

Non-Gaussian statistics of concentration fluctuations in free liquid diffusion

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We show that the three-point skewness of concentration fluctuations is nonvanishing in free liquid diffusion, even in the limit of vanishingly small mean concentration gradients. We exploit a high-Schmidt reduction of non-linear Landau-Lifshitz hydrodynamics for a binary fluid, both analytically and by a massively parallel Lagrangian Monte Carlo simulation. Non-Gaussian statistics result from nonlinear coupling of concentration fluctuations to thermal velocity fluctuations, analogous to the turbulent advection of a passive scalar. Concentration fluctuations obey no central limit theorem, counter to the predictions of macroscopic fluctuation theory for generic diffusive systems.

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Introduction. The origin of macroscopic hydrodynamics from microscopic molecular dynamics is a vexing open problem in physics, with various competing proposals such as Zwanzig-Mori coarse-graining methods [1,2], hydrodynamic scaling limit (HSL) [3] and macroscopic fluctuation theory (MFT) [4], renormalization group (RG) [5] and effective field theory (EFT) [6], or kinetic theory for low-density gases [7]. The problem became even more complex with the theoretical discovery [8] and experimental verification [9] of generic spatial long-range nonequilibrium correlations. Such second-order correlations are predicted by linearized fluctuating hydrodynamics [10] and have been interpreted in MFT as central limit theorem (CLT) corrections to a leading-order law of large numbers. Important topics of ongoing research are the dynamical emergence of these correlations [11] and the higher-order correlations [4,12], especially as the latter can be measured experimentally in some condensed-matter systems, such as atomic superfluids [13]. Indeed, the universal validity of MFT has been challenged by the prediction of non-Gaussian statistics of charge density fluctuations in Dirac metals based on nonlinear fluctuating hydrodynamics [14], with higher statistics different from MFT predictions for generic diffusive systems [12].

In this Letter, we show that non-Gaussian statistics appear already in a very commonplace example: the free diffusion of a solute in a liquid solvent, such as a drop of dye in water. Long-range correlations in free liquid diffusion were long ago observed in terrestrial experiments by light

scattering [15]. Although quenched at large scales by buoyancy effects on Earth, they are observed up to system size in ongoing low-gravity space experiments [16,17]. The concentration second-order correlations were successfully predicted by linearized fluctuating hydrodynamics [18] and fluctuations are thus widely expected to be Gaussian [19]. However, in a landmark work [20], Donev, Fai, and Vanden-Eijnden (hereafter, DFV) succeeded to explain these fluctuations in a liquid at rest by a nonlinear advection equation $\partial_t c + \mathbf{u} \cdot \nabla c = D_0 \Delta c$, where c is the concentration of the solute, $\mathbf{u}$ is the thermal velocity field of the solvent liquid governed by linearized fluctuating hydrodynamics, and D_0 is the bare diffusivity. In agreement with the EFT interpretation, there is an explicit high-wave-number cutoff in this model taken to be on the order of the radius σ of the solute molecule. In the limit of high Schmidt number $\nu/D_0 \gg 1$ appropriate to most liquid mixtures, DFV showed that this system reduces to a version of the Kraichnan model of turbulent scalar advection [21,22]:

$$\partial_t c + \mathbf{w} \circ \nabla c = D_0 \Delta c, \quad (1)$$

where $\circ$ denotes the Stratonovich product and $\mathbf{w}$ is a Gaussian random velocity with zero mean and covariance $\langle w_i(\mathbf{x}, t) w_j(\mathbf{x}', t') \rangle = R_{ij}(\mathbf{x}, \mathbf{x}') \delta(t - t')$, where $\mathbf{R} = \frac{2k_B T}{\eta} \mathbf{G}$, with $\mathbf{G}$ the Green's function of the Stokes operator (Oseen tensor). The DFV theory leads naturally to a renormalization of the bare diffusivity D_0 , so that the mean concentration field satisfies a Fickian diffusion equation $\partial_t \bar{c}(\mathbf{x}, t) = D \Delta \bar{c}(\mathbf{x}, t)$, in which the diffusivity at macroscopic scales is given by the Stokes-Einstein relation $D = k_B T / 6\pi \eta \sigma \gg D_0$, where T is temperature and $\eta = \rho \nu$ the shear viscosity of the solvent. DFV explained the emergence of long-range correlations as closely analogous to a turbulent cascade of an advected scalar. Just as in the Kraichnan model [22], closed equations hold

$$\begin{aligned} \partial_t C_{12} = & D(\Delta_{\mathbf{x}_1} + \Delta_{\mathbf{x}_2}) C_{12} + \frac{1}{2} R_{ij}(\mathbf{x}_1, \mathbf{x}_2) \nabla_{x_1^i} \nabla_{x_2^j} C_{12} \\ & + R_{ij}(\mathbf{x}_1, \mathbf{x}_2) \nabla_{x_1^i} \bar{c}_1 \nabla_{x_2^j} \bar{c}_2 \end{aligned} \quad (2)$$

