Chaotic mixing in effective compressible flows

R. Volk,[1,*] C. Mauger,[2] M. Bourgoin,[3] C. Cottin-Bizonne,[4] C. Ybert,[4] and F. Raynal[2]

[1]*Laboratoire de Physique de l'ENS de Lyon, CNRS UMR5672 and Université de Lyon, Lyon, France*
[2]*LMFA, CNRS UMR5509, École Centrale Lyon, INSA de Lyon and Université de Lyon, Lyon, France*
[3]*LEGI, CNRS UMR5519, Université Joseph Fourier, Université de Grenoble, Grenoble INP, France*
[4]*Institut Lumière Matière, CNRS UMR5306, Université Claude Bernard Lyon 1, Université de Lyon, Lyon, France*

We study numerically joint mixing of salt and colloids by chaotic advection and how salt inhomogeneities accelerate or delay colloid mixing by inducing a velocity drift $\mathbf{V}_{\mathrm{dp}}$ between colloids and fluid particles as proposed in recent experiments [J. Deseigne *et al.*, Soft Matter **10**, 4795 (2014)]. We demonstrate that because the drift velocity is no longer divergence free, small variations to the total velocity field drastically affect the evolution of colloid variance $\sigma^2 = \langle C^2 \rangle - \langle C \rangle^2$. A consequence is that mixing strongly depends on the mutual coherence between colloid and salt concentration fields, the short time evolution of scalar variance being governed by a new variance production term $P = -\langle C^2 \nabla \cdot \mathbf{V}_{\mathrm{dp}} \rangle / 2$ when scalar gradients are not developed yet so that dissipation is weak. Depending on initial conditions, mixing is then delayed or enhanced, and it is possible to find examples for which the two regimes (fast mixing followed by slow mixing) are observed consecutively when the variance source term reverses its sign. This is indeed the case for localized patches modeled as Gaussian concentration profiles.

PACS number(s): 47.61.Ne, 47.51.+a, 47.52.+j

I. INTRODUCTION

Mixing of a scalar field C by laminar flows with chaotic trajectories in a bounded or periodic domain is often characterized by the evolution of its variance $\langle C^2 \rangle$, a quantity known to decrease with time when the flow is incompressible and no source of scalar is present [1]. The case of mixing in compressible flows has received less attention: Vergassola and Avellaneda showed that a compressible flow can modify scalar transport either in stationary cellular flows or random delta correlated flows [2]; in the context of reactive flows, compressibility was proved to have a strong influence on chemical reactions or population growth [3,4] because it controls the local density of fluid particles. Surprisingly, if most flows encountered in nature are incompressible, advection diffusion by an effective compressible flow field arises naturally when mixing large molecules, colloids, or living cells in moderate Reynolds number flows. Even in the case of flow tracers, the presence of background inhomogeneities will result in a drift velocity $\mathbf{V}_{\mathrm{drift}}$ between the fluid flow $\mathbf{V}(\mathbf{r},t)$ and the transported species. This situation is encountered in a large variety of situations: thermophoresis (Soret effect) leads to a drift velocity proportional to the temperature gradient [5,6], diffusiophoresis is responsible for focusing and defocusing of colloids due to salt gradients [7,8], and chemotaxis allows living cells to move with a drift velocity linked to the local gradient of food [9]. In these three cases, the drift term is generally not divergence free because the inhomogeneous field does not satisfy the Laplace equation.

A recent experimental study showed how chaotic mixing of colloids is tuned by diffusiophoresis [10]. In this paper we demonstrate by means of numerical simulations that it is the compressible nature of the drift velocity which is responsible for this tuning and that it may produce unexpected effects such as an increase of scalar variance at small times.

---

*romain.volk@ens-lyon.fr

II. EQUATION AND FLOW FIELD

We study the mixing of colloids and salt with the respective concentrations $C(\mathbf{r},t)$ and $S(\mathbf{r},t)$ under the action of the velocity $\mathbf{V}(\mathbf{r},t)$. In the presence of salt gradients, electrokinetic effects result in a drift velocity $\mathbf{V}_{\mathrm{dp}} = \alpha \nabla \log S$ between the colloids and the fluid motion, with α being a constant with the dimension of a diffusion coefficient whose magnitude and sign depend on the precise nature of the salt and colloids [7,8]. Starting from a situation with initial concentration profiles $C_0(\mathbf{r})$ and $S_0(\mathbf{r})$, the time evolution of the concentrations is then given by the coupled advection diffusion equations:

