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What is mixing and can it be complex?

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Abstract

While the concept of mixing is commonly used in science and engineering, its exact interpretation may vary between different disciplines. In the present work, we analyse the concept of mixing in context of mechanical mixing, the ergodic theory, modelling of turbulent reacting fluid flows and complex competitive systems. Although mixing represents a dissipative process, which is responsible for irreversible increase of molecular disorder, mixing nevertheless can be associated with emergence of complexity under certain conditions. This dual role of mixing is noted and examined here. The appendix discusses three fundamental hypotheses, which are related to understanding of mixing and were introduced by Boltzmann.

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1. Introduction: mechanical mixing

Mixing is commonly understood as blending of two (or more) gases or liquids until a uniform mixture is achieved. Mixing preserves the identity of participating molecules and is thus different from chemical reactions. If molecules have little interactions, the resulting mixture is called an ideal mixture and characterized by maximal possible disorder and maximal possible entropy. Alternatively, interactions between molecules can reduce molecular chaos and the entropy of mixing falls below its maximal value.

The process of mixing of white and black fluids is schematically presented in figure 1. The ordered state before mixing figure 1(i) is replaced by blobs of one fluid floating in the other as shown in figure 1(ii). The following figure 1(iii) demonstrates maximal randomization of the mixture with the molecules of the black fluid distributed randomly in the white fluid. If the mixture is treated as continuum, then a homogeneous grey colour becomes distributed uniformly in the domain (figure 1(iv)). Mixing is closely related to the process of diffusion (i.e. diffusion of the scalar representing the concentration of the black admixture into white liquid), although diffusion usually involves spatial transport while mixing is conventionally referred to the local effect of the diffusion. The black area (i.e. the number of black pixels) is exactly the same in figures 1(i)–(iii). In figure 1(iv) the image is slightly coarsened so that the grey area is larger than the black area in figure 1(i) but the intensity of the dark colour is reduced proportionally. If two liquids are immiscible, then mixing can not proceed beyond the stage shown in figure 1(ii) since the thermodynamic states with fully mixing liquids

have prohibitively high energy levels when these liquids are immiscible.

The entropy of complete ideal mixing of two components can be expressed by the following equation:

$$\Delta S_{\text{mix}} = -k_B N_m (X_1 \ln(X_1) + X_2 \ln(X_2)), \quad (1)$$

where $X_1 + X_2 = 1$ are the molar fractions, k_B is the Boltzmann constant (per molecule) and N_m is the total number of molecules in the system. The process of mixing increases entropy by ΔS_{mix} and is the most fundamental example of a thermodynamically irreversible process: mixing of two fluids might be relatively easy but the mixture can never spontaneously unmix without external interference. While the equations of classical mechanics and of quantum mechanics are reversible in time, mixing is not. The question of the reasons behind the existence of a preferred direction in time and consistency of the second law of thermodynamics with mechanical laws has been discussed from the times of Ludwig Boltzmann and still awaits its full resolution (see appendix A.1).

2. Ergodic mixing

The concept of mixing is also used in ergodic theory, which studies the behaviour of large Hamiltonian systems (i.e. dynamical systems preserving the total energy). These systems may have a very large dimension. For example, if a system involves N_m molecules and each molecule has at least 6 degrees of freedom (i.e. position and velocity), then the dimension of this system can be estimated as $6N_m$, which is

