Examination of the $\tau_2/\tau_1$ ratio provides an even clearer picture; this ratio is calculated to be 3.3 from the MD simulations, in good agreement with the extended jump model prediction of 4.0, whereas the purely diffusive model yields a value of 6 (27).

Therefore the extended jump model, whose parameters are determined in the accompanying simulations, is shown to be fully consistent with the experimental reorientation times and is clearly supported by MD simulations. These results thus call for a reinterpretation of the many experimental data for which water rotation is assumed to be purely diffusive in character.

Further confirmation of the molecular mechanism presented here could emerge from the resolution of the remaining controversial issues for water reorientation, such as the experimental isotope effect in the reorientation times ($t_1$), and a possible laser OH excitation frequency dependence of the reorientation times ($t_2$, $t_3$, $t_4$) and angular displacement ($t_5$).

References and Notes
20. In Csaïka and Chandler’s paper on some aspects of H-bond breaking in water (as opposed to reorientation), jumps occur in producing a predefined broken H-bond final state, which is an unstable state, without a new partner in most cases and with the former accepting water still in the first hydration shell (32). This process is to be distinguished from that of the present work, where jumps terminate in a new stable state, with a new partner, and with the former partner now in the second hydration shell (Fig. 1).
26. The $\tau_1$ time is currently available only through MD simulations; but promising time-resolved hyper-Rayleigh scattering techniques should allow its determination for water in the near future (32).
31. T. Buckup, personal communication.
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The Role of Pair Dispersion in Turbulent Flow
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Mixing and transport in turbulent flows—which have strong local concentration fluctuations—are essential in many natural and industrial systems including reactions in chemical mixers, combustion in engines and burners, droplet formation in warm clouds, and biological odor detection and chemotaxis. Local concentration fluctuations, in turn, are intimately tied to the problem of the separation of pairs of fluid elements. We have measured this separation rate in an intensely turbulent laboratory flow and have found, in quantitative agreement with the seminal predictions of Batchelor, that the initial separation of the pair plays an important role in the subsequent spreading of the fluid elements. These results have surprising consequences for the decay of concentration fluctuations and have applications to biological and chemical systems.

Turbulent mixing of liquids and gases is ubiquitous in nature (1); it is the basis of all industrial fluid mixing processes, and it determines the spread of pollutants or bioagents in the atmosphere (2) and oceans (3). Biological organisms in marine ecosystems also exploit it for their survival (4–6). A crucial component of turbulent mixing is the fluctuation of local concentration. The rate of destruction of ozone in the atmosphere, for example, is largely determined by these fluctuations rather than by the mean concentration (7), as is the toxicity of gas leaks or air pollution. It is natural to relate these concentration fluctuations to the separation of two nearby fluid elements; i.e., pair dispersion ($\delta$, $\kappa$).

In a quiescent fluid, the relative dispersion of two fluid elements (or tracer particles) is dominated by diffusion. The particles undergo Brownian motion, and the mean square separation between them grows linearly in time. In a turbulent flow, however, if the two particles are separated by distances smaller than the characteristic size of the largest eddies in the flow, they will separate faster (superdiffusively). At large separation times and distances, the local correlations responsible for the superdiffusive separation will no longer be present, and, on average, the relative dispersion will again be linear in time.

Despite almost 80 years of scientific inquiry into relative dispersion (2, 9–17), no clear experimental verification of the theoretical predictions has emerged. One critical unresolved question is the extent to which the initial separation of the fluid particles influences their subsequent motion. Our measurements in a laboratory water flow (18, 19) in very intense turbulence suggest that the initial separation remains important for all but the most violent flows on Earth. This observation has consequences for such varied problems as pollution control; combustion modeling; hazardous chemical control; and even the understanding of how animals locate food, predators, and mates (5, 6).

