Chapter 9

Non-equilibrium fluctuations in a free diffusion experiment studied with SNFS

In this chapter, we describe a measurement of the power spectrum of the nonequilibrium fluctuations that arise during a free diffusion experiment. In Sect. 9.1 we discuss the origin of such fluctuations; in Sect. 9.2 we describe the physical system we studied; the results are shown in Sect. 9.3. The optical setup has been already described in Sect. 4.8.

9.1 Nonequilibrium fluctuations in free diffusion processes.

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 on matter. The general belief is that while the process occurs over quite microscopic distances, nothing peculiar should occur at any other lengthscale, except the molecular one where the random molecular diffusion takes place.

It has been recently shown that, quite unexpectedly, gigant fluctuations are present during the diffusive remixing of two miscible phases of a binary mixture not too far from its critical point [13]. A fluctuating hydrodynamic description has been developed [20], which indicates that gigant nonequilibrium fluctuations should be present during the diffusive remixing of fluids in general; moreover, it has been shown that the fluctuations can be considered the origin of the whole Fick flow [21].

The presence of the fluctuations has been detected experimentally during the free diffusive remixing occurring in ordinary liquid mixtures and in macromolecular solutions [22, 23]. The measurements concerned an ordinary, low molecular weight liquid mixture, an aqueous solution of a low molecular weight solid, a 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.

A free diffusion experiment begins filling a cell with the two liquids, with the denser solution in the lower part to avoid convective instability. The two horizontal layers are initially separated by a fairly sharp meniscus. As soon as the two liquids came into contact, the diffusive remixing begins, and the meniscus repidly becomes smeared. The concentration profile inside the sample, initially a step function as a function of the height z, gradually evolves into an s-shaped function [24], until eventually, after a few days, the concentration becomes uniform throughout the sample.

During the free diffusion process described above, intense fluctuations arise. Their power spectrum $S(\vec{q})$, with $\vec{q}$ in the horizontal direction, is given by:

$$S(q) = S_0 \frac{1}{1 + \left[\frac{q}{q_{RO}}\right]^4}. \tag{9.1}$$

The roll-off wave vector q_{RO} is given by:

$$q_{RO} = \sqrt[4]{\frac{\beta g \nabla c}{\nu D}} \tag{9.2}$$

where g is the gravity acceleration, ν is the kinematic viscosity, D is the diffusion coefficient, and $\beta = \frac{1}{\rho}\frac{\partial \rho}{\partial c}_p, T$ is the solutal expansion coefficient, a quantity that increases as increases the mismatching of the two liquids. The gradient ∇c can be assumed roughly connstant in the region between the fluids, where diffusion takes place, and vanishes outside. The sample-dependent prefactor in Eq. (9.1) is given by:

$$S_0 = K_B T \left(\frac{\partial n}{\partial c}\right)^2 \frac{\Delta c}{\rho \beta g} \tag{9.3}$$

where Δc is the total concentration difference across the sample.

The power spectrum $S(q)$ dislpays a q^{-4} power low divergence at large wave vectors, $q \gg q_{RO}$, and a saturation at a constant value at small wave vectors, $q \ll q_{RO}$. The q^{-4} power low is interpreted as the result of of the coupling of velocity fluctuations with concentration fluctuations, while the saturation 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 $\beta g \nabla c$, and the the low wave vector value of the power spectrum S_0 is roughly constant as free diffusion takes place, since the concentration near the upper and lower windows of the cell are initially constant.

The 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 detail in [20] and [25]. 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 $\tau_{visc} = a^2/\nu$, ν 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 life time 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 power spectrum at high wavevectors. As the wavevector increases, the velocity fluctuation lives for a shorter time, and can displace the parcel of a smaller amount, and this gives a factor q^{-2}; moreover, the displaced parcel will be dissipated as q^{-2}. 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 wavevectors.

9.2 The cell.

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 liquid sample we used was an aqueous solution of glycerol, with a weight fraction of 0.3. It was diffused into pure water. The cell was filled with the two liquids, with the denser solution in the lower part to avoid convective instability. The two horizontal layers are initially separated by a fairly sharp meniscus. As SNFS is an image forming technique, at least for big objects, we were able to thoroughly check the sample for spurious disturbances at the interface before starting collecting data. As soon as the two liquids came into contact, diffusion takes place, and the nonequilibrium fluctuations arise.

The main difficulty is to fill the cell, keeping the interface between the two liquids as regular as possible. We used a Flowing Junction Cylindrical Cell (FJCC), a prototype developed for the study of nonequilibrium fluctuations in microgravity [26]. From Eq. (9.2) we see that the roll off depends on the intensity of g, the gravitational acceleration. As g decreases, gravity acts at increasingly shorter wavevectors, and the divergence of fluctuations at small q