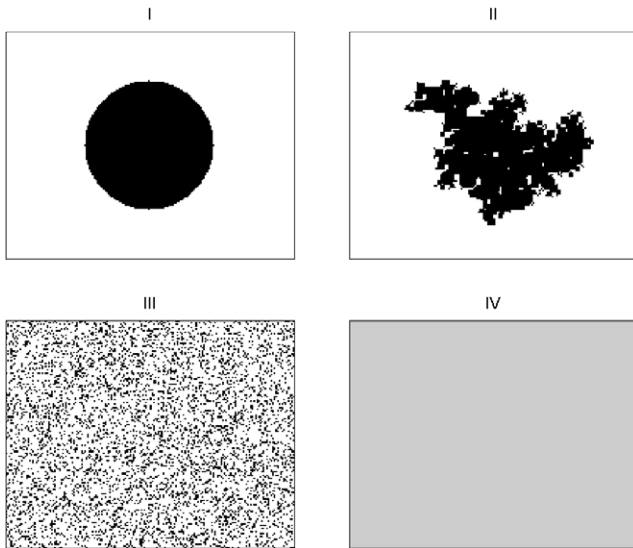


Figure 1. Schematic of the mixing process proceeding from ordered state (i) to disordered states (iii) and (iv). The number of black pixels is the same in (i), (ii) and (iii). Panel (iv) has the same average intensity of the black colour as the other figures.

extremely large. Following Gibbs term of extension-in-phase, we call this combined space as the extended phase space. Evolutions of Hamiltonian systems are measure-preserving, i.e. any volume in the extended phase space is not changed as each point in this volume evolves in time according to the laws of mechanics.

While each state of a system can be represented by a single point in the $6N_m$ -dimensional extended phase space, the mathematical treatment practiced in statistical physics and thermodynamics involves ensembles of systems, which are represented by volumes in the same extended phase space. The fundamental premise, which states that macroscopic averages evaluated for the ensembles must correspond to the averages over a sufficiently long period of time evaluated for a single system, is called the ergodic hypothesis. This premise can be written as

$$\frac{\int_{\mathcal{D}} f(\mathbf{y}) P(\mathbf{y}) d\mathbf{y}}{\int_{\mathcal{D}} P(\mathbf{y}) d\mathbf{y}} = \lim_{\tau \rightarrow \infty} \frac{1}{2\tau} \int_{-\tau}^{+\tau} f(\mathbf{y}(t)) dt, \quad (2)$$

where \mathcal{D} is the accessible domain, f is an arbitrary function of a stationary random process $\mathbf{y}(t)$ and $P(\mathbf{y})$ is the probability density function (PDF) of this process. This hypothesis was first introduced by Boltzmann, formulated in the form of equation (2) by Paul and Tatiana Ehrenfest and proven for different specific conditions in a number of theorems due to von Neumann, Birkhoff, Kolmogorov, Sinai and others (see appendix A.2).

Ergodic mixing can be understood through analogy between evolution of volumes in the extended phase space with mixing of fluids. This analogy was first introduced by Gibbs in his fundamental work [1], which laid the foundations of statistical physics. Ergodic mixing can be described by the same figure 1, which in this case illustrates the extended phase space. The ensemble of states is initially confined to the black region in figure 1(i). The evolution of the system changes the shape of the region but does not alter its volume (figures 1(ii) and (iii)) but after a sufficiently long period of time, the

trajectories become densely distributed in the domain \mathcal{D} permissible by the equations of motion (figure 1(iii)). Any averaging or coarsening results in a uniform distribution (figure 1(iv)). The time averages for a common selected trajectory become the same as the averages over the whole domain \mathcal{D} . Mixing is thus sufficient for ergodicity.

Although Gibbs analogy provides an excellent illustration of the concept of ergodic mixing, mechanical mixing and ergodic mixing are not exactly equivalent. For example, immiscible liquids cannot be mixed mechanically (as considered in the previous section), while the dynamic system represented by the molecules of these liquids may reach the state of ergodic mixing over the permissible domain in the extended phase space. This apparent paradox has a simple explanation: the states of a complete mechanical mixture of the liquids have prohibitively high energy levels and do not belong to the permissible domain \mathcal{D} .

3. Interactive mixing

The term ‘interactive mixing’ is interpreted here as exchanges of properties that are often used in computer simulations of mechanical mixing and diffusion, especially in the context of modelling of turbulent reacting flows.