We measured relative dispersion in a water flow at high turbulence levels by using optical particle tracking. This technique has been used for a number of years in turbulence research (13, 20) but was limited to the measurement of low–turbulence level flows, because tracer-particle motions must be resolved over times comparable to the smallest time scale of the turbulence [i.e., the Kolmogorov time scale $\tau_{0} = (\nu \epsilon)^{-1/2}$, where $\nu$ is the kinematic viscosity and $\epsilon$ is the energy dissipation rate per unit mass]. In intense turbulence, these times are often very small. The turbulence level is generally quantified by the Reynolds number, which measures the ratio of the nonlinear inertial forces to the linear viscous forces. Here we report the Reynolds number based on the Taylor microscale, $R_{T} = \sqrt{\left(15\nu^2 L/\nu^2\right)}$, where $L$ is the Taylor microscale.
where $\nu$ is the root mean square (rms) velocity of the turbulent fluctuations and $L$ is the largest length scale of the turbulence. In our water flow at $R_e = 815$, which is the highest Reynolds number reported in this work, $\tau_\eta = 0.54$ ms; therefore, very fast detectors must be used to resolve the fine structure of the flow. Previously, by using silicon strip detectors from high-energy physics experiments (18, 19), we extended the particle tracking technique to flows with high turbulence levels. Such detectors, however, are unsuitable for measuring the statistics of many tracer particles at once. We therefore used three Phantom v7.1 digital cameras from Vision Research, Inc. (Wayne, NJ), which record 27,000 pictures per second at a resolution of 256 × 256 pixels (Fig. 1A). This camera system can be used to track several hundred particles at once (21). An example of two such simultaneously measured particle tracks is shown in Fig. 1B.

We generated turbulence between coaxial counter-rotating baffled disks in a closed chamber with a volume of approximately 0.1 m$^3$ (Fig. 1A). We made measurements in a sub-volume of roughly $5 \times 5 \times 5$ cm$^3$ in the center of the tank, where the mean flow is statistically zero. Polystyrene tracer particles 25 $\mu$m in diameter, comparable to the Kolmogorov length scale $\eta = (v/\epsilon)_{1/4}$, which is the smallest scale of the turbulence, were illuminated by two frequency-doubled, pulsed Nd–yttrium-aluminum-garnet (Nd:YAG) lasers, with a combined power of roughly 150 W. The particle positions were measured with a precision of roughly 0.1 pixels (21), corresponding to about 20 $\mu$m in the flow. Further description of this flow has been reported previously (18, 19).

By analyzing our measured particle tracks, we investigated the time evolution of the mean square separation between two fluid elements. Predictions for the superdiffusivity of this pair dispersion in turbulence date back to 1926, when Richardson (10) suggested that it should grow in time as $t^3$. By applying Kolmogorov’s scaling theory (22), Obukhov (23) specified that in the inertial range of turbulence, where the only relevant flow parameter is the energy dissipation rate per unit mass $\epsilon$, the pair dispersion should grow as $gt^3$, where $g$ is a universal constant. Batchelor (11) refined this work, predicting that the mean square separation should scale as $t^3$ for times shorter than a characteristic timescale $t_0$, which depends on the initial separation of the pair.

By defining $\Delta(t)$ as the separation of two fluid elements at time $t$ and defining $\Delta_0$ as the initial separation between the fluid elements, Batchelor predicted that for $\Delta_0$ in the inertial range

$$\left( \frac{\Delta(t) - \Delta_0}{\Delta_0} \right)^2 = \frac{11}{3} C_2 (\epsilon \Delta_0)^{2/3} t^2$$

for $t < t_0 = \left( \frac{\Delta_0^3}{\epsilon} \right)^{1/3}$ (Eq. 1)

where $C_2$ is the universal constant in the inertial range scaling law for the Eulerian second-order velocity structure function with a well-known value of approximately 2.13 (24). In the classical cascade model of turbulence, $t_0$ may be identified as the time for which the two fluid elements “remember” their initial relative velocity as they move in the same eddy of size $\Delta_0$. At times on the order of $t_0$, this eddy breaks up, and the growth of the pair separation is expected to undergo a transition to Richardson-Obukhov scaling.