$$\frac{\partial S}{\partial t} + \boldsymbol{\nabla} \cdot S\mathbf{V} = D_s \nabla^2 S, \tag{1}$$

$$\frac{\partial C}{\partial t} + \boldsymbol{\nabla} \cdot C(\mathbf{V} + \mathbf{V}_{\mathrm{dp}}) = D_c \nabla^2 C, \tag{2}$$

$$\mathbf{V}_{\mathrm{dp}} = \alpha \boldsymbol{\nabla} \log S, \tag{3}$$

where D_s and D_c are, respectively, the diffusion coefficients of the salt and colloids. In this situation, salt is mixed by the velocity field $\mathbf{V}$ independently of the colloids, while the colloid concentration is also coupled to the salt concentration through the drift velocity $\mathbf{V}_{\mathrm{dp}}$. In order to study the impact of the salt gradients on colloid mixing, we restrict ourselves to two-dimensional (2D) situations; we achieve chaotic mixing using a time periodic velocity field, the so-called sine flow that has been a standard tool for studies of chaos in spatially smooth flows [1,11,12]. We recall it is T periodic with two subcycles for which the velocity field is $\mathbf{V}(\mathbf{r},t) = (\sin(y),0)$ for $nT \leqslant t < (n+1/2)T$ and $\mathbf{V}(\mathbf{r},t) = (0,\sin(x))$ for $(n+1/2)T \leqslant t < (n+1)T$, which ensures the velocity field is divergence free at any time. For given initial concentration profiles $C_0(\mathbf{r})$ and $S_0(\mathbf{r})$, Eqs. (1) and (2) are solved with periodic boundary conditions using a pseudospectral method with a resolution of 512^2 for a square box of length $L = 2\pi$. We use an Adams-Bashford temporal scheme with order 2 and $dt = 0.002$ to ensure the scalar gradient and Laplacian are
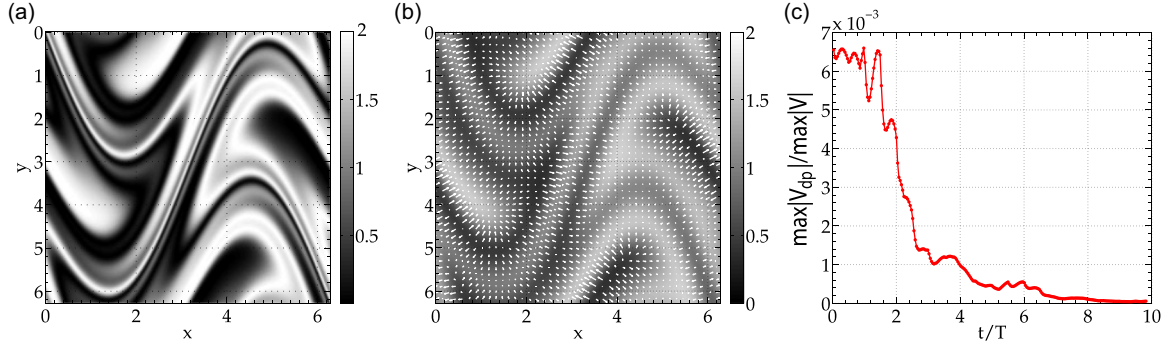
FIG. 1. (Color online) (a) Colloid concentration field at $t = 5T$ in the reference case ($D_c = 10^{-4}$, Pe = 65 000) for an initial concentration $C_0 = 1 + \sin(x)$. (b) Salt concentration field at $t = 5T$ for $S_0 = 1.01 + \sin(x)$ ($D_s = 10^{-2}$, $Pe_s = 650$) together with the corresponding drift velocity field $\mathbf{V}_{dp} = \alpha\nabla\log S$ with $\alpha = 0.001$. (c) Corresponding time evolution of nondimensional maximum drift velocity, $\max|\mathbf{V}_{dp}|/\max|\mathbf{V}|$.

well resolved for diffusivities in the range $D_c \in [10^{-4}, 10^{-2}]$, which corresponds to Péclet numbers in the range Pe = $\max|\mathbf{V}|L/D_c \in [0.065, 6.5]10^4$. For all simulations shown here we set $T = 0.8L/\max|\mathbf{V}|$; in this regime of nonglobal chaos (see Poincaré sections in Figs. 3–10 of Ref. [13]), as in many natural situations, one can distinguish between thin structures developing due to stretching and folding and poor mixing in regular regions which govern the long time decay of scalar variance [1]. Figure 1(a) displays the colloid concentration field obtained in the reference case $\mathbf{V}_{dp} = \mathbf{0}$, with Péclet number Pe = 65 000 and an initial profile $C_0(\mathbf{r}) = 1 + \sin(x)$, after five cycles of mixing.

