

MIXING

The word mixing is used both as a general term defining the operation of putting two or more substances together in order to achieve uniformity and as a mathematical term defining the property of random processes. Mixing as an operation is widespread both as a natural phenomenon and an industrial process. Putting milk into coffee, preparing cement, and pushing a car accelerator pedal involve mixing liquids, granular materials, and gases. On a molecular scale, it is diffusion which provides mixing. When diffusion is caused solely by the gradient of concentration $\theta(\mathbf{r}, t)$, it is described by the second-order partial differential equation

$$\frac{\partial \theta}{\partial t} = \operatorname{div}(\kappa \nabla \theta). \quad (1)$$

When the diffusivity κ is constant, (1) is a linear parabolic equation which can be solved by using the Green function: $\theta(\mathbf{r}, t) = (4\pi\kappa t)^{-d/2} \int \exp[-(\mathbf{r} - \mathbf{r}')^2/4\kappa t] \theta(\mathbf{r}', 0) d\mathbf{r}'$.

The diffusivity of gases in gases is of order $10^{-1} \text{ cm}^2 \text{s}^{-1}$ so it would take many hours for an odor to diffuse across the dinner table. Similarly, to diffuse salt to a depth of 1 km in the ocean molecular diffusion would take 10^7 years. It is the motion of fluids that provides large-scale mixing in most cases. In a moving fluid, θ satisfies the advection-diffusion equation:

$$\frac{\partial \theta}{\partial t} + (\mathbf{v} \cdot \nabla) \theta = \operatorname{div}(\kappa \nabla \theta). \quad (2)$$

If the velocity gradient is λ then one can define a diffusion scale $r_d = \sqrt{\kappa/\lambda}$ comparing advective and diffusive terms in (2). Fluid motion and molecular diffusion provide for mixing at the scales respectively larger and smaller than r_d . Inhomogeneous flow brings into contact fluid parcels with different values of θ thus producing large gradients that are then eliminated by molecular diffusivity. How fast mixing proceeds and how concentration variance decays in time depends on how inhomogeneous the flow is.

When a velocity field fluctuates, the simplest quantity (and often most important) is the concentration averaged over velocity, $\langle \theta(\mathbf{r}, t) \rangle$. The behavior of this quantity is determined by the properties of Lagrangian velocity $\mathbf{V}(t) = \mathbf{v}[\mathbf{q}(t), t]$ which is taken on the trajectory that satisfies $d\mathbf{q}/dt = \mathbf{v}[\mathbf{q}(t), t]$. For times longer than the Lagrangian correlation time, $\langle \theta(\mathbf{r}, t) \rangle$ also satisfies the diffusion equation

$$\left[\partial_t - (\kappa \delta_{ij} + D_{ij}) \nabla_i \nabla_j \right] \langle \theta(\mathbf{r}, t) \rangle = 0,$$

with so-called eddy diffusivity

$$D_{ij} = \frac{1}{2} \int_0^\infty \langle V_i(0) V_j(s) + V_j(0) V_i(s) \rangle ds.$$

If we release a single spot of, say, a pollutant then its average position is given by $\langle \theta(\mathbf{r}, t) \rangle$. On the other hand, the evolution of the spot itself depends on the spatial properties of the velocity field. In considering hydrodynamic mixing at a given scale, one usually distinguishes between two qualitatively different classes of velocity fields: spatially smooth and nonsmooth. Velocity can be considered spatially smooth on a given scale if the velocity gradient does not change much across the scale. Comparing the inertial term $(\mathbf{v} \cdot \nabla) \mathbf{v}$ to the viscous term $\nu \Delta \mathbf{v}$ in the Navier-Stokes equation for fluid motion, one defines the viscous scale η similarly to r_d . Turbulent flows are smooth at scales smaller than η (viscous interval) and non-smooth at larger scales (inertial interval). Fluid particles separate exponentially with time in smooth flows and according to power laws in nonsmooth flows. Despite the fact that the fluid viscosity ν (momentum diffusivity) is caused by the same molecular motion as κ (diffusivity of a substance), their ratio varies widely depending on the type of material. That ratio is called the Schmidt number or Prandtl number when θ is temperature. The Schmidt number is very high for viscous liquids and also for colloids and aerosols, since the diffusivity of, say, micron-size particles (e.g., cream globules in milk and smoke in the air) is six to seven orders of magnitude less than the viscosity of the ambient fluid. In those cases, $r_d \ll \eta$. At scales less than η , the flow is spatially smooth and the velocity difference between two fluid particles can be presented as $\mathbf{v}(\mathbf{q}_1, t) - \mathbf{v}(\mathbf{q}_2, t) = \hat{\sigma}(t) \mathbf{R}(t)$ so that the separation $\mathbf{R} = \mathbf{q}_1 - \mathbf{q}_2$ obeys the ordinary differential equation

$$\dot{\mathbf{R}}(t) = \sigma(t) \mathbf{R}(t),$$

leading to the linear propagation $\mathbf{R}(t) = W(t) \mathbf{R}(0)$. The main statistical properties of $\mathbf{R}(t)$ can be established at the limit when t exceeds the correlation time of the strain matrix $\hat{\sigma}(t)$. The basic idea (going back to the works of Lyapunov, Furstenberg, Oseledec and many others and developed in the theory of dynamical chaos) is to consider the positive symmetric matrix $W^T W$ which determines R . The main result states that in almost every realization of $\hat{\sigma}(t)$, the matrix $t^{-1} \ln W^T W$ stabilizes as $t \rightarrow \infty$. In particular, its eigenvectors tend to d fixed orthonormal eigenvectors \mathbf{f}_i . To understand that intuitively, consider some fluid volume, say a sphere, which evolves into an elongated ellipsoid at later times. As time increases, the ellipsoid is more and more elongated and it is less and less likely that the hierarchy of the ellipsoid axes will change. The

