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RAPID COMMUNICATIONS

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Universal behavior of nonequilibrium fluctuations in free diffusion processes

Doriano Brogioli, Alberto Vailati,* and Marzio Giglio
Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia, Università di Milano, via Celoria 16, 20133 Milano, Italy

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We show that giant nonequilibrium fluctuations are present during the free diffusive remixing occurring in ordinary liquid mixtures and in macromolecular solutions. The static structure factor of the fluctuations is measured by using a quantitative shadowgraph technique. We show that structure factors at different times and from different samples can be rescaled onto a single master curve without any adjustable parameter, thus giving strong evidence that nonequilibrium fluctuations are a universal feature of free diffusion processes.

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Diffusion is the fundamental mass transfer mechanism in many natural and technological processes. The diffusive transport can be interpreted by the simple molecular random-walk model. A more refined description requires the understanding of direct interaction between the diffusing particles and possibly hydrodynamic interactions. Both types of interactions may produce appreciable changes in the magnitude of the effective diffusion coefficient D but, at any extent, diffusion is believed to give rise to an intimate and homogeneous remixing of matter. The general belief is that while the process occurs over quite macroscopic distances, nothing peculiar should occur at any other lengthscale, except the molecular one where the random walk molecular diffusion takes place.

We have recently shown that, quite unexpectedly, giant fluctuations are present during the diffusive remixing of two miscible phases of a binary mixture not too far from its critical point [1]. We have developed a fluctuating hydrodynamic description [2] which indicates that giant nonequilibrium fluctuations should be present during the diffusive remixing of fluids in general. So far, however, there is still no experimental evidence of the universality of the process.

In this Rapid Communication we report on the observation of giant fluctuations in the free diffusion processes occurring in two ordinary, low molecular weight liquid mixtures, an aqueous polymer solution and a protein solution, thus giving evidence that these anomalous fluctuations are a universal feature associated with spontaneous diffusion across a macroscopic gradient. The main result of this work is that the time-sequences for the static structure factor, measured during the free diffusion process in different samples, can be rescaled onto a unique master curve without any adjustable parameter.

Although low angle light scattering techniques are very suitable to study long-range correlated fluids, their sensitivity is hampered by the divergence of stray light at small wave vectors. The data presented in this paper were collected by using the shadowgraph projection technique. Shadowgraphy has traditionally been used to obtain a qualitative mapping of inhomogeneities in the index of refraction. However, very recently the technique has been reintroduced as a powerful quantitative tool to assess the features of long wavelength fluctuations in fluids [3,4].

We have investigated the free diffusion process that takes place when two miscible fluids are brought in contact, the mixing between adjoining regions being kept as little as possible before a measurement sequence. The samples investigated are concentrated aqueous solutions of urea (44% w/w), glycerol (38% w/w), polyethylene glycol 1000 (20% w/w), and lysozyme (16% w/w). All of these samples were diffused into pure water. The cell was filled with water first, the

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*Author to whom correspondence should be addressed. FAX: 39-02-2392-T12. Electronic address: vailati@fisica.unimi.it

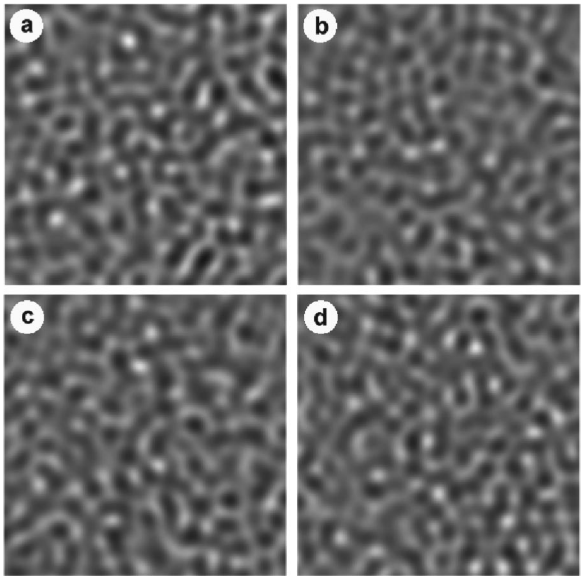

FIG. 1. Shadowgraph images of the nonequilibrium concentration fluctuations during the free diffusion process in aqueous solutions. (a) urea, (b) glycerol, (c) polyethylene glycol 1000, and (d) lysozyme. The images were recorded about 13 min after the start of the diffusion process. The side of each picture corresponds to 5 mm in real space.