When diffusiophoresis comes into play, the drift term $\mathbf{V}_{dp} = \alpha\nabla\log S$ depends on the instantaneous salt gradients. In order to be consistent with experiments [8,10], we set $\alpha = 0.001$ and $D_s = 0.01$ for all simulations, which corresponds to a Péclet number $Pe_s = 650$ for the salt. We define the initial salt concentration profile $S_0 = 1 + \sin(x) + s$, with $s = 0.01$ being an offset accounting for the unavoidable homogeneous background concentration of ionic species (buffer solution). As observed in experiments [10], one expects the drift term to modify colloid mixing depending on whether the initial colloid concentration field $C_0(x)$ is correlated, or anticorrelated, with the initial salt concentration profile $S_0(x)$. For all Péclet numbers we study the evolution of colloid concentration variance $\langle(C - \langle C\rangle)^2\rangle$ for two different initial profiles $C_0 = 1 \pm \sin(x)$ and compare the results to the reference case $\alpha = 0$. The drift velocity, which does not depend on $C(\mathbf{r}, t)$, is displayed in Fig. 1(b) together with the corresponding salt concentration field computed at $t/T = 5$. With the chosen parameters, the modification of the total velocity field acting on the colloids, $\mathbf{V} + \mathbf{V}_{dp}$, is never larger than 1%, as shown in Fig. 1(c). However, we will demonstrate that this small variation leads to a strong alteration of mixing because $\mathbf{V}_{dp}$ is not divergence free [Fig. 1(b)].

III. MIXING TIME

In Fig. 2, we display the evolution of the mixing time T_{mix} needed to decrease the initial colloid concentration variance by a factor of 2, as a function of the Péclet number Pe = $\max|\mathbf{V}|L/D_c$. As already observed in experiments [10],

when salt and the colloid are initially injected together [salt-in configuration, $C_0(\mathbf{r}) = 1 + \sin x \sim S_0(\mathbf{r})$], mixing is approximately 15% slower than in the reference case $\alpha = 0$. On the contrary, when salt and colloids are injected separately [salt-out configuration, $C_0(\mathbf{r}) = 1 - \sin x$ and $S_0(\mathbf{r}) = 1.01 + \sin x$], the mixing is nearly 20% faster. This result supports the idea that the action of diffusiophoresis can be seen as a modification of colloid transport properties through an effective diffusivity D_{eff} corresponding to an effective Péclet number Pe = $\max|\mathbf{V}|L/D_{eff}$. Using the curves $T_{mix}(\text{Pe})$, well fitted by a power law for the reference case (as usual for nonglobal chaos), one would then find $Pe_{eff} \sim 1.5Pe$ and $Pe_{eff} \sim 0.5Pe$ for the salt-in and salt-out configurations, respectively. This means that a correction to the velocity field smaller than 1% leads to a 50% change in the colloid effective diffusivity. This result proved to be quite robust when performing the same simulations with $T = 1.6L/\max|\mathbf{V}|$ (not shown here). In this
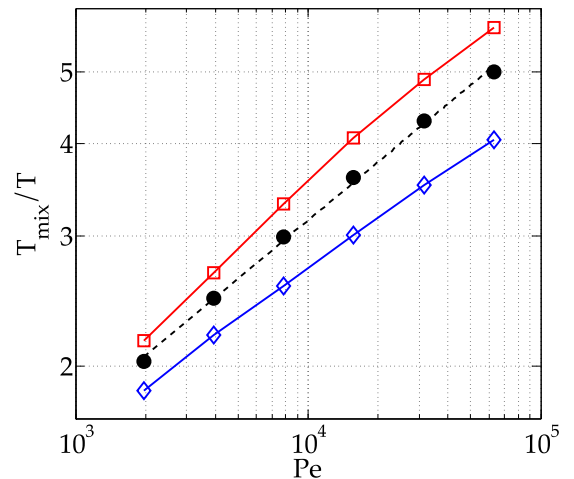