3.1. Conservative mixing

The process of mixing can be simulated by a sufficiently large number of notional particles, randomly walking from the region of their initial confinement (such as the black region in figure 1(i)) and diffusing to occupy the whole domain (as in figure 1(iii)). The fundamental similarity between diffusion (mixing) and random walks was established first in physics and then in mathematics. Einstein’s work on Brownian motion [2], Kolmogorov’s work on forward and backward equations [3] and many other publications can be cited in this context. In fluid mechanics, Lagrangian particles, which follow the fluid flow (with or without random walk) are conventionally used to evaluate scalar transport. In this case the scalar is represented by the concentration of the particles. In principle, this approach can be used to characterize turbulent reacting flows, which might involve hundreds of different chemical species, but representing each scalar by a large number of particles within each small volume would be prohibitively expensive and impractical. The success of Lagrangian simulations in turbulent flows is related to the effective use of another type of particles—Pope particles (i.e. notional Lagrangian particles possessing a set of scalar properties and being subject to interactive mixing [4–6]). Lagrangian particles without properties and interactive mixing are distinguished here by referring to them as ‘elementary’.

The goal of making Lagrangian simulations of scalar transport computationally efficient inevitably leads us from elementary particles to Pope particles. Indeed, the same set of elementary particles can be economically used to model different scalars provided the particles carry different ‘marks’ corresponding to different scalars. These marks become particle properties. It appears then that performing interactive mixing of these properties can radically improve the accuracy of the simulations [7]. In the last few decades,

all Lagrangian simulations of turbulent reacting flows in Reynolds-averaged Navier–Stokes (RANS)-PDF [4], large eddy simulations-filtered density function (LES-FDF) [8] or LES-PDF [9] conditions, have been performed using Pope particles, while the use of elementary particles was confined to a very specific problem of evaluating turbulent dispersion of a single scalar, mostly in atmospheric applications. Interactive mixing can be conducted by different mixing schemes. Curl’s mixing

$$\begin{cases} \dot{X}^{(p)} = (1 - \alpha)X^{(p)} + \alpha \frac{X^{(p)} + X^{(q)}}{2} \\ \dot{X}^{(q)} = (1 - \alpha)X^{(q)} + \alpha \frac{X^{(p)} + X^{(q)}}{2} \end{cases} \quad (3)$$

and interactions by exchange with the mean (IEM)-type mixing (mixing by interactions by exchange with the mean)

$$\dot{X}^{(p)} = (1 - \alpha)X^{(p)} + \alpha \langle X \rangle \quad (4)$$

represent the oldest and most simple interactive mixing schemes [4]. The acute symbol is used to denote the scalar values after mixing and α specifies the extent of mixing. In Gurl’s mixing, particles interact with each other by forming groups of two particles (p and q in (3)), while particles interact only with the mean in (4). Note that conventional IEM mixing is continuous, while we use a discrete time version here by analogy with Curl’s mixing. Values $\mathbf{y}^{(p)} = (\mathbf{x}^{(p)}, \mathbf{X}^{(p)})$ comprising coordinates \mathbf{x} and scalar properties \mathbf{X} are assigned to each particle p .

Elementary particles with $\mathbf{y}^{(p)} = (\mathbf{x}^{(p)})$ move independently from each other and, consequently, the joint PDF of k particles satisfies the disorder condition

$$P_k(\mathbf{y}^{(1)}, \mathbf{y}^{(2)}, \dots, \mathbf{y}^{(k)}) = P_1(\mathbf{y}^{(1)})P_1(\mathbf{y}^{(2)}) \dots P_1(\mathbf{y}^{(k)}). \quad (5)$$

While the particles remain independent from each other in IEM mixing, this is not necessarily true for Curl’s mixing. The disorder condition may generally be incorrect for Pope particles (with $\mathbf{y}^{(p)} = (\mathbf{x}^{(p)}, \mathbf{X}^{(p)})$) due to interactions between the particles and a likelihood of stochastic dependences between $\mathbf{X}^{(p)}$ and $\mathbf{X}^{(q)}$ for $p \neq q$. Since both IEM and Curl’s mixing emulate the same physical process (i.e. physical mixing), it is unlikely that stochastic dependencies between the particles may become significant and in most cases can be neglected [4]. A more rigorous analysis of particle dependencies given in [7] confirms this statement. In statistical physics, the hypothesis of molecular disorder, which is similar to (5) and is discussed in appendix A.3, is one of the most fundamental properties of molecular dynamics.