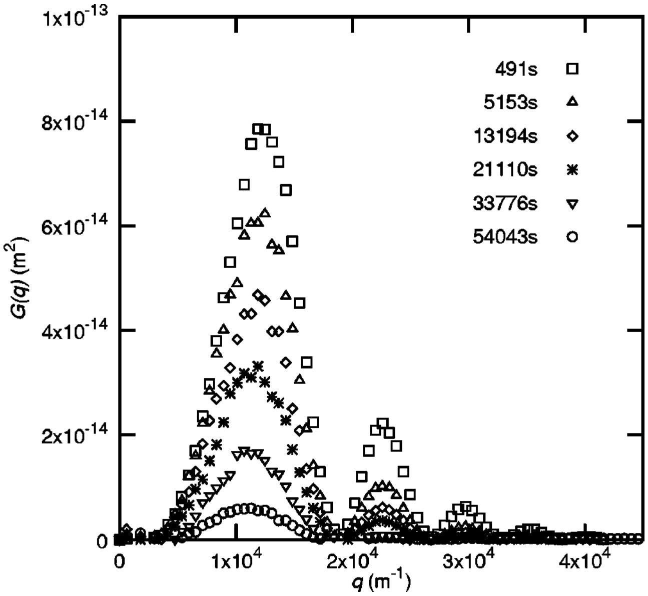

FIG. 2. Power spectrum $G(q)$ of the shadowgraph signal measured during the free diffusion process in the water-urea sample and plotted as a function of wave vector q. The oscillations in $G(q)$ are due to the sinusoidal dependence of the shadowgraph transfer function $T(q)$ on q^2.

denser solution being carefully injected from below, so as to smear the interface as little as possible. The two horizontal layers are initially separated by a fairly sharp meniscus. As shadowgraphy is an image forming technique, we were able to thoroughly check the sample for spurious disturbances at the interface before starting to collect data. As soon as the two phases came into contact, the diffusive remixing began, and the meniscus rapidly became smeared. The concentration profile inside the sample, initially a step function as a function of the height z, gradually evolved into an s-shaped function [5], until eventually, after a few days, the concentration became uniform throughout the sample.

The sample was illuminated by a time incoherent plane wave coming from a red LED coupled to a multimode fiber and propagating in the vertical direction through a 20 mm high cell. The intensity distribution on a plane 17.5 cm away from the cell was imaged onto a charge-coupled-device (CCD) camera as a function of time. Typical shadowgraph images of the giant concentration fluctuations in the four mixtures obtained a few minutes after the start of the diffusion process are shown in Fig. 1. The images are virtually indistinguishable. Although a typical lengthscale can be appreciated in Fig. 1, we will shortly show that this is partially due to the peculiar oscillating shadowgraph transfer function. The static structure factor of the non equilibrium fluctuations $S(q)$ has been investigated with quantitative shadowgraph analysis of Ref. [3]. Roughly 100 shadow images are collected in quick sequence (typically over a few sec) in order to accumulate adequate statistics, and the process is repeated in order to follow the diffusion process. The images are 512×512 pixels wide and span 256 gray levels. From these images we can derive the static spectrum of the fluctuations, which is related to the index of refraction fluctuations by the relation

$$\langle \delta n(\mathbf{q},k_z=0)\,\delta n(\mathbf{q}',k_z=0)\rangle = \delta(\mathbf{q}-\mathbf{q}')S(\mathbf{q}), \qquad (1)$$

where $\mathbf{q}$ and $\mathbf{q}'$ are two-dimensional vectors, representing the two components k_x and k_y of the three-dimensional wave vector.

