquad (1)$$

where the diffusiophoretic (DP) mobility D_{DP} has the dimension of molecular diffusivity.[24] While the theoretical expression of D_{DP} includes the particle's surface charge and salt-type corrections,[19,24] it is typically much larger than the bare colloid diffusion coefficient ($D_{DP}/D \gg 1$), and close to small molecule fast diffusivities (here $D_{DP} \simeq 290$ μm^2 s^{-1} (ref. 17)). In contrast, because both PEG and Rhodamine B bear no charge, and have intrinsic fast diffusivities, we do not expect diffusiophoresis to affect solute transport, in line with results from Fig. 3A.

Coming back to the colloidal suspension mixing problem, it is now possible to propose a rationalization of the observed salt effects on the basis of this diffusiophoretic mechanism. As sketched in Fig. 3B, the salt concentration fields C_s exhibit strong gradients localized at the edges of the stretched filaments, thereby triggering a supplementary DP migration of the nearby colloids toward high salt concentrations, see eqn (1). This will induce an accelerated spreading of the colloid profile for salt-out and conversely inhibit mixing for salt-in, in full agreement with the observed behavior in Fig. 3A. This effect is measured systematically for colloids, for all flow velocities or SHM geometries probed as shown in the inset of Fig. 4 where the salt-in and salt-out mixing lengths, normalized by the saltless reference case y_m^0, are plotted against the Peclet number. Finally we need to emphasize that this effect shows up here although the salt concentration remains quite low (20 mM). This is a key consequence of the log dependency in eqn (1)
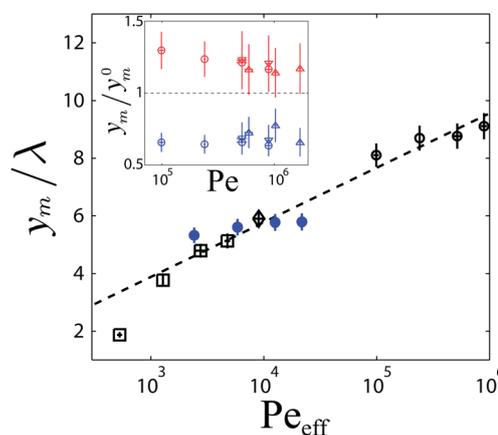

Fig. 4 Reduced mixing length y_m/λ as a function of – effective – Péclet number Pe$_{eff}$ for different velocities, molecular species and salt content (SHM geometrical parameters as in Fig. 1). No salt: Rhodamine B ($\square$), Rhodamine PEG5000 ($\diamondsuit$), saltless 200 nm colloids ($\bigcirc$); 20 mM LiCl salt contrast: salt-out 200 nm colloids ($\bullet$); Pe$_{eff}$ calculated according to eqn (7). The black dashed line represents a log evolution of Pe$_{eff}$. Inset: salt effects on mixing length for colloids y_m/y_m^0 as a function of the Pe number, for different SHM geometrical characteristics. Salt-less mixing length y_m^0 is used as a normalization for saltless (red) and salt-out (blue) data. SHM specifications as in Fig. 1 except for α: $\alpha_1 = 0.35$ ($\bigcirc$), $\alpha_2 = 0.40$ ($\triangle$) and $\alpha_3 = 0.36$ (∇).

allowing a response independent of the nominal solute concentration, in the limit of negligible background buffer,[19] and thus even for traces of solutes as recently demonstrated.[18]

Going beyond this analysis towards a more quantitative description of this effect constitutes an important challenge. It involves the coupling of two intrinsically complex mechanisms: the description of mixing and its complex interplay between flow deformation and local transport; together with the description of a molecular-scale non-equilibrium phenomenon controlling here local colloid dynamics. A first step in this direction can be performed by considering the simplified coupling framework proposed by Ranz for the chaotic laminar mixing process.[26] It consists of considering the reference frame of a stretched filament, whose axes are aligned with maximal compression and stretching directions, and reducing the homogenization to a 1D cross-filament dynamics.

For solute species where transport is only ruled by diffusion and flow-advection (*i.e.* single solute or saltless colloids), the Ranz model writes:

$$\partial_t c - \gamma x \partial_x c = D \partial_x^2 c, \tag{2}$$

with x being the direction perpendicular to the filament interface, and $\gamma \propto U$ is the principal strain rate. Transverse filament thickness evolves as $s(t) \sim s_0 \exp(-\gamma t)$, with $s_0 = w/2$ being the initial width. This equation is solved by a change of variables $\xi = x/s(t)$ and $\tau = D \int_0^t dt'/s^2(t')$, yielding a simple diffusion equation from which concentration profiles are obtained.[26,27] This yields a mixing time for purely advection–diffusion dynamics in the form:

$$t_m^0 = \frac{1}{2\gamma} \log(\text{Pe}/2), \tag{3}$$

where the Peclet number is defined in the model as $\text{Pe} = \gamma s_0^2/D \propto Uw/2D$. This predicts a logarithmic dependence of the mixing length $y_m^0 = U t_m^0$ in terms of the Peclet number. Despite the simplicity of the Ranz model, it is well consistent with our experimental results for single species mixing (Fig. 3A), in agreement with the literature.[10,21,27]