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for second cumulants $\mathcal{C}_{12} = \mathcal{C}(\mathbf{x}_1, \mathbf{x}_2, t)$, also

$$\begin{aligned} \partial_t \mathcal{C}_{123} = & D[\Delta_{\mathbf{x}_1} + \Delta_{\mathbf{x}_2} + \Delta_{\mathbf{x}_3}] \mathcal{C}_{123} \\ & + R_{ij}(\mathbf{x}_1 - \mathbf{x}_2) \nabla_{x_1^i} \nabla_{x_2^j} \mathcal{C}_{123} + R_{ij}(\mathbf{x}_1 - \mathbf{x}_3) \nabla_{x_1^i} \nabla_{x_3^j} \mathcal{C}_{123} \\ & + R_{ij}(\mathbf{x}_2 - \mathbf{x}_3) \nabla_{x_2^i} \nabla_{x_3^j} \mathcal{C}_{123} \\ & + R_{ij}(\mathbf{x}_1 - \mathbf{x}_2) [\nabla_{x_1^i} \bar{c}_1 \nabla_{x_2^j} \mathcal{C}_{23} + \nabla_{x_2^j} \bar{c}_2 \nabla_{x_1^i} \mathcal{C}_{13}] \\ & + R_{ij}(\mathbf{x}_1 - \mathbf{x}_3) [\nabla_{x_1^i} \bar{c}_1 \nabla_{x_3^j} \mathcal{C}_{23} + \nabla_{x_3^j} \bar{c}_3 \nabla_{x_1^i} \mathcal{C}_{12}] \\ & + R_{ij}(\mathbf{x}_2 - \mathbf{x}_3) [\nabla_{x_2^i} \bar{c}_2 \nabla_{x_3^j} \mathcal{C}_{13} + \nabla_{x_3^j} \bar{c}_3 \nabla_{x_2^i} \mathcal{C}_{12}] \quad (3) \end{aligned}$$

for triple cumulants $\mathcal{C}_{123} = \mathcal{C}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, t)$ of concentration fluctuations, and so forth. In these equations, gradients of the lower-order cumulants appear as source terms. It was shown recently [23] that the DFV model yields second-order correlations in the form observed experimentally [15,24]: $\mathcal{C}_{12} \propto |\nabla \bar{c}(t)|^2 \sigma r_{12}$, where $\nabla \bar{c}(t)$ is the mean concentration gradient and $r_{12} = |\mathbf{x}_1 - \mathbf{x}_2|$.

It was pointed out also in Ref. [23] that the higher-order cumulants of concentration fluctuations should not vanish in the DFV theory, just as they do not in turbulent scalar cascades. The structure of the source terms in the closed equations (2), (3), etc. suggests that, in general, the P th-order cumulant $\mathcal{C}_{12\dots P} \propto (\nabla \bar{c})^P$. If so, not only are cumulants for all $P > 2$ nonvanishing, but also when normalized by the $P/2$ power of the second cumulant $\mathcal{C}_{12}$ they will remain nonzero in the limit $|\nabla \bar{c}| \rightarrow 0$. Such higher cumulants nondimensionalized by the second cumulant generalize the concepts of skewness and kurtosis, and their nonvanishing indicates persistent non-Gaussianity as $|\nabla \bar{c}| \rightarrow 0$. A main assumption of MFT [4] is that macroscopic diffusion equations arise as a “law of large numbers” in a hydrodynamic scaling limit [3] where macroscopic gradients become arbitrarily weak on the microscopic scale. The experimentally observed second cumulants of concentration fluctuations are then interpreted in MFT as “central limit theorem” corrections, predicted to become Gaussian in the limit [3,4].

To address these questions, we consider here the simplest situation [23] with initial concentration profile $c_0(\mathbf{x}) = \frac{c_0}{2}(1 + \text{erf}(\frac{z}{2\sqrt{D\tau}}))$ in infinite three-dimensional space and gradients nonzero only in the z direction. The parameter τ with units of time is introduced to set the magnitude of the initial concentration gradient as $|\nabla c_0| = c_0/\sqrt{4\pi D\tau}$. Our problem setup idealizes laboratory experiments [15,24] on free diffusion with initial interfaces in concentration, but where the spatial domain was finite and gravity appeared. Following DFV, we ignore initial local equilibrium fluctuations of concentration, which are orders of magnitude smaller than the nonequilibrium fluctuations of interest (see Fig. 2 from Ref. [15]). Note that the mean concentration $\bar{c}(\mathbf{x}, t)$ obtained by evolving the error function profile under the diffusion equation keeps the same form, but with $\tau \mapsto t + \tau$. To probe the non-Gaussian statistics, we will calculate the three-point skewness function $\mathcal{S}_{123} = \mathcal{C}_{123}/(\mathcal{C}_{13}\mathcal{C}_{23}\mathcal{C}_{12})^{1/2}$.