The spectrum is derived as follows. For each image, the shadowgraph signal is given by

$$i(\mathbf{x}) = \frac{1}{\gamma}\,\frac{I(\mathbf{x})-I_0(\mathbf{x})}{I_0(\mathbf{x})}, \qquad (2)$$

where $I(\mathbf{x})$ is the intensity distribution as measured by the CCD sensor, $I_0(\mathbf{x})$ the blank intensity distribution with no fluctuations in the cell, and the coefficient γ characterizes the nonlinear response of the CCD detector [6]. The background term $I_0(\mathbf{x})$ is determined by averaging over an image sequence, so that the resulting image contains only contributions coming from nonuniform illumination of the sample, as the fluctuations are averaged to zero.

The shadowgraph signal power spectrum $G(q)$ can be calculated by means of two-dimensional FFT of the shadograph signal $i(\mathbf{x})$, $G(\mathbf{q}) = |\mathcal{F}[i(\mathbf{x})]|^2$, followed by the azimuthal average of the transformed matrix. The spectrum of non equilibrium fluctuations $S(q)$ can then be derived from the relation

$$G(q) = T(q)S(q), \qquad (3)$$

where $T(q)$ is the shadowgraph transfer function [3],

$$T(q) = \left[2k\sin\left(\frac{zq^2}{2k}\right)\right]^2 T_S(q), \qquad (4)$$

where z is the distance between the sample midplane and the plane imaged onto the CCD sensor, and k is the wave vector of the probe beam. The term $T_S(q)$ describes the source

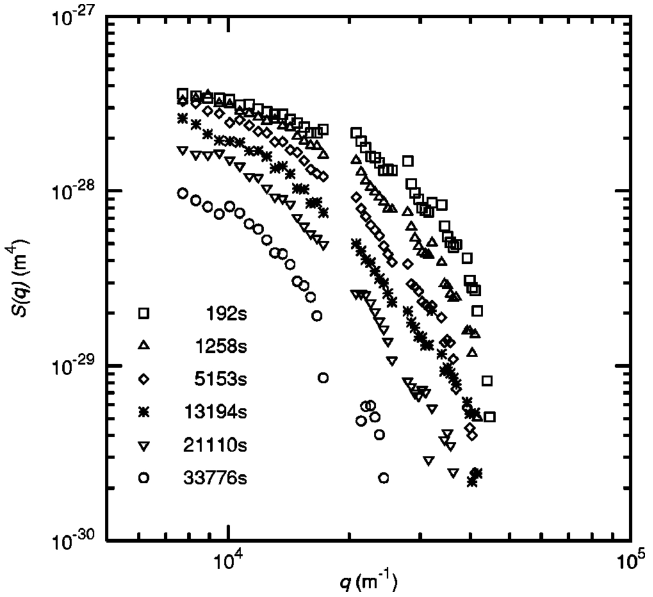

FIG. 3. Structure factor $S(q)$ of the concentration fluctuations measured during the free diffusion process in the water-urea sample and plotted as a function of wave vector q. Data around the zeroes of the shadowgraph transfer function have been omitted.

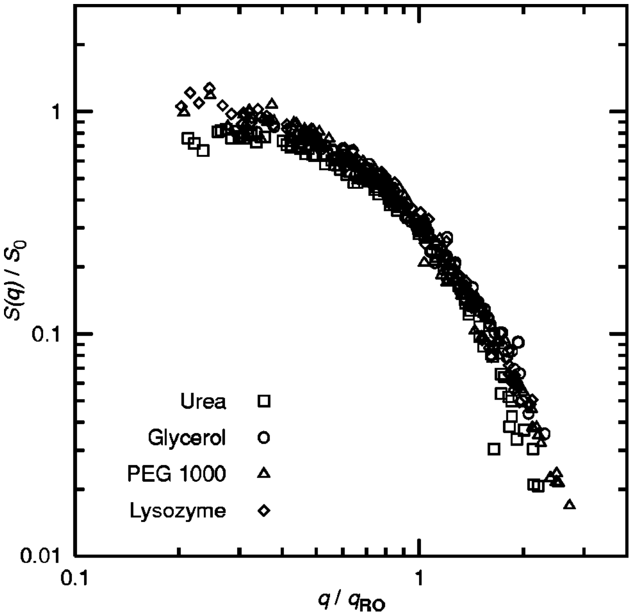

FIG. 4. Plot of the scaled static structure factor measured during the free diffusion process in aqueous solutions. The time sequences from individual samples are plotted by scaling the wave vector q with the time-dependent roll-off wave vector q_{RO} calculated from Eq. (6). The structure factors are scaled by the sample-dependent amplitude S_0 calculated from Eq. (8).