3.2. Competitive mixing and complexity

A system, which is in a state of complete disorder (5), cannot be complex since it is fully characterized by one-particle PDF $P_1(\mathbf{y})$ and has relatively small number of effective degrees of freedom corresponding to that of a single particle. (The same statement applies to the opposite case of deterministically constrained systems—these systems cannot be complex due to a limited number of degrees of freedom they possess). Consequently, interactive mixing, which can

introduce dependencies between particles, is a principal factor that is necessary for the emergence of complexity in these systems. This necessity, however, does not imply sufficiency. For example, conservative mixing considered in the previous subsection, is generally compliant with (5), exactly or approximately, and does not make the system complex. A number of recent publications [10–13] indicate that another version of particle interactions—competitive mixing combined with random mutations—may bring complexity into the system under certain conditions discussed below.

If mutations in a system with competitive mixing belong to the class of mutations called Gibbs mutations, then this system can be characterized by competitive thermodynamics [13]. This limits the system complexity as thermodynamically consistent behaviour is associated with particle disorder. If mutations are not Gibbs compliant, the behaviour of the system depends on the transitivity of the competition rules. The case of transitive rules is qualitatively similar to the transitive systems with Gibbs mutations. This, again, restricts the complexity of the system. The restrictions of competitive thermodynamics, however, gradually disappear for intransitive competitions. First, competitive thermodynamics might acquire quite unusual intransitive features, which in conventional thermodynamics are banned by its zeroth law. Stronger intransitivity removes thermodynamic restrictions and the system can become more complex. Competitive cooperation, formation of structures and complex cyclic behaviour has been observed in competitive systems with strongly intransitive competition localized in physical space [13]. Under these conditions, interactive mixing is associated with partially ordered, complex behaviour.

4. Concluding remarks

While exact definition of mixing may vary from one field of science to another, there is common qualitative understanding of this term across the disciplines. Mixing is a fundamentally dissipative process that is characterized by loss of information, entropy increase and irreversibility. Interactive mixing (while shearing many common features associated with general mixing) may also exhibit complex behaviour. This may seem unexpected but there is no contradiction here—evolutionary emergence of complexity is accompanied by dissipative loss of information and increase of entropy.

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Appendix. Three Boltzmann hypotheses

This appendix presents three hypotheses introduced by Ludwig Boltzmann in his studies of kinetic theory of gases and can help to understand different aspects of mixing. Our preference is given to conveying the meaning of the hypotheses by using modern terminology and understanding, rather than reproducing Boltzmann’s exact words (which in many cases were written in German).

A.1. Thermodynamic time

This hypothesis was formulated by Boltzmann in response to his critics and in attempt to reconcile the time-symmetric behaviour of conventional mechanics with the time asymmetric nature of thermodynamics and kinetic theory [14–16]. If two gases, say nitrogen and oxygen, are placed into separated parts of a fixed volume and the separating membrane is then removed, the gases irreversibly mix to form a uniform mixture (this example was used by Boltzmann in his polemics in *Nature* [14]). Mechanically, this mixing process can be reversed but, obviously, we never observe this reversal in the real world. One should not overlook that the temporal boundary conditions in this experiment are strongly time-asymmetric: we manage to set the non-equilibrium initial conditions but cannot do the same to the final conditions. Why is this the case? We can set the initial conditions because we can use available exergy in form of electricity to separate air into N_2 and O_2 and prepare the experiment. Where does this exergy come from? Electricity is generated by fossil fuels, whose energy comes from the sun. The sun's gravitational thermo-nuclear factory is possible due to highly ordered non-equilibrium state of the early Universe. Thus, any question pertaining to the asymmetry of local temporal boundary conditions is inevitably related to the temporal boundary conditions imposed on the Universe.

In science of the late 19th century, the Universe was deemed to be infinite in size and eternal while the modern cosmology believes that the Universe was born around 14 billion years ago and might be limited in size. The arguments of Boltzmann, which were directed at his contemporaries, thus need to be translated into context of modern science.