We focus first on the early-time, transient regime when non-equilibrium correlations begin to emerge. In fact, in the free-decay problem where the mean gradient decreases in time as $|\nabla \bar{c}| \sim c_0/\sqrt{4\pi D(t + \tau)}$, the largest cumulants in absolute magnitude appear near the end of this early-time regime [25]

and thus should present the largest experimental signal. This early-time regime was first investigated theoretically by DFV [20] whose results for the spectral structure function of concentration were confirmed in physical space to have the form [25]

$$\begin{aligned} & C(r_{12}, \theta_{12}, Z_{12}, t) \\ & \simeq \frac{3c_0^2}{8\pi} \times \frac{\sigma}{r_{12}} (1 + \cos^2 \theta_{12}) \\ & \times \left[E_1 \left(\frac{Z_{12}^2 + \frac{1}{4}z_{12}^2}{2D(t + \tau)} \right) - E_1 \left(\frac{Z_{12}^2 + \frac{1}{4}z_{12}^2}{2D\tau} \right) \right], \\ & Dt \lesssim \sigma^2 \ll r^2, \quad (4) \end{aligned}$$

where r_{12}, θ_{12} are spherical coordinates (omitting azimuthal angle) of the separation vector $\mathbf{r}_{12} = \mathbf{x}_1 - \mathbf{x}_2$ of the two points, $Z_{12} = (z_1 + z_2)/2$ is the mean of their vertical positions, $z_{12} = r_{12} \cos \theta_{12}$ is the vertical coordinate of $\mathbf{r}_{12}$, and $E_1(x)$ is the exponential integral function (see Eq. (6.6.1) of Ref. [26]). The result (4) is derived from Eq. (2) by a short-time, large- r asymptotic expansion in which the source term is evaluated with the infinite-space Oseen tensor $G_{ij} = \frac{1}{8\pi r}(\delta_{pq} + \frac{r_i r_j}{r^2})$ and treated as the leading term on the right-hand side, the diffusion term being regarded as a small perturbation. Formula (4) then results from direct time integration of the source term. The triple cumulant $\mathcal{C}_{123}$ can be evaluated in the analogous asymptotic scheme. With the symmetries of the interface problem, the triple cumulant is specified at each time t by the triangle in $\mathbb{R}^3$ with vertices $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3$ or, more geometrically, by the lengths of its three sides r_{13}, r_{23}, r_{12} , by two Euler angles β, γ specifying its orientation, and by the vertical position $Z = z_3$ (see Sec. A of the Supplemental Material [27]). The asymptotic solution for short times $Dt \lesssim \sigma^2$ and large triangles $\min_{p,q} R_{pq} \gg \sigma$ is obtained by integrating in time the six source terms on the right-hand side of Eq. (3), treating the diffusion terms as a perturbation. Although the calculation is straightforward in principle, the resulting expression for $\mathcal{C}_{123}$ is quite lengthy. See Sec. A of the Supplemental Material for details of the derivation and the full analytical result [27].

Especially relevant to the validity of a central limit theorem is $\mathcal{C}_{123}$ in the weak-gradient limit $|\nabla c_0| \rightarrow 0$ or, equivalently, $\tau \rightarrow \infty$. The analytical expressions simplify in that limit so that, for example, the result analogous to Eq. (4) for general particle pair p, q becomes [25]

$$\begin{aligned} & \mathcal{C}(r_{pq}, \theta_{pq}, Z_{pq}, t) \simeq \frac{3}{2} \sigma Dt \frac{|\nabla c_0|^2}{r_{pq}} (1 + \cos^2 \theta_{pq}), \\ & D\tau \gg \max \{r_{pq}^2, Z_{pq}^2\} \gg \sigma^2 \gtrsim Dt. \quad (5) \end{aligned}$$

The latter conditions for all pairs p, q guarantee not only that $\sigma|\nabla c_0|/c_0 \ll 1$ but also that the triangle with vertices $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3$ lies entirely in the interface region where the mean concentration gradient $\sim |\nabla c_0|$ is nearly a space-time constant. The time integrals of the six forcing terms on the right-hand side of Eq. (3) can be computed in the same manner, yielding $\mathcal{C}_{123} \propto |\nabla c_0|^3 (\sigma Dt)^2 / r^3$ (where r is some combination of r_{13}, r_{23}, r_{12} depending on β, γ), so that skewness $\mathcal{S}_{123} \propto (\sigma Dt/r^3)^{1/2}$ is growing in time and independent of $|\nabla c_0|$, even as $|\nabla c_0| \rightarrow 0$. See Appendix A for a sketch of