To distinguish between Batchelor and Richardson-Obukhov scaling, the inertial range must be large, so that there will be a large separation between the eddy turnover time $T_e$ and the Kolmogorov time $\tau_\eta$. To achieve such a wide range of scales, the turbulence level must be high because $R_e \sim (T_e/\tau_\eta)$. Based on evidence from direct numerical simulation (25), a turbulence level of at least $R_e = 600$ to 700 is required to see true inertial range scaling of a Lagrangian quantity such as relative dispersion. Previous experimental and computational studies of dispersion have been limited by their low turbulence levels ($R_e < 300$) (12–15, 17) and have not been conclusive. High turbulence levels are obtained in kinematic simulation models (16), but such models may not be suited to the pair dispersion problem (26).

Figure 2 shows measurements of relative dispersion for turbulence levels up to $R_e = 815$. We found that for experimentally accessible initial separations, our data scales as $t^3$ for more than two decades in time, with no hint of classical Richardson-Obukhov $t^3$ scaling. This behavior holds throughout the entire

![Fig. 1.](https://example.com/fig1.png) **Fig. 1.** (A) Sketch of the experimental setup. Three high-speed cameras were used to record the three-dimensional tracks of tracer particles in intense turbulence. The particles were illuminated by two high-power lasers. (B) A pair of measured particle trajectories at $R_e = 690$. The small spheres mark every 30th position. The color of the spheres indicates the magnitude of each particle’s absolute velocity in units of m/s. The particles enter the measurement volume as indicated by the arrows and separate under the influence of the turbulence.

![Fig. 2.](https://example.com/fig2.png) **Fig. 2.** Evolution of the mean square particle separation. The mean square separation between particle pairs is plotted against time for 50 different initial separations at a turbulence level of $R_e = 815$, with the time axis normalized by the Kolmogorov scales. Each curve represents a bin of initial separations 1 mm wide ($\approx 43\eta$), ranging from 0 to 1 mm to 49 to 50 mm. The curves are scaled by the constant $(\bar{h} L_c \epsilon \Delta_0)^{1/3}$ (Eq. 1). The data collapse onto a single universal power law. The bold black line is the power law predicted by Batchelor (11). Because the smallest $\Delta_0$ measured is not in the inertial range, we do not expect it to scale perfectly as $t^2$, and indeed it does not scale as well as the larger $\Delta_0$. The inset shows the same curves scaled simply by the Kolmogorov length, for which we see no scale collapse. For both plots, we see no Richardson-Obukhov $t^3$ scaling.
inertial range, even for large initial separations (up to 70% of the largest length scale of the turbulence). When we scaled our relative dispersion data by the constant predicted by Batchelor, given in Eq. 1, the curves collapsed onto a single \( r^3 \) power law. The line drawn in Fig. 2 is \( C_2 (\Delta_0 r^3)^{2/3} \).

In Fig. 2, where time is plotted in units of \( \tau_0 \), the data for different initial separations deviate from the \( r^3 \) law at times that vary with \( \Delta_0 \). If, however, we scale time by Batchelor's \( t_0 = (\Delta_0 r^3)^{1/3} \) (Fig. 3), the data for each initial separation deviate from Batchelor's prediction at the same universal value of roughly 0.1 \( \tau_0 \), irrespective of turbulence level.

For the quantities plotted in Figs. 2 and 3, we see no Richardson-Obukhov \( r^3 \) scaling. We also, however, measured other statistics that, dimensionally, should obey the same scaling laws. One such quantity is exit time statistics (I4). Our measurements of such statistics showed no clear \( r^3 \) behavior. Another measure of relative dispersion is shown in Fig. 4, in which we plot \( \langle (\Delta t r^3)^{2/3} \rangle - \Delta_0 2^{2/3} \) as a function of \( t / t_0 \). For small initial separations for which \( (T_0/t_0) \) is of order 10, we see a transition to a scaling law consistent with the Richardson-Obukhov prediction for times greater than roughly \( t_0 \), irrespective of turbulence level. For larger initial separations for which \( (T_0/t_0) \) is smaller, however, no such scaling is seen, as shown in the inset to Fig. 4. The existence of a transition at times on the order of \( t_0 \) shows that the initial separation is an important parameter for relative dispersion and cannot be neglected.