It is now possible to extend this framework to include the supplementary colloid DP migration. While the salt concentration C_s is still ruled by eqn (2), the cross-filament dynamics of the colloid concentration c in salt-in and salt-out now writes:

$$\partial_t c - \gamma x \partial_x c + \partial_x[V_{\text{DP}} c] = D_c \partial_x^2 c, \tag{4}$$

with V_{DP} given by (1), and D_c is the colloid diffusivity. In the reduced variables (ξ, τ_s) associated with salt dynamics, eqn (4) transforms into

$$\partial_{\tau_s} c + \partial_\xi \left[\left(\frac{s V_{\text{DP}}}{D_s} \right) c \right] \simeq 0, \tag{5}$$

where a diffusive term of order $D_c/D_s \ll 1$ was neglected, with D_s being the salt diffusivity. Information on the filament interface position $\xi = \Xi(\tau_s)$ can be obtained using the method of characteristics, leading to $d\Xi/d\tau_s = s(\tau_s)V_{\text{DP}}(\Xi(\tau_s), \tau_s)/D_s$. For short

times and small interface displacements τ_s, $\xi \ll 1$, the salt concentration $C_s(\xi, \tau_s)$ decreases to $c_0(1 + \xi/\sqrt{\pi\tau_s})/2$ and one may obtain an expression for the interface displacement $\Delta\Xi = \Xi(\tau_s) - \Xi(0)$ as:

$$\Delta\Xi \simeq \pm 2 \frac{D_{\text{DP}}}{D_s} \sqrt{\frac{\tau_s}{\pi}}, \tag{6}$$

valid for short times; the sign $\pm$ corresponds to the salt-out and salt-in cases respectively.

Let us now focus on the salt-out case. One defines the reduced mixing time τ_s^{out} as the time when the interface reaches the next colloidal suspension filament ($\xi = \pm 1/2$). This is obtained as $\tau_s^{\text{out}} = D_s/2D_{\text{eff}}$, where we introduced an effective diffusion coefficient defined as $D_{\text{eff}} = 8D_{\text{DP}}^2/(\pi D_s)$, in line with Abécassis *et al.*[17,19,20] One deduces accordingly,

$$y_m^{\text{out}} \equiv U \times t_m^{\text{out}} = \frac{U}{2\gamma} \log(\text{Pe}_{\text{eff}}/2), \tag{7}$$

where we defined an effective Péclet number in the form $\text{Pe}_{\text{eff}} = 2\gamma s_0^2/D_{\text{eff}} = (2D_c/D_{\text{eff}})\text{Pe}$.

A comparison with eqn (3) suggests that in the salt-out configuration the effect of diffusiophoresis can be mapped onto the classical mixing framework, provided the bare molecular diffusivity D_c is replaced by an effective diffusivity $D_{\text{eff}}/2$ ($D_{\text{eff}} = 157 \ \mu\text{m}^2 \ \text{s}^{-1}$). Accordingly the relevant Peclet number is defined in terms of the effective diffusion coefficient D_{eff}. Since $D_{\text{eff}} \gg D_c$, we now expect large particles to mix as fast as small molecules in the co-mixing configuration. While the mixing length is only a weak (logarithmic) function of the Peclet number, the huge change in effective diffusion leads to a quantitative change in the mixing efficiency. This prediction is tested in Fig. 4 where the experimental mixing lengths y_m/λ obtained for various velocities and salt configurations are plotted against the effective Peclet number Pe_{eff} defined above. Although we do not expect this generalized Ranz model to capture the full complexity of the mixing process, it indeed provides an insightful framework that well captures the importance and basic mechanisms of this molecular co-mixing phenomenon.

Finally, in contrast to the salt-out configuration, the analysis for the salt-in case requires accounting for the – until now neglected – diffusive transport, which becomes the dominant mechanism for mixing at long time intervals. While the above framework indeed predicts focusing of the colloid profiles at early times – thus with no possible diffusivity mapping, a full quantitative analysis is far more complex and we leave it for future investigations.

In conclusion, we demonstrate that traces of salt can considerably impact the chaotic mixing of suspensions: here synthetic colloids, but it generalizes to charged molecules,[15,17] silica[19] or clay particles, *etc.* This arises from a shift in molecular transport, with canonical diffusion overtaken by diffusiophoresis. Unlike physically applied fields, the chemical driving force under diffusiophoresis evolves under flow as a mirror of the colloid distribution, thus providing especially relevant and efficient transport unusually bridging across widely separated scales.

Beyond the here-demonstrated interest at the microfluidic scale, we stress that diffusiophoresis should show up whenever

colloids, particles or molecules evolve in an inhomogeneous chemical background. Combined with the fact that chaotic mixing can be viewed as a prototypal building block for turbulent mixing, this suggests that tuning the local transport properties may yield possible implications at upper-scales,[28] in a broad range of situations from bio-reactors to estuaries where fresh water full of sediments meets the salty seawater, see *e.g.* ref. 29. Indeed, in the context of marine biology, the local non-equilibrium dynamics of bio-organisms, revealed at the micro-scale, has been hinted as a crucial factor for ocean-scale distribution.[30–34]

Acknowledgements

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