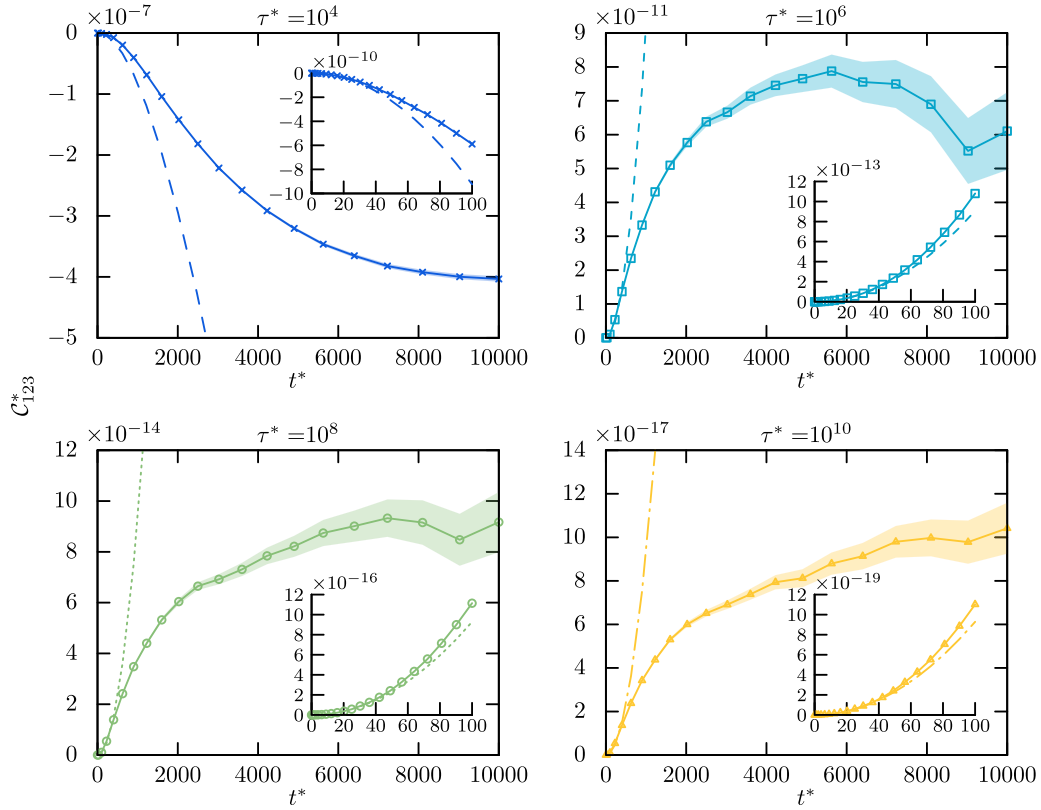


FIG. 1. Triple cumulants for the vertical equilateral triangle with side lengths $r^* = 50$ and for initial mean concentration profiles with $\tau^* = 10^4, 10^6, 10^8$, and 10^{10} going from left to right, top to bottom, respectively. Solid lines with symbols and shades show the numerical results and corresponding errors from the Lagrangian Monte Carlo computation. Dashed lines correspond to the analytical expression (Sec. A of the Supplemental Material [27]), valid asymptotically for short times, as highlighted by the insets. For corresponding results on the combined second cumulant $(C_{13}C_{23}C_{12})^{1/2}$ used to calculate the three-point skewness, see Appendix B, Fig. 4.

the calculation and Sec. A of the Supplemental Material for full details [27].

These conclusions may be confirmed and extended by an independent evaluation of the concentration cumulants with a Lagrangian Monte Carlo method, first employed for passive scalars in the Kraichnan model of turbulent advection [28–30] and recently applied by us to liquid mixing [25]. In this method, the DFV model (1) is solved for $D_0 = 0$ at the three points $\mathbf{x}_p$, $p = 1, 2, 3$, in one realization of the thermal velocity $\mathbf{w}$ by setting $c(\mathbf{x}_p, t) = c_0(\xi_p(t))$, where $d\xi_p/dt = \mathbf{w}_p$, $\xi_p(0) = \mathbf{x}_p$, $p = 1, 2, 3$, with $\mathcal{W} = (\mathbf{w}_1, \mathbf{w}_2, \mathbf{w}_3)$ a nine-dimensional Gaussian white noise with covariance

$$\langle w_{pi}(t)w_{qj}(t') \rangle_\xi = R_{ij}(\xi_p(t), \xi_q(t))\delta(t - t'), \quad (6)$$

for $p, q = 1, \dots, 3$ and $i, j = 1, \dots, 3$. By repeating this numerical integration for independent realizations $\mathcal{W}^{(n)}$, $n = 1, \dots, N$, the triple cumulant can then be evaluated by an empirical average over samples

$$C_{123} \simeq \frac{1}{N} \sum_{n=1}^N c'^{(n)}(\mathbf{x}_1, t) c'^{(n)}(\mathbf{x}_2, t) c'^{(n)}(\mathbf{x}_3, t), \quad (7)$$