Boltzmann time hypothesis. The perceived direction of time is linked to the direction of entropy increase and determined by the temporal boundary conditions imposed on the Universe (or the observable part of it).

On the face of the problem, this hypothesis seems to deal with definitions more than with the physics declaring that the second law of thermodynamics determines the direction of time rather than the direction of time determines how the second law should be applied (one may recall the famous chicken and egg question). The thermodynamic time hypothesis is nevertheless a physical hypothesis that leads to quite astonishing corollary (which was also noticed by Boltzmann)—if different temporal boundary conditions are set over different parts of the material world, the perceived time can run in these parts in the opposite directions.

The exact mechanism of enacting the direction of time remains unknown. The laws of both classical mechanics and quantum mechanics are time-symmetric. Boltzmann's time hypothesis can act solely through the temporal boundary conditions in otherwise time-symmetric mechanics of the Universe, or the hypothesis can be enacted by the temporal boundary conditions causing a slight temporal bias in the behaviour of the matter filling the Universe. The bias is so small that we do not detect it in conventional mechanical laws. If exists, this bias is likely to be related to the

process of quantum decoherence, theoretically hidden at the interface of classical and quantum mechanics. Roger Penrose [17] suggested another fundamental hypothesis that weak interactions of gravitational fields and quantum coherent states are slightly time-asymmetric causing decoherence. The direction of time still awaits its full physical explanation.

A.2. Ergodic theory

The conventional description of thermodynamic systems is based on averages, which in mathematics are most conveniently evaluated over ensembles (i.e. over a large set of conceptually identical systems) while a specific thermodynamic system is in its single specific micro-state at every specific moment. How then the averages are related to the realistic system in its specific state? The answer to this question is given by the ergodic hypothesis in physics and, more broadly, by ergodic theory in mathematics. The 'ergodic' terminology was introduced by Boltzmann following the assumption that the dynamic system under consideration is Hamiltonian and its total energy is preserved. Time evolution of these systems is confined to finite domains and preserves volumes in the extended phase space. The properties established by the ergodic theory are generally expected to be valid almost everywhere (i.e. possibly with exception of subdomains of zero volumes). A good review of the ergodic theory written for physicists can be found in [18]; see also remark on p. 207 of [15].

Boltzmann ergodic hypothesis. If a dynamic system is confined to a finite domain and observed over a sufficiently long period of time, then almost every selected trajectory of the system fills the domain with a uniform density.

This hypothesis, which presumes that the mixing conditions are complied with on average over a large period of time, can be called weak mixing. The ergodic hypothesis strengthens the formulation of Poincare recurrence theorem by suggesting mixing instead of recurrence. Ergodic mixing, which is illustrated in figure 1 and requires that the mixing conditions are satisfied at a fixed time moment rather than on average, is also called *strong mixing* (to distinguish it from weak mixing). Weak mixing follows from strong mixing but not vice versa. For example, pendulum oscillations comply with the conditions of weak mixing but not with the conditions of strong mixing. Weak mixing is equivalent to the conventional ergodic conditions (2), which were first given in this form by Paul and Tatiana Ehrenfest [20].

While the physical explanation of the ergodicity of thermodynamic systems was given by Boltzmann, it took a few decades to prove the corresponding mathematical theorems. The ergodic property requires an additional ergodicity condition imposed on dynamic transformations in a Hamiltonian system: no subdomain in the extended phase space can evolve to be mapped on itself; the whole domain and, possibly, small domains of measure zero are exempted from this requirement. The volume in the extended phase space is commonly referred to as the measure. Evolutions of dynamic systems complying with this condition are called ergodic transformations and ergodicity of the transformations is necessary for ergodicity of the system. Indeed, imagine

that the whole domain is divided into two (or more) subdomains that are mapped onto themselves. Then any dynamic trajectory starting in one of the subdomains will be forever confined to this subdomain violating ergodicity (2). For ergodic transformations, any function $f(\mathbf{y})$, which is not changed by this transformation, must be constant almost everywhere (otherwise the domains bounded by the lines of constant f are mapped onto themselves, which is not permitted). The famous Birkhoff theorem [19] proves that this condition of ergodic transformations is sufficient for Ehrenfest ergodicity (2). As many mathematical theories, the ergodic theory applies almost everywhere, i.e. while neglecting any properties confined to domains of zero measure.