characteristics, and for a source of uniform intensity it reduces to the Airy function [3]. In the shadowgraph setup used here the source is the exit plane of a multimode fiber illuminated by a LED. Although in this case a bell-shaped function is still satisfactory to describe $T_S(q)$, it is difficult to assess *a priori* its typical width. Therefore, we decided to determine experimentally the overall transfer function $T(q)$. This was accomplished by performing measurements with a δ-correlated sample $[S(q)=\text{const}]$. The corresponding $G(q)$ was fitted with Eq. (4) so to obtain the oscillation frequency of the sinusoidal term and the source width [we assumed a Gaussian shaped $T_S(q)$].

Figure 2 shows the time evolution of the azimuthally averaged signal power spectrum $G(q)$ during the free diffusion process in the urea-water sample. The fast oscillations of $G(q)$ are due to the sinusoidal dependence of the shadowgraph transfer function on q^2 [see Eq. (4)]. The shadowgraph layout is arranged so that the oscillations of the transfer function are fast compared to the typical decay range of $S(q)$. The structure factor $S(q)$ is obtained by dividing $G(q)$ by the measured transfer function $T(q)$.

The time evolution of $S(q)$ for the urea-water sample is presented in Fig. 3, where we decided to omit data in regions around the zeros of the transfer function. A remarkable aspect of Fig. 3 is that the data are plotted in absolute units, without the need of any calibration procedure. This is because in the shadowgraph technique one measures both the reference beam and the shadowgraph intensity fluctuations with the same CCD sensor. This allows the direct calculation of the dimensionless shadowgraph signal defined by Eq. (2). The structure factor in Fig. 3 displays the features already observed during the free diffusion process in a near-critical binary mixture: a q^{-4}-compatible power-law divergence at large wave vectors, which has been interpreted as the result of the coupling of velocity fluctuations with concentration fluctuations, and the saturation at a constant value at small wave vectors, which is due to a stabilizing effect of gravity on long wavelength fluctuations. Moreover, the roll-off wave vector where the transition between the two regimes occurs gets smaller as time goes by, and the low wave vector value of the structure factor is initially constant. As we will see these two features of the structure factor are related to features of the macroscopic concentration profile. The observed nonequilibrium concentration fluctuations are originated from the coupling of velocity fluctuations with concentration fluctuations due to the presence of a macroscopic concentration gradient. This can be understood by simple naive arguments, discussed in much detail in Refs. [2] and [7]. Suppose that a small parcel of fluid of linear size a undergoes a velocity fluctuation. This fluctuation will displace the parcel until the viscous drag will stop it in a time given approximately by $\tau_{visc}=a^2/\nu, \nu$ being the kinematic viscosity. If the displacement of the parcel occurs in a direction parallel to the macroscopic concentration gradient, the parcel will be surrounded by fluid with different concentration. The lifetime of this concentration fluctuation is $\tau_{diff}=a^2/D$, and is much larger than the viscous time τ_{visc}, as $D \ll \nu$. Thus, in the presence of a macroscopic gradient, the effect of a short-living velocity fluctuation is to induce a long-lasting concentration fluctuation. Once a concentration fluctuation has been created, two mechanisms may contribute to its relaxation: diffusion and buoyancy. If the spatial extent of the fluctuation is small, then the fluctuation will soon disappear due to diffusion. This mechanism gives rise to the q^{-4} divergence of the static structure factor at intermediate wave vectors. However, if the fluctuation is large enough, the buoyancy force acting on it will be able to restore the fluctuation in the layer of fluid having the same density in a time shorter than the diffusive one. This gives rise to the frustration of the q^{-4} divergence at smaller wave vectors.