where $c'^{(n)}(\mathbf{x}, t) = c^{(n)}(\mathbf{x}, t) - \bar{c}(\mathbf{x}, t)$. This scheme yields the exact cumulants without restriction to short times and larger, but it is subject to slow Monte Carlo convergence and can require a large number N of samples. In the original

application to turbulent advection [28–30], a number of samples $N \simeq 10^7$ sufficed, but our problem is much more demanding. First, the correlations between thermal velocity fluctuations decay with distance, opposite to the growing correlations for turbulent velocities. Second, we consider a problem of free decay rather than a statistical steady state as in the turbulence studies [28–30], and the decaying mean concentration field generates higher cumulants with absolute magnitude decreasing in time. For these reasons, accurate results for our case required $N \simeq 10^{14}$ samples, which we only achieved by a CUDA-MPI (Compute Unified Device Architecture library combined with Message Passing Interface paradigms) implementation designed to leverage the massive parallel-processing capabilities of GPUs (Graphic Processing Units). For more details on the numerics, see Ref. [25] and Sec. B of the Supplemental Material [27]. All results are calculated in dimensionless form, with $r^* = r/\sigma$, $t^* = 2Dt/\sigma^2$, and $c^* = c/c_0$.

We present in Fig. 1 the triple cumulant C_{123}^* at three points forming an equilateral triangle with side length $r_{13}^* = r_{23}^* = r_{12}^* = 50$ and lying in a plane perpendicular to $z = 0$ ($\gamma = 0$, $\beta = \pi/2$). (Results for another value $r^* = 100$ are presented in Sec. C of the Supplemental Material, which lead to the same conclusions [27]). The Lagrangian numerical results for four values of $\tau^* = 10^4$ – 10^{10} are seen generally to grow in magnitude with t^* and then roughly to saturate, within increasing Monte Carlo error. They agree well with

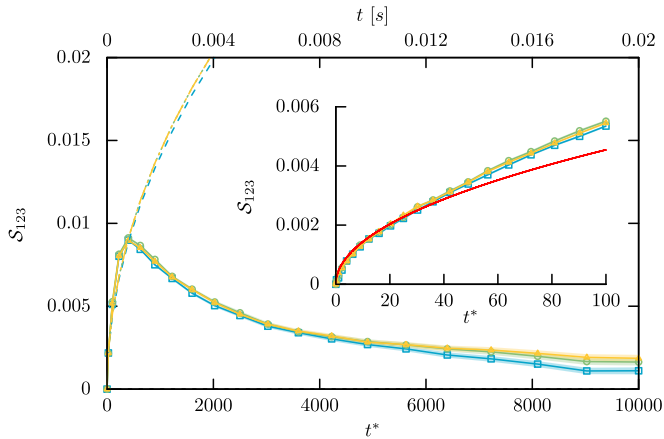


FIG. 2. Three-point skewness for the vertical equilateral triangle with side lengths $r^* = 50$ and small concentration gradients. [Colors and symbols are coded as in Fig. 1 for $\tau^* = 10^6$ (cyan squares), 10^8 (green circles), and 10^{10} (yellow triangles), The result for $\tau^* = 10^4$ can be found in Sec. C of the Supplemental Material [27]]. Solid lines with symbols and shades represent the numerical Lagrangian results and Monte Carlo errors, while dashed lines show the analytical prediction. The times t in seconds on the upper axis are calculated with reference values $\sigma = 10$ nm and $D = 2.2 \times 10^{-5}$ mm²/s for which the maximum skewness is achieved in about 4 ms. Short-time behavior is enlarged in the inset, with the red line showing the short-time asymptotic prediction for vanishing concentration gradient.

the analytic predictions for shorter t^* , as seen especially in the insets. The nonvanishing triple cumulants demonstrate non-Gaussianity of the concentration statistics. Note the intriguing change in sign between $\tau^* = 10^4$ and $\tau^* = 10^6$. For $\tau^* > 10^6$, however, the triple cumulants appear to become qualitatively similar and simply decreasing in magnitude with increasing τ^* , consistent with the estimate $C_{123} \propto |\nabla c_0|^3$. The latter scaling is confirmed by the plot of the three-point skewness S_{123} in Fig. 2, in which the results for the three largest τ values, differing over four orders of magnitude, essentially collapse. Note that the skewness from the Lagrangian Monte Carlo also agrees well with the asymptotic prediction at short t^* (inset) but thereafter attains a maximum value of about 0.01 and then slowly decreases in t^* , possibly to a nonzero quasisteady value. Our main conclusion is unaffected if the skewness vanishes as $t^* \rightarrow \infty$ but, crucially, it is essentially τ independent, not only in the early-time regime but over the entire t^* range studied. Thus, there is no central limit theorem with zero skewness in the limit of vanishing gradients, $\nabla c_0 \rightarrow 0$. Figure 2 constitutes the main result of this Letter.