In any practical application of relative dispersion, the initial source will have finite size and therefore have a nonzero \( \Delta_0 \). Our data show that \( t_0 \) accurately quantifies the transition between the Batchelor scaling regime and the Richardson-Obukhov regime. Consequently, a clear \( r^3 \) scaling law requires not only a large separation between \( T_0 \) and \( \tau_0 \) but also a large separation between \( T_0 \) and \( \tau_0 \) For the initial separations accessible in our experiments, the maximum value of the ratio of \( (T_0/t_0) \) was of order 10, with no fully developed \( r^3 \) scaling. In order to apply the Richardson-Obukhov scaling law to a practical situation, then, \( (T_0/t_0) \) must be much larger than 10, which implies the necessity of a high turbulence level.

For most flows on Earth, both natural and industrial, the turbulence levels are quite small: typically, \( R \leq 1000 \). Very turbulent atmospheric flows, such as warm clouds or the atmospheric boundary layer (27), have turbulence levels of about \( R \sim 10^4 \). Even the most violent flows on Earth, such as plinian volcanic eruptions, have similar turbulence levels. If we consider a pair of particles with an initial separation of roughly 1 m, such as might be found in the smokestack of an industrial plant, for a turbulence level of \( R \sim 10^3 \), \( (T_0/t_0) \) is only about 30, assuming typical atmospheric flow parameters (28).

An important consequence of these results is that in almost all flows with industrial or biological significance, the initial separation \( \Delta_0 \) will influence the subsequent spreading of the two fluid elements throughout the entire period of their turbulent superdiffusive separation. This can explain, for example, measurements of the decay of the fluctuations of a passive scalar injected into the flow (29). This decay became slower as the separation between two sources was increased. These results may, in turn, explain why the spatial arrangement of odor sources plays such an important role in the way crayfish and other crustaceans, as well as organisms both larger and smaller (6), navigate their marine environments (5).

We observed that Batchelor’s prediction is fulfilled for more than two decades in time at high turbulence levels. Although our data may be somewhat contaminated by the inhomogeneity and anisotropy present in our specific flow, the observed scale collapse onto the Batchelor law appears very robust. In addition, we showed that the initial separation of the particle pair remains important in most flows in nature up to times of order \( t_0 \), which itself depends on the initial separation. We observed a transition near \( t_0 \) only when \( (T_0/t_0) \) was of order 10 or larger. Therefore, a large separation between \( T_0 \) and \( t_0 \) is required to see a fully developed Richardson-Obukhov scaling regime, requiring a turbulence level beyond the reach of current experiments and higher than will occur in most practical situations.

References and Notes
Late Quaternary Atmospheric CH$_4$

Isotope Record Suggests Marine Clathrates Are Stable

Todd Sowers

One explanation for the abrupt increases in atmospheric CH$_4$ that occurred repeatedly during the last glacial cycle involves clathrate destabilization events. Because marine clathrates have a distinct deuterium/hydrogen (D/H) isotope ratio, any such destabilization event should cause the D/H ratio of atmospheric CH$_4$ ($\delta DCH_4$) to increase. Analyses of air trapped in the ice from the second Greenland ice sheet project show stable and/or decreasing $\delta DCH_4$ values during the end of the Younger and Older Dryas periods and one stadial period, suggesting that marine clathrates were stable during these abrupt warming episodes. Elevated $\delta DCH_4$ values may be the result of a lower ratio of net to gross wetland CH$_4$ emissions and an increase in petroleum-based emissions.