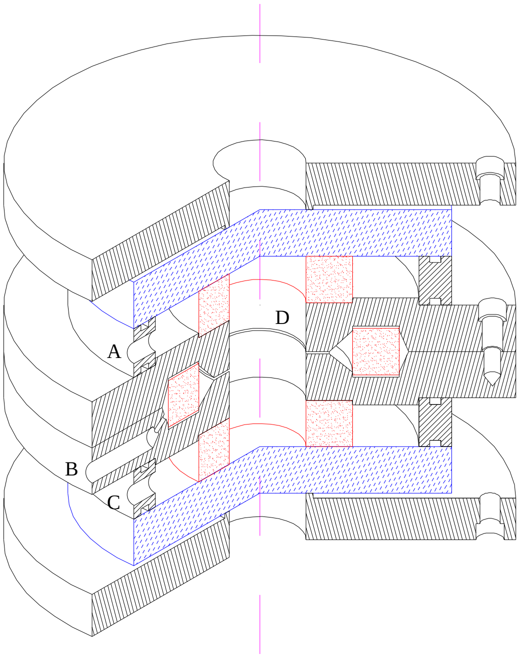

Figure 9.1: The Flowing Junction Cylindrical Cell, developed for measurements of non equilibrium fluctuations in free diffusion experiments in microgravity. The gray parts are made of perspex. The glass windows are blue in the drawing. The two liquids are injected through the holes: water in hole A and a solution of water and glycerol in hole C. They fill, respectively, the upper and the lower part of the cell. The two liquids come into contact in the middle of the cell, and the solution they form flows through the slit D and is extracted from the hole C. The porous rings, red in the drawing, make the flow more regular.

becomes more evident. From Eq. (9.3) we see that the intensity of the power spectrum for small wave vectors increases linearly in $1/g$. This divergence of the intensity of fluctuations on g will be studied in an experiment performed on the Intarnational Space Station. A drawing of the prototype cell is shown in Fig. 9.1; a picture can be seen in Fig. 9.2. Two pipes feed the cell with the two liquids, in the present study water and a solution of water and glycerol, with a small pressure. The liquids enter in two ring-shaped chambers, from which they flow in the cylindrical cell passing throug porous elements. The flow is quite symmetric, due to the presence of the porous rings. The two liquids fill the cell, water on the top and glycerol on the bottom; they come into contact in the middle of the cell, and are pushed out the cell through a circular slit. The outgoing liquid is collected in a third chamber, passes through another porous

Figure 9.2: A picture of the Flowing Junction Cylindrical Cell.

ring, and is collected by a pipe.

The FJCC can be filled also in microgravity, since it is based on the flow of liquids. However, gravity greatly simplifies this task: since the denser fluid is in the lower part of the cell, big fluctuations, created by macroscopic motions, relax due to buoyancy, while small fluctuations disappear quickly due to diffusion.

9.3 Results.

Although low angle light scattering techniques are very suitable to study long range correlated fluids, their sensitivity is hampered by the divergence of stry light at small wave vectors. The data presented in [22, 23] 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 [15, 16].

The main problem of shadowgraph is the oscillatory behaviour of its transfer function: see Eq. (3.37). The scattering intensities around the zeroes of the transfer function cannot be measured: for example, in Fig. 3 of [22], the values of $S(q)$ are missing for $q \approx 2 \cdot 10^4 \mathrm{m}^{-1}$. Moreove, the region in which the zeroes are too frequent cannot be considered in the data analysis. The overall wavevector range covered about one decade.

We measured the scatterig intensities at different times after the beginning of the diffusion process. The power spectra measured with SNFS are shown in Fig. 9.3. They show the q^{-4} divergence and the saturation for small wavevectors. The roll off wavevector is about $10^4 \mathrm{m}^{-1}$, and is compatible with the value given by Eq. (9.2)

The data cover about two decades in wavevectors: about ten times the range covered with shadowgraph. The quality must be compared with data shown in Fig. 2 of [13], obtained with SALS on a similar, but quite peculiar system: the wavevector range covered by SNFS is slightly more wide. Moreover, it should be noticed that SALS gives no reliable results for the present system, that is for the nonequilibrium fluctuations in the free diffusion of simple fluids, due to stray light, since the scattering is weak and the wavelength associated to the process is quite long. The results we present are the best obtained for such a system up to now.

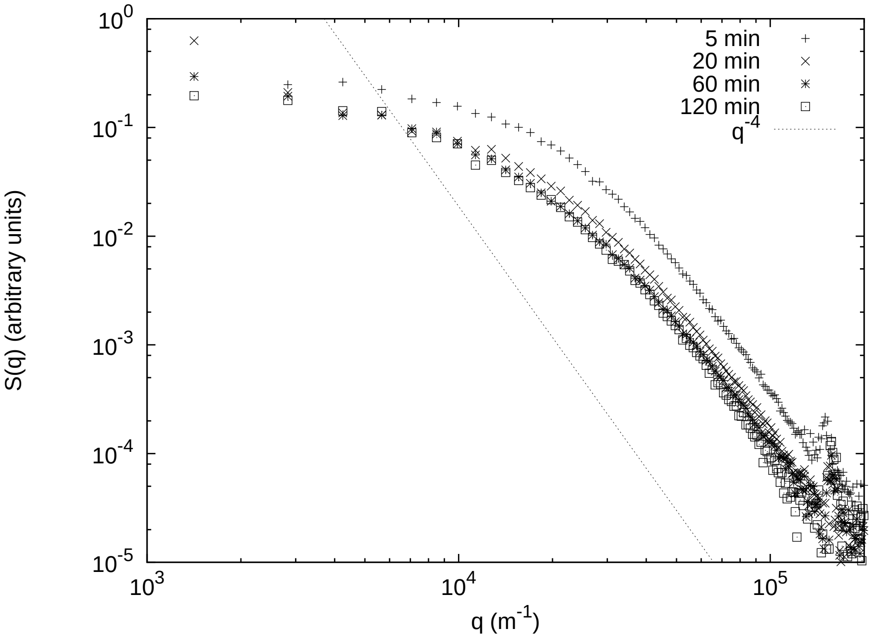

Figure 9.3: Measured power spectrum of non equilibrium fluctuations in the free diffusion process of glycerol in water.