We have thus shown that nonlinear Landau-Lifschitz fluctuating hydrodynamics for a binary mixture, in the high-Schmidt limit appropriate to liquid diffusion, implies non-Gaussian statistics of concentration fluctuations. An experimental test of these predictions might be feasible by light-scattering methods [31,32]. We have considered free diffusion of an initial inhomogeneous concentration field, but it would be interesting to investigate also nonequilibrium steady states. Beyond correlations, other statistics could show turbulentlike, non-Gaussian features such as fat tails in probability density functions (PDFs) [33]. Note, however, that this can occur only for multipoint variables such as

concentration increments, as the PDF of the single-point concentration indeed becomes Gaussian as $\nabla c_0 \rightarrow 0$: see Appendices and more comparisons with turbulence (Sec. D of the Supplemental Material [27]). Buoyancy effects of gravity that are known to quench long-range concentration correlations can be incorporated into the DFV model [20] and it is worth understanding their influence on non-Gaussianity. In low-gravity environments, in contrast, thermal noise effects are observed to propagate to the system size and thus non-Gaussian statistics occurring in liquid diffusion may have critical importance for space exploration [17].

Our results contradict the naïve expectations of MFT that statistics of fluctuations should become Gaussian in the limit of weak gradients. These predictions of MFT are rigorous central limit theorem results for simple toy models of particle diffusion, such as Kawasaki lattice gases, in a suitable “hydrodynamic scaling limit” [3,4]. However, it is not at all clear how to formulate a “hydrodynamic scaling limit” for the problem of liquid diffusion and recent work has shown that the HSL, even when mathematically applicable in principle, may be physically unattainable [34,35]. Furthermore, the DFV model accurately predicts other effects missed by MFT, such as renormalization of the bare diffusivity [20,36] that is commonly observed in molecular dynamics studies [37,38]. The latter renormalization as well as the non-Gaussian statistics calculated in the present study is due to nonlinear coupling of the diffusive mode with the momentum mode, which is a general phenomenon predicted by renormalization group [5] but not included in MFT analyses of diffusion [4]. It was a fundamental insight of the Kraichnan model that relative advection even by a Gaussian velocity field, such as thermal velocity fluctuations in this study, will produce non-Gaussian multipoint statistics for the advected scalar [21,22]. The non-Gaussian diffusive statistics predicted in Dirac fluids arise from a similar mechanism [14]. The magnitude of the skewness that we observe is not large (only 0.01 at maximum in the case considered in Fig. 2) but nonvanishing as $\nabla c_0 \rightarrow 0$, indicating persistent nonlinear coupling of concentration and velocity fluctuations. We have thus confirmed and extended the claims of earlier work that “nonequilibrium fluctuations do not represent merely a perturbation of a macroscopic state” [20,39,40]. Our results imply that MFT and HSL cannot be a universally valid explanation for origin of hydrodynamic behavior, not even for the familiar example of liquid diffusion.

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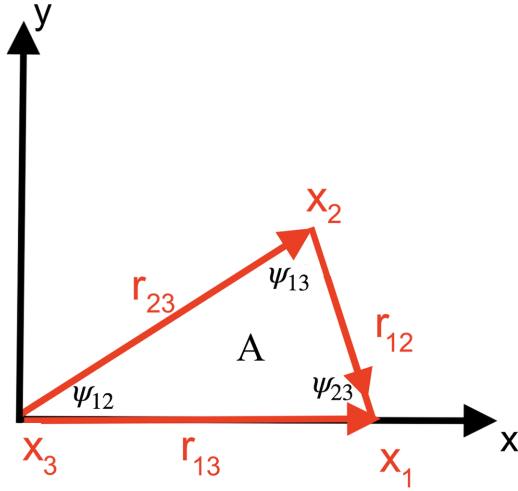


FIG. 3. Illustration of the triangle formed by vertices $\mathbf{x}_1$, $\mathbf{x}_2$, $\mathbf{x}_3$ in reference position in the horizontal plane.

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the European Union nor the granting authority can be held responsible for them.

Data Availability. The data that support the findings of this article are openly available [41].

Appendix A: Sketch of analytical computation of triple cumulants. We give here a brief sketch of the calculation of the triple cumulant of the concentration fluctuations, asymptotically for large separations and for short times. We refer to Fig. 3 for a sketch of the three points in the triple cumulant, forming the vertices of a triangle in the plane perpendicular to the mean gradient. The triangle is shown in the reference position that we adopt, before rotation by Euler angles β , γ into general orientation. The side lengths r_{13} , r_{23} , r_{12} and the interior angles ψ_{13} , ψ_{23} , ψ_{12} specify the geometry of the triangle. The source terms on the right-hand side of Eq. (3) for the triple cumulant that arise from gradients of the mean and second cumulant of the concentration depend on both the geometry of the triangle and its orientation and displacement along the gradient. The latter dependencies appear in the second cumulant C_{pq} through the azimuthal angle θ_{pq} and the mean displacement Z_{pq} , which ultimately can all be calculated knowing the geometry, orientation, and displacement of the triangle. Using these variables and the symmetries of the problem, the six source terms can all be calculated; for example, the first one, $F_{123} = R_{ij}(\mathbf{x}_1 - \mathbf{x}_2) \nabla_{x_i} \bar{c}_1 \nabla_{x_j} C_{23}$, becomes