The ice core record of atmospheric CH$_4$ changes covering the past 650,000 years exhibits two primary frequencies. Over long time scales (greater than 10,000 years) atmospheric CH$_4$ changes have a substantial amount of variance concentrated in the precessional bandwidth (19,000 and 23,000 years) (1, 2) that is considered to be an integral part of tropical climate throughout the late Pleistocene. One hypothesis that accounts for this observation involves an energized hydrologic cycle during periods of elevated low-latitude insolation. The invigorated hydrologic cycle promotes an increase in wetland extent driving a concomitant increase in CH$_4$ emissions that raise atmospheric CH$_4$ levels during warm periods. Embedded within the precession signal are millennial- and century-scale variations that are tightly coupled to Greenland temperature (3, 4). In general, increasing atmospheric CH$_4$ levels are synchronous with, or slightly lag (by a few decades), the surface temperature increase over Greenland (5). Assessing the nature of these abrupt CH$_4$ events is important for understanding how ecosystems and climate are connected and in estimating the degree to which future CH$_4$ levels may contribute to changes in Earth’s radiation budget.

There are two competing explanations for the abrupt CH$_4$ increases. One hypothesis holds that the terrestrial biosphere is capable of rapidly increasing CH$_4$ emissions in response to abrupt changes in the hydrologic cycle that are teleconnected to surface temperatures over Greenland (3, 4). The other explanation involves the sudden release of marine clathrates situated along the continental margin where episodic destabilization events may have been triggered by enhanced ventilation (warming) of upper thermocline waters (6). The majority of the released CH$_4$ ultimately travels across the air-sea interface leading to atmospheric CH$_4$ increases.

Model estimates of changes in the primary CH$_4$ sink (tropospheric hydroxyl radical) during the last glacial termination suggest that the observed CH$_4$ variations must be due in large part to changes in the sources as opposed to changes in the rate of removal (7). The isotopic composition of atmospheric CH$_4$ therefore provides additional information on the relative contribution of the various sources. Variations in the D/H ratio of atmospheric CH$_4$ ($\delta DCH_4$) can be used to infer variable clathrate contributions on the basis of their elevated $\delta D$ values compared with all terrestrial CH$_4$ sources (Fig. 1). Methane clathrates within the continental margin sediments are formed almost exclusively by CO$_2$ reduction or thermal cracking of longer chain hydrocarbons, whereas terrestrial CH$_4$ emissions are primarily aceticlastic in nature (8, 9). During CO$_2$ reduction, all the methyl hydrogen atoms come directly from porewater H$_2$ that is in isotopic equilibrium with the porewater (10). The resulting $\delta DCH_4$ values are lower than the porewater $\delta D_{H_2O}$ due to a ~180 per mil (‰) biologically induced isotope effect associated with CO$_2$ reduction (9, 11). Marine clathrate $\delta DCH_4$ values from 13 nearshore sites scattered throughout the Northern Hemisphere are surprisingly constant (~189 ± 27‰; error is SD) given the diverse nature of the geologic and sedimentologic settings and the varying proportions of microbial and thermogenic CH$_4$ at each site (12, 13). In contrast, CH$_4$ production in terrestrial ecosystems is dominated by acetogenesis (acetate fermentation) where three-fourths of the hydrogen atoms in the emitted methane originate from the methyl group associated with the acetate substrate. The remaining hydrogen comes from the local water with the resulting terrestrial $\delta DCH_4$ values generally ranging from ~250 to ~380‰, with the local $\delta DCH_4$ value strongly influenced by the $\delta D$ of precipitation (8, 9).

An atmospheric $\delta DCH_4$ record (Fig. 2) was generated from the second Greenland ice sheet project (GISP II) ice core using a previously described technique with an external precision of ±4.2‰ (14). The general picture of $\delta DCH_4$ variations associated with the deglaciation shows a progressive decrease in $\delta DCH_4$ as the concentration of CH$_4$ increases, opposite to that predicted by increasing clathrate contributions due to warming associated with the termination. During the last glacial maximum (LGM), $\delta DCH_4$ values were generally ~5‰ higher than the Bolling/Allerod values (~15 to 13 thousand years ago (ka)) and ~20‰ higher than early Holocene values. There are three factors that can be reasonably constrained as contributing to the elevated $\delta DCH_4$ values during the LGM. All three factors are temperature dependent, so