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limiting eigenvalues

$$\lambda_i = \lim_{t \rightarrow \infty} t^{-1} \ln |W \mathbf{f}_i| \quad (3)$$

define the so-called Lyapunov exponents. The major property of the Lyapunov exponents is that they do not depend on the starting point if the velocity field is ergodic.

Consider now a pollutant spot with size l released within a spatially smooth velocity and assume that the Peclet number l/r_d is large. The above consideration shows, in particular, that the spot will acquire an ellipsoid form. The direction that corresponds to the lowest Lyapunov exponent (necessarily negative in an incompressible flow) contracts until it reaches r_d , and further contraction is stopped by molecular diffusion. Since the exponentially growing directions continue to expand then the volume grows exponentially and the value of θ inside the spot decays exponentially in time. For an arbitrary large-scale initial distribution of θ , the concentration variance decays exponentially in a spatially smooth flow since this is how fast velocity inhomogeneity contracts θ “feeding” molecular diffusion which eventually decreases the variance. Even though it is diffusion that diminishes θ , the rate of decay is independent of κ , it is usually of order of the typical velocity gradient.

If the Schmidt number is small while the Reynolds number of the flow is large then the velocity field at scales larger than r_d cannot be considered spatially smooth. That means that the velocity difference $\delta v(r)$ measured between two points distance r apart scales as r^a with $a < 1$ (of course, δv is random and the statement pertains to the moments). For example, for the energy cascade in incompressible fluids, a is close to $1/3$. The equation $\dot{\mathbf{R}} = \delta \mathbf{v}(\mathbf{R}) \propto R^a$ suggests that interparticle distance grows by a power law: $R(t) \propto t^{1/(1-a)}$. The volume of any spot also grows so that scalar variance decays by a power law: $\langle \theta^2 \rangle \propto t^{d/(1-a)}$. Such estimates are supported by a rigorous theory only for a velocity field short-correlated in time. In this case, one can also show that the probability distribution $P(\theta, t)$ takes the self-similar form $t^{d/2(1-a)} Q(t^{d/2(1-a)} \theta)$ which is likely to be the case for a general scale-invariant velocity. On the contrary, $P(\theta, t)$ does not change in a self-similar way in a spatially smooth flow.

In finite vessels, the long-time properties of fluid mixing are usually determined by slowest parts, namely the walls, where the velocity gradient may become zero, and corners with recirculating eddies.

In multiphase flows, not only mixing but also segregation can occur. The physical reason for that is a centrifugal force: when fluid streamlines are curved, heavier particles move out while lighter particles move in. It is a matter of everyday experience that air bubbles are trapped inside the sink vortex while heavy particles gather outside the vortices (which is used, in particular, for flow visualization).

Granular mixing is strikingly different from fluid mixing. In a granular flow, collisions of grains are inelastic and friction between grains makes it possible for static configurations (such as arches) to support a load and distribute stresses. As a result, granular motion has nonlocal properties and no effective hydrodynamic description based on average over local kinetics (like Equation (2)) is available. When a container partially filled with grains is vertically shaken with accelerations larger than the gravitational acceleration, convective rolls are observed with grains rising at the center and falling along the walls. Contrary to fluid convection, however, the grains move faster and mix better near the walls. Granular flows can also demonstrate segregation. The most celebrated example is the so-called Brazil nut effect whereby large particles (Brazil nuts) rise to the top of shaken container of mixed nuts.

The use of the term “mixing” in mathematics is based on the notion (introduced by Josiah Gibbs) that evolution is mixing when it leads asymptotically in time to some equilibrium invariant measure. Formally, one defines the evolution operator U_t acting on some phase space A and denotes the measure of any subset B as $P(B)$. The evolution is mixing if for any $B, C \in A$ one has $\lim_{t \rightarrow \infty} P(A \cap U_t B) = P(A)P(B)$. One can also define weak mixing property where $\lim_{t \rightarrow \infty} t^{-1} \int P(A \cap U_s B) ds = P(A)P(B)$. Mixing of a random process or dynamical system means ergodicity, that is equality between temporal and phase-space average.

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See also Diffusion; Entropy; Granular materials; Intermittency; Kolmogorov cascade; Lagrangian chaos; Lyapunov exponents; Turbulence

Further Reading

Chate, H., Villermaux, E. & Chomaz, J.-M. (editors). 1999. *Mixing: Chaos and Turbulence*, New York: Kluwer
 Falkovich, G., Gawędzki, K. & Vergassola, M. 2001. Particles and fields in fluid turbulence. *Reviews of Modern Physics*, 73: 913–975

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