A.3. Molecular disorder

The famous H-theorem proved by Boltzmann is based on molecular mechanics and on an additional hypothesis—the hypothesis of molecular disorder or the *Stosszahlansatz* [15]. Without this hypothesis, the Boltzmann kinetic equation formulated for one-particle PDF $P_1(\mathbf{y})$ remains unclosed as a part of the Bogolubov–Born–Green–Kirkwood–Yvon chain linking $P_1(\mathbf{y}^{(1)})$ to $P_2(\mathbf{y}^{(1)}, \mathbf{y}^{(2)})$, $P_2(\mathbf{y}^{(1)}, \mathbf{y}^{(2)})$ to $P_3(\mathbf{y}^{(1)}, \mathbf{y}^{(2)}, \mathbf{y}^{(3)})$ and so on. Although the hypothesis of molecular disorder is confirmed for gases by reasonable accuracy of the resulting Boltzmann kinetic equation, proving this hypothesis from first principles is a complex problem, which is not resolved in a general case.

Boltzmann hypothesis of molecular disorder. Molecules are statistically independent from each other (or can be treated as being statistically independent from each other).

Equation (5) is an important mathematical consequence of the hypothesis, which is used in the derivation of the Boltzmann kinetic equation and proof of Boltzmann's H-theorem. It is easy to see that this hypothesis cannot be exact, at least because the properties of two molecules become correlated after their collision. It may be the case that the hypothesis can be proven solely from the laws of mechanics as an approximate or asymptotic property but this would have a clearly unwanted consequence. Since the laws of mechanics are time-symmetric, our prediction of an equilibrium future, given the non-equilibrium present can be extended to predicting an equilibrium past given the non-equilibrium present. This should not be a surprise: if the only information we have about surrounding world is its present, we should be predicting equilibrium states as both its future and its past. Equilibrium states are the most probable states after all. Even our memories of more non-equilibrium Universe in the past are then interpreted as an illusion due to an odd fluctuation (the so-called Boltzmann brain).

The answer for mounting paradoxes is, of course, to adjust the theory to our experience. Since we do not know the exact physical working of the unidirectional time flow, we might use a fix—the causality principle. In physics, causality is time-asymmetric: the future depends on the past but not vice versa. Applying causality to the hypothesis of molecular disorder is also time-asymmetric: two molecules are stochastically independent before but not after their collision. According to causality, independence of molecules

before collision is very probable but after collision it is not. Hence, although trajectories of molecules can be inverted so that two gases O_2 and N_2 might unmix in the example of appendix A.1, we would judge the probability of this event as most unlikely, since a much more likely behaviour is predicted by the H-theorem: moving towards the equilibrium of the uniform mixture of these gases. We cannot, however, apply the H-theorem backward in time, since this would contradict the causality principle (post-collisional states of molecules are not independent!).

We must conclude that the hypothesis of molecular disorder, although not exact, is a reasonable physical assumption (although not a mathematical theorem) which is confirmed by the validity of the Boltzmann kinetic equation and is most likely to be supported by measurements of molecular statistics in gases if we could perform them. Finding rigorous mathematical justifications for this assumption might indeed be useful but perhaps not as important as explaining the physical reasons responsible for the direction of time. It might be noted that a thermodynamical system has a temperature at a given moment of time and not while being averaged over a large or infinite time period, as required by the ergodic theorems. Why might this be the case? The explanation is in validity of the hypothesis of molecular disorder: since molecules are independent we can average over the ensemble of molecules (Boltzmann statistics) rather than over the ensemble of systems (Gibbs statistics). Our everyday use of conventional thermodynamics gives the strongest support in favour of the hypothesis of molecular disorder.

While the hypothesis of molecular disorder is a reasonable approximation for conventional thermodynamic systems, we argue that this hypothesis breaks down when complexity emerges. A complex system has a sophisticated hierarchy of structures, and the elements within these structures are no longer stochastically independent.

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