FIG. 2. (Color online) Mixing time T_{mix}/T as a function of the Péclet number Pe = $\max|\mathbf{V}|L/D_c$ as measured from time evolution of the variance $\sigma^2 = \langle C^2\rangle - \langle C\rangle^2$ with and without diffusiophoresis. For all cases $S_0 = 1.01 + \sin x$ with $D_s = 10^{-2}$ and $D_c = \in [10^{-4}, 10^{-2}]$. Circles: reference case with no diffusiophoresis $C_0 = 1 + \sin(x)$ and $\alpha = 0$. Dashed line: power law fit with exponent $\gamma = 0.26$. Squares: salt-in case $C_0 = 1 + \sin x$, $\alpha = 0.001$. Diamonds: salt-out case $C_0 = 1 - \sin(x)$, $\alpha = 0.001$.
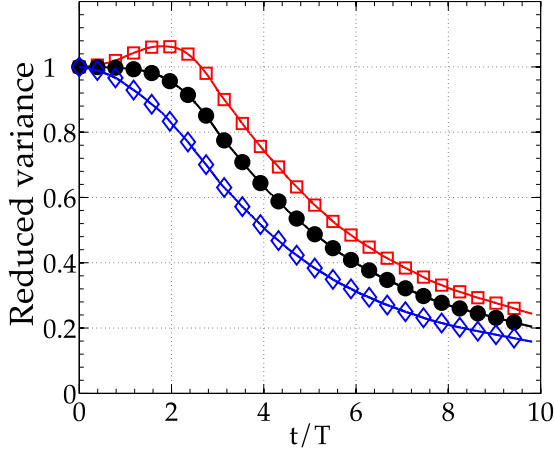
FIG. 3. (Color online) Time evolution of nondimensional colloid concentration variance $\sigma^2(t)/\sigma^2(0)$ with $\sigma^2(t) = \langle C^2 \rangle - \langle C \rangle^2$ and $S_0 = 1.01 + \sin(x)$, $D_s = 10^{-2}$, $D_c = 10^{-4}$. Circles: reference case with no diffusiophoresis $C_0 = 1 + \sin x$, $\alpha = 0$. Squares: salt-in case $C_0 = 1 + \sin x$, $\alpha = 0.001$. Diamonds: salt-out case $C_0 = 1 - \sin x$, $\alpha = 0.001$.

regime of global chaos we did not observe any significant difference concerning diffusiophoresis: if mixing is indeed enhanced with T_{mix} varying linearly with log(Pe), we found for all configurations (salt-in, salt-out) that T has a weak impact on the measured effective Péclet numbers.

IV. COMPRESSIBLE EFFECTS

However, this mean field approach based on T_{mix}, if interesting for interpreting the long time behavior, may not catch the short time evolution of colloid variance when concentration gradients are not generated yet, so that diffusion is negligible. As displayed in Fig. 3, if one always observes a decrease of scalar variance at small times in the salt-out and reference cases, the salt-in case is more appealing: the variance first increases for $t/T \leqslant 2$ before decreasing for $t/T \geqslant 2$. This short-time increase is incompatible with an effective diffusivity which would predict a variance decreasing with rate $d\langle C^2 \rangle/dt = -2D_{\text{eff}}\langle (\nabla C)^2 \rangle$, where $\langle \cdot \rangle$ stands for spatial averaging over one period of the flow. For a better understanding of the colloid variance evolution, one may then come back to Eq. (2) and derive an equation for the scalar energy C^2 valid for compressible flows. One obtains

$$\frac{1}{2}\frac{\partial C^2}{\partial t} + \nabla \cdot \left[(\mathbf{V} + \mathbf{V}_{\text{dp}})\frac{C^2}{2} - D_c C \nabla C \right]$$
$$= -D_c(\nabla C)^2 - \frac{C^2}{2}\nabla \cdot \mathbf{V}_{\text{dp}}.$$