$$F_{123} = \frac{k_B T}{4\pi\eta r_{12}} \bar{c}'(z_1) \left\{ (\cos\theta_{23} - \cos\psi_{13} \cos\theta_{12}) \frac{\partial C_{23}}{\partial r_{23}} + \frac{\sin^2\theta_{23} + \cos\theta_{12}(\cos\theta_{12} + \cos\psi_{13} \cos\theta_{23})}{r_{23}} \frac{\partial C_{23}}{\partial(\cos\theta_{23})} + \frac{1}{2}(1 + \cos^2\theta_{12}) \frac{\partial C_{23}}{\partial Z_{23}} \right\},$$

and similarly for all six source terms.

Following the asymptotic scheme outlined in the main text for the second cumulant, the leading-order contribution to the triple cumulant for large separations and short times is obtained simply by integrating in time the contributions from these six source terms. We here discuss only the simplifications that occur in the time $\tau \rightarrow \infty$. First, the mean concentration gradient becomes t independent to leading order: $\nabla \bar{c} \sim \nabla c_0 \sim c_0 / \sqrt{4\pi D \tau}$. In that case, one must evaluate time integrals only of the derivatives of the second cumulants. These are easily evaluated for large τ from Eq. (5) to be

$$\int_0^t \frac{\partial C}{\partial r_{pq}}(r_{pq}, \cos\theta_{pq}, Z_{pq}, s) ds \sim -\frac{3}{4} |\nabla c_0|^2 \frac{\sigma}{r_{pq}^2} (1 + \cos^2\theta_{pq}) D t^2$$

and

$$\int_0^t \frac{\partial C}{\partial(\cos\theta_{pq})}(r_{pq}, \cos\theta_{pq}, Z_{pq}, s) ds \sim \frac{3}{2} |\nabla c_0|^2 \frac{\sigma}{r_{pq}} \cos\theta_{pq} D t^2,$$

with other contributions asymptotically smaller. Combining the contributions from the six source terms and recalling that $D = k_B T / 6\pi\eta\sigma$, one obtains $C_{123} \propto |\nabla c_0|^3 (\sigma D t)^2 / r^3$ as claimed in the main text. It follows from this result that the three-point skewness S_{123} will remain finite in the limit of weak gradients or $\tau \rightarrow \infty$, at least for the large-separation, short-time regime. See Sec. A of the Supplemental Material for complete details of the calculation and also a short matlab code to evaluate the triple cumulant as a function of time in this regime, for any choice of the three points [27].

Appendix B: Numerical results for second cumulants. To obtain the Lagrangian Monte Carlo results for the three-point skewness S_{123} plotted in Fig. 2, not only are the results required for the triple cumulant C_{123} plotted in Fig. 1 but also required are the second cumulants C_{13} , C_{23} , C_{12} . The results for the second cumulant from the same Lagrangian Monte Carlo scheme were presented in our earlier paper [25] and these were compared there with the large-separation, short-time approximation (4). However, for completeness, we present here a similar comparison for the particular combination $(C_{13} C_{23} C_{12})^{1/2}$ that appears in our definition of the three-point skewness. In Fig. 4, we show this combination for the same three points and for the same τ values as that for the triple cumulants plotted in Fig. 1. An interesting observation is that the Monte Carlo errors are much smaller for the