A more refined description of the fluctuations can be obtained by time-dependent fluctuating hydrodynamics [2]. It can be shown that the cumulative $S(q)$ of a diffuse interface is the sum of contributions from different layers, and in the hydrodynamic regime is best approximated by

$$S(q,t)=S_0\frac{1}{1+\left[\frac{q}{q_{RO}(t)}\right]^4}, \tag{5}$$

where the roll-off wave vector q_{RO} is given by

$$q_{RO}(t)=\left[\frac{\beta g\nabla c(t)}{\nu D}\right]^{1/4}, \tag{6}$$

g being the gravity acceleration, ν the kinematic viscosity, D the diffusion coefficient, and $\beta=\rho^{-1}(\partial\rho/\partial c)_{p,T}$ the solutal expansion coefficient. ∇c is the largest concentration gradient in the profile at a certain time [1,2],

$$\nabla c=\frac{\Delta c}{\sqrt{4\pi Dt}}. \tag{7}$$

The sample-dependent prefactor in Eq. 5 is given by

$$S_0=\frac{1}{(2\pi)^2}k_BT\left(\frac{\partial n}{\partial c}\right)^2\frac{\Delta c}{\rho\beta g}, \tag{8}$$

where Δc is the total concentration difference across the sample. During a run, q_{RO} changes as a function of time because of the changes in ∇c. The theoretical values for q_{RO} have been calculated from Eq. (6), and structure factors from each time sequence are presented in Fig. 4 as a function of the calculated reduced wave vector q/q_{RO}.

For each sample the observed change in q_{RO} during the free diffusion barely spans a factor of 2, while the data in each run span almost three decades in time. From Fig. 4, one can notice that structure factors from individual time sequences collapse onto a unique curve, thus confirming the validity of Eqs. (5), (6), and (8) to describe the time-dependent features of the nonequilibrium structure factor.

In order to check the consistency between data for different mixtures, the experimental structure factors measured during the free diffusion process in different samples have been normalized by dividing them by the calculated value of S_0, the sample-dependent prefactor that appears in Eq. (5) (S_0 varies by roughly a factor of 2 for the samples investigated). As can be noticed in Fig. 4, the data from different samples collapse nicely into a single master curve, which reproduces the fast q^{-4} divergence at larger wave vectors as well as the gravity-induced saturation effect at smaller q. We point out that the data in Fig. 4 are scaled according to the values calculated from Eq. (8) with no adjustable parameters. The $S(q)/S_0$ curves coalesce to 1 as $q/q_{RO}\rightarrow 0$ and this shows that there is good agreement between the measured and calculated values of S_0.

The present work gives strong experimental evidence that giant nonequilibrium fluctuations are a truly universal feature of diffusion across a macroscopic gradient in ordinary liquid mixtures and macromolecular solutions. The rescaling of the experimental results shows that the time-dependent fluctuating hydrodynamics model [2] is successful in quantitatively describing the typical features of the structure factor, namely the q^{-4} divergence and its saturation at small wavevectors. It also correctly accounts both for the time-dependent and the sample-related features of the static structure factor. Our results may have important consequences in the processes where macroscopic concentration gradients are present. In particular, as the roll-off wave vector gets very small under microgravity conditions, the fluctuations are predicted to grow enormously large at small wave vectors, and this may have important consequences on many diffusion-controlled experiments in microgravity.

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[5] E.L. Cussler, *Mass Transfer in Fluid Systems* (Cambridge University Press, Cambridge, England, 1984).

[6] The nonlinearity in the response of the CCD detector is described by the power law $I(\mathbf{x})\propto[j(\mathbf{x})]^{\gamma}$, where $j(\mathbf{x})$ is the intensity of the light impinging onto the CCD. The linearization of this relation for small intensity fluctuations yields Eq. (2), where $i(\mathbf{x})=\delta j(\mathbf{x})/j(\mathbf{x})$. The contrast γ can be measured independently by using a sample with a well known intensity probability distribution $P(I)$. In our case the calibrating sample was a ground glass illuminated by the spatially filtered 632.8 nm line of a He-Ne laser beam, so that the CCD camera was illuminated by a speckle field with a Gaussian probability distribution.

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