This equation, although similar to the classical scalar energy budget, contains an additional term proportional to the drift velocity field compressibility $\nabla \cdot \mathbf{V}_{\text{dp}}$ that does not vanish in the present case. When averaging over one flow period, all terms written as a divergence disappear, and one obtains a new global scalar energy budget valid for compressible flows:

$$\frac{1}{2}\frac{d\langle C^2 \rangle}{dt} = -D_c\langle (\nabla C)^2 \rangle - \left\langle \frac{C^2}{2}\nabla \cdot \mathbf{V}_{\text{dp}} \right\rangle. \quad (4)$$
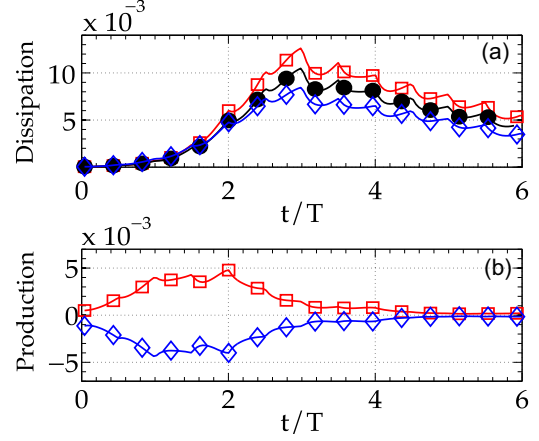

FIG. 4. (Color online) (a) Time evolution of colloid concentration dissipation $|\varepsilon_c| = D_c \langle (\nabla C)^2 \rangle$. Circles: reference case with no diffusiophoresis. Squares: salt-in case. Diamonds: salt-out case. (b) Corresponding time evolution of production term $P = -\langle C^2 \nabla \cdot \mathbf{V}_{\text{dp}} \rangle / 2$.

Because mean scalar concentration remains conserved even in the case of compressible flows, this equation also gives the evolution of scalar variance $\sigma^2 = \langle C^2 \rangle - \langle C \rangle^2$. Therefore scalar variance in compressible flows results in the competition between scalar dissipation $\varepsilon_c = -D_c\langle (\nabla C)^2 \rangle$ and production $P = -\langle C^2 \nabla \cdot \mathbf{V}_{\text{dp}} \rangle / 2$, the latter being proportional to the mutual coherence between C^2 and the total flow field compressibility $\nabla \cdot \mathbf{V}_{\text{dp}}$. This equation, well verified in our case at any time step, helps us understand the evolution of scalar variance in the presence of diffusiophoresis. As seen in Fig. 4(a), dissipation alone cannot explain the observed differences in scalar variance at short times; indeed, for large-scale initial concentration profiles, ε_c remains weak until small-scale fluctuations have been created by stretching and folding. For the two first mixing cycles $t/T \leqslant 2$, the evolution of the variance is then governed by the production term $P = -\alpha\langle C^2 \nabla^2 \log S \rangle / 2$, positive for the salt-in configuration and negative for the salt-out configuration, as demonstrated in Fig. 4(b). This effect disappears when the salt has been mixed. Considering the Péclet number of the salt (Pe$_s$ = 650), Fig. 2 shows the mixing time is of the order of two mixing cycles, which means salt is totally mixed at $t = 2T_{\text{mix}} \sim 4T$. For $t \geqslant 4T$ both the drift velocity field and the production term have become very weak [Figs. 1(c) and 4], so that the decay of variance is mainly governed by scalar dissipation thereafter. We may then conclude that diffusiophoresis is globally impacting mixing because compressibility modifies the colloid concentration field at small times while regular mixing of this modified initial condition follows, shifted in time.

Up to now we have dealt with modal ($\sin x$) and therefore "nonlocalized" initial conditions for C_0 and S_0. However, since mixing in the presence of diffusiophoresis is governed by the coherence between salt and colloid concentration, it strongly depends on initial conditions. Therefore it is interesting to look at more realistic situations where the initial condition is a patch of fluid. For instance, one can compare situations of a patch of salt plus colloids introduced in pure water (salt-in situation) to
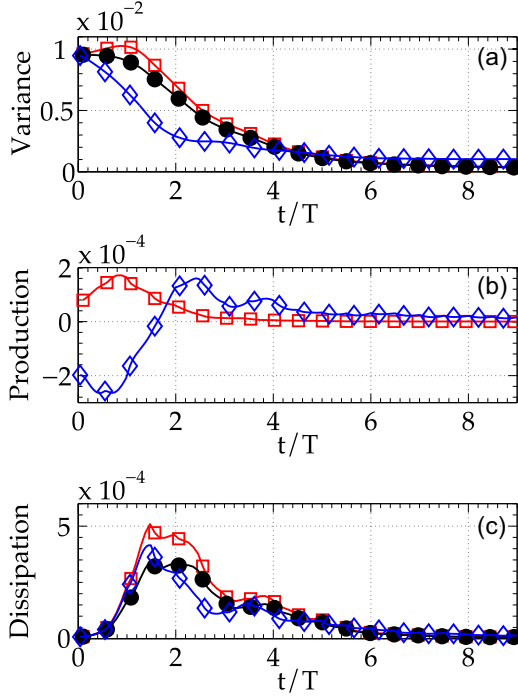
FIG. 5. (Color online) (a) Time evolution of colloid concentration variance for a patch of salt $S_0 = 0.01 + \exp[-4(x^2 + y^2)]$ with $D_s = 10^{-2}$, $D_c = 10^{-4}$. Circles: reference case with no diffusiophoresis $C_0 = \exp[-4(x^2 + y^2)]$, $\alpha = 0$. Squares: salt-in case $C_0 = \exp[-4(x^2 + y^2)]$ and $\alpha = 0.001$. Diamonds: salt-out case $C_0 = 1 - \exp[-4(x^2 + y^2)]$ and $\alpha = 0.001$. (b) Time evolution of production term $P = -\langle C^2 \nabla \cdot \mathbf{V}_{\mathrm{dp}} \rangle / 2$. (c) Corresponding time evolution of dissipation term $|\varepsilon_c| = D_c \langle (\nabla C)^2 \rangle$.