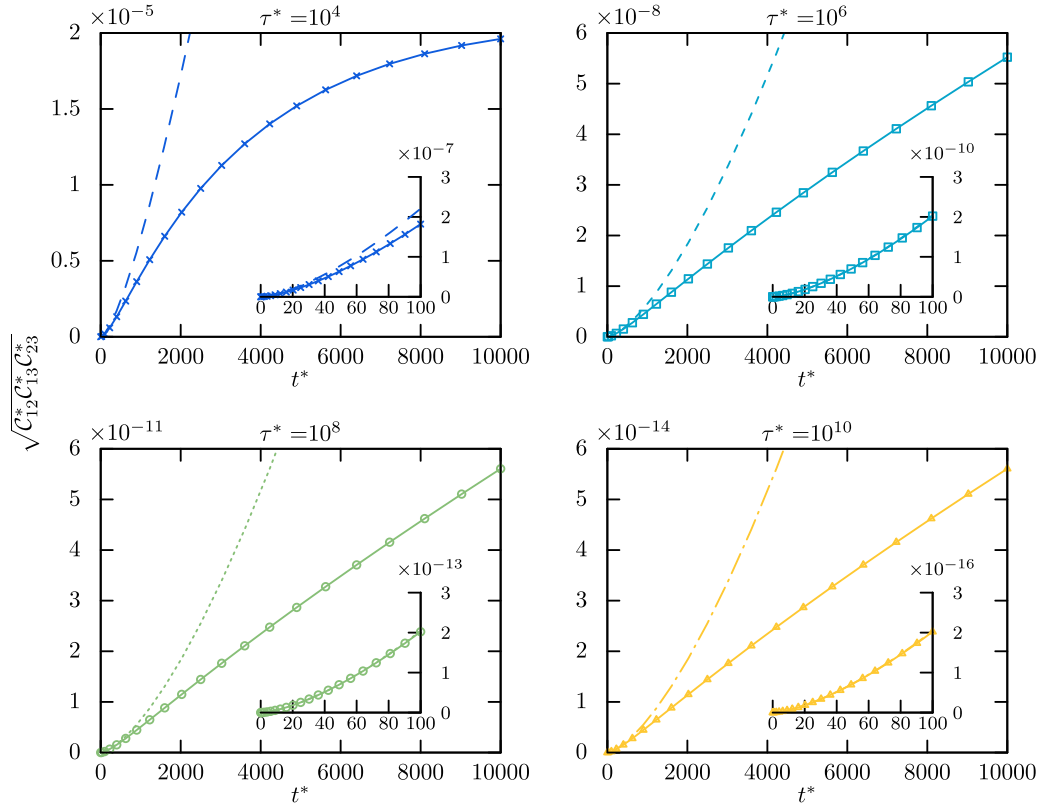


FIG. 4. Combined second cumulants $(C_{13}C_{23}C_{12})^{1/2}$ for the vertical equilateral triangle with side lengths $r^* = 50$ and for initial mean concentration profiles with $\tau^* = 10^4$, 10^6 , 10^8 , and 10^{10} going from left to right, top to bottom, respectively. Solid lines with symbols and shades represent numerical results and dashed lines the analytical prediction. Monte Carlo error is too small to be visible at this scale.

second cumulants than for the triple cumulants. In fact, it is these small error bars that, by standard propagation of error formulas, led to the relative smaller errors in the three-point skewness in Fig. 2 relative to the triple cumulant in Fig. 1. We have also plotted in Fig. 4 the predictions of the large-separation, short-time asymptotics. It can be seen especially in the insets of the figures, which enlarge into the short-time region, that the agreement between the analytical and numerical results is excellent. This close agreement provides a good check on both methods.

Appendix C: One-point PDFs of concentration fluctuations. Although it is not immediately obvious how to calculate the PDF of concentration fluctuations at multiple space points, it is easy in our model for $D_0 = 0$ to evaluate the PDF at a single point by using the fact that $c(\mathbf{x}, t) = c_0(\boldsymbol{\xi}(t))$, where $\boldsymbol{\xi}(0) = \mathbf{x}$ and $d\boldsymbol{\xi}/dt = \mathbf{w}$ is a white-noise process with covariance $\langle w_i(t)w_j(t') \rangle = 2D\delta_{ij}\delta(t - t')$. Since our nondimensionalization corresponds to taking $2D = 1$, this gives $c^*(z^*, t^*) = c_0^*(z^* + \sqrt{t^*}N)$ in dimensionless variables, with N a standard normal random variable. From our adopted initial concentration profile $c_0^*(\zeta^*) = \frac{1}{2}(1 + \text{erf}(\frac{\zeta^*}{\sqrt{2\tau^*}}))$, it is then straightforward to find the PDF of the concentration $c^*(z^*, t^*)$.

Because $c_0^*(\zeta^*)$ is a nonlinear function, this random variable is in general non-normal. For example, when $t^* = \tau^*$,

the theory of inverse transform sampling implies that $c^*(0, t^*)$ has a uniform distribution on the unit interval $[0, 1]$ of concentration values and for increasing $t^* > \tau^*$ its PDF becomes more peaked at values $c^* = 0$ and $c^* = 1$. On the other hand, in the opposite limit of weak concentration gradients, $\tau^* \gg t^*$, $(z^*)^2/2$, the result

$$c_0^*(\zeta^*) \simeq \frac{1}{2} \left(1 + \left(\frac{2}{\pi \tau^*} \right)^{1/2} \zeta^* \right)$$

implies that

$$c^*(z^*, t^*) \simeq \frac{1}{2} \left(1 + \left(\frac{2t^*}{\pi \tau^*} \right)^{1/2} N \right)$$

and converges to a Gaussian random variable with mean $\frac{1}{2}$ and standard deviation $\propto \nabla c_0^*$. It should be noted that a similar result holds also for $D_0 > 0$, since this amounts simply to replacing $D \mapsto D + D_0$.

Thus, the single-point statistics of the concentration indeed become Gaussian in the limit $\nabla c_0 \rightarrow 0$. This fact underlines the nontriviality of our results for multipoint statistics, which remain non-Gaussian in this same limit.

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