the one of a patch of salty solution surrounded by well-mixed, salt-free colloids (salt-out situation). These situations can be reproduced with Gaussian profiles $S_0 = \exp[-4(x^2 + y^2)]$ for which the salt-in and salt-out configurations would correspond to $C_0 = \exp[-4(x^2 + y^2)]$ and $C_0 = 1 - \exp[-4(x^2 + y^2)]$, respectively. For these Gaussian initial concentration profiles, if the no-salt and salt-in configurations lead to similar variance evolutions as the ones in Fig. 3, one observes an unexpected evolution with two time scales for the salt-out configuration [Fig. 5(a)]. After very fast mixing at short times $t \leqslant 2T$, colloids start to mix at a reduced speed so that, finally, the salt-out configuration is less efficient for mixing on long time scales. This again can be understood by looking at the evolution of the production term displayed in Fig. 5(b), a quantity much larger than dissipation at small times for these still large-scale initial configurations [Fig. 5(c)]. Indeed, if P remains always positive for the salt-in case as shown in Fig. 5(b), it is negative at short times for the salt-out case before becoming positive for $t \geqslant 1.8$.

This is because the salt-out case (with $C_0 = 1 - \exp[-4(x^2 + y^2)]$) corresponds to a situation where colloids are present almost everywhere compared to the salt-in case $C_0 = \exp[-4(x^2 + y^2)]$. Because salt mixes much more efficiently than colloids, the patch of salt spreads rapidly as time increases, until the front of salt concentration (with high gradients of salt responsible for diffusiophoresis) enters regions with initially homogeneous colloid concentration and
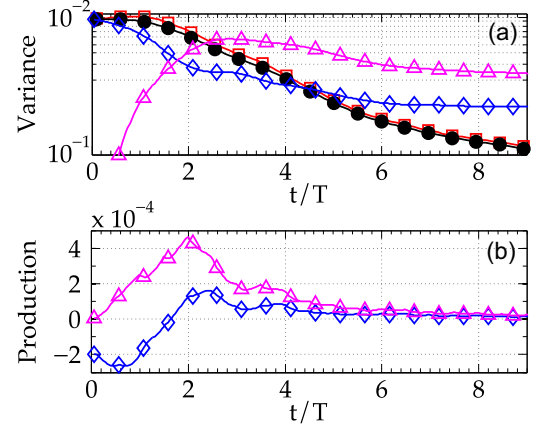

FIG. 6. (Color online) (a) Circles, squares, and diamonds are the same as in Fig. 5(a), plotted in semilogarithmic coordinates. Triangles: corresponding demixing configuration with an homogeneous initial colloid concentration $C_0 = 1$. (b) Time evolution of production term $P = -\langle C^2 \nabla \cdot \mathbf{V}_{\mathrm{dp}} \rangle / 2$ for the same salt-out configuration as in Fig. 5(b) (diamonds) and the demixing configuration (triangles).

starts to unmix. To better understand the salt-out configuration we simulated a pure demixing configuration with an initial homogeneous concentration $C_0 = 1$, for which initial variance, production, and dissipation vanish. These results, presented in log scale in Fig. 6(a), show that if the long time behavior of the salt-in and reference cases are identical, the variance decrease of the salt-out case is much slower, similar to the one of pure demixing. In this latter case, variance production increases at short time because the concentration increases in regions where $\nabla \cdot \mathbf{V}_{\mathrm{dp}}$ is negative and decreases in regions where $\nabla \cdot \mathbf{V}_{\mathrm{dp}} > 0$. As a consequence the concentration pattern created has a strong correlation with $\nabla \cdot \mathbf{V}_{\mathrm{dp}}$, and the production term reaches a very high value after two cycles of mixing [Fig. 6(b)], leading to a very slow variance decrease, as already observed for the salt-out case.

V. CONCLUSION

We have studied 2D chaotic mixing of colloids under the action of diffusiophoresis, which produces a velocity drift and makes colloids no longer be tracers of the flow motion. We have demonstrated that this very small drift, which leads to a correction to the velocity field smaller than 1%, is responsible for an important change in mixing because it strongly modifies the topology of the total flow, which is no longer divergence free. This compressibility is at the origin of the scalar variance production term $P = -\langle C^2 \nabla \cdot \mathbf{V}_{\mathrm{dp}} \rangle / 2$, necessary to understand (i) the evolution of scalar variance at small times, not explained in the framework of effective diffusion for the salt-in case, and (ii) acceleration or delay of mixing depending on the coherence between salt and colloid concentration fields. One remarkable property of this compressible effects is the capacity to unmix an initially homogeneous colloidal solution by simply adding salt gradients. If the present results were obtained on the physical case of colloid mixing in the presence of chemical gradients, they are more general and may play an important role in cell dynamics because the

total flow is compressible [9]. Effective flow compressibility should also apply to temperature gradients (Soret effect) and may help us understand older experiments of DNA trapping and amplification in laminar thermally driven flows [6], the Laplacian of the temperature field being an image of the local DNA concentration. Finally, we note these compressibility effects are not a manifestation of only laminar mixing. They are also observed in particle laden turbulent flows providing the particles do not follow the fluid motions because they have inertia [14,15] or because they are sensitive to gravitational field [16]. Bridging between the different results, this suggests

the possibility of a common frame of description for turbulent clustering and diffusiophoretic mechanisms via compressible effects.

[1] R. Pierrehumbert, Chaos Solitons Fractals **4**, 1091 (1994).

[2] M. Vergassola and M. Avellaneda, Phys. D (Amsterdam, Neth.) **106**, 148 (1997).

[3] P. Perlekar, R. Benzi, D. R. Nelson, and F. Toschi, Phys. Rev. Lett. **105**, 144501 (2010).

[4] S. Pigolotti, R. Benzi, M. H. Jensen, and D. R. Nelson, Phys. Rev. Lett. **108**, 128102 (2012).

[5] C. Soret, Arch. Sci. Phys. Nat. Geneva **2**, 48 (1879).

[6] D. Braun and A. Libchaber, Phys. Rev. Lett. **89**, 188103 (2002).

[7] J. L. Anderson, Annu. Rev. Fluid Mech. **21**, 61 (1989).

[8] B. Abécassis, C. Cottin-Bizonne, C. Ybert, A. Ajdari, and L. Bocquet, New J. Phys. **11**, 075022 (2009).

[9] J. Muñoz García, Z. Neufeld, and C. Torney, New J. Phys. **12**, 103043 (2010).

[10] J. Deseigne, C. Cottin-Bizonne, A. D. Stroock, L. Bocquet, and C. Ybert, Soft Matter **10**, 4795 (2014).

[11] F. J. Muzzio, M. M. Alvarez, S. Cerbelli, M. Giona, and A. Adrover, Chem. Eng. Sci. **55**, 1497 (2000).

[12] K. Ngan and J. Vanneste, Phys. Rev. E **83**, 056306 (2011).

[13] *Handbook of Industrial Mixing: Science and Practice*, edited by E. L. Paul, V. A. Atiemo-obeng, and S. M. Kresta (Wiley-Interscience, Hoboken, NJ, 2003).

[14] M. Maxey, J. Fluid Mech. **174**, 441 (1987).

[15] R. A. Shaw, Annu. Rev. Fluid Mech. **35**, 183 (2003).

[16] W. M. Durham, E. Climent, M. Barry, F. De Lillo, G. Boffetta, M. Cencini, and R. Stocker, Nat. Commun. **4**, 2148 (2013).