Giant fluctuations in diffusion in freely-suspended liquid films.

Doriano Brogioli

January 18, 2013

Abstract

Recent works have shown that non-equilibrium concentration fluctuations arise during free diffusion in simple, three-dimensional fluids. In this paper, I extend the theory of non-equilibrium fluctuations to two-dimensional systems, and I evaluate the root mean square amplitude of the fluctuations in the presence of an uniform concentration gradient. I find that, in this case, fluctuations are expected to be extremely strong. Experimentally, two-dimensional liquid systems are approximated by freely suspended liquid films; diffusion is studied with I discuss the effect of the drag due to the fluids surrounding the film, that is the main known difference between real films and ideal two-dimensional liquids. In order to check experimentally this theory, I provide an evaluation of the power spectrum of the fluctuations that should arise during the diffusion of a spot with a gaussian profile, that can be directly compared with the results from a fluorescence recovery after photobleaching (FRAP) experiment. I propose that this kind of experiment could provide informations on the physical properties of membranes. PACS: 68.15.+e Liquid thin films, 68.65.-k Low-dimensional systems, 47.10.+g Fluid dynamics, 05.40.-a Fluctuations phenomena, 05.70.Ln, Nonequilibrium thermodynamics, 66.10.Cb Diffusion.

1 Introduction

Fick’s flow arises whenever a concentration gradient is present in a multicomponent fluid. The presence of this flux is the evidence of non-equilibrium condition; recently, fluctuations much stronger than equilibrium ones have been reported in systems made by couples of ordinary miscible fluids. These non-equilibrium fluctuations are originated by the termally excited velocity fluctuations, that displace volumes of fluid in layers with different concentrations. Also, it has been shown that this effect is the only origin of the Fick’s flow. Until now, the performed experiments and the developed theory concerned three-dimensional fluids, where fluctuations, though stronger than the equilibrium ones, are always very weak, and can be considered the low-frequency tail of a process that happens mainly at the molecular level. In this paper, I use the
theory of non-equilibrium fluctuations [6] to show that, in two dimensions, the fluctuations are very strong, and that they have a macroscopic, non negligible component. The calculation of the Fick's flow in an ideal two-dimensional liquid gives the already known divergence, that here I interpret as the effect of the divergence of the fluctuations at long wavelengths; the usual Saffman formula [7] can be obtained when considering the drag due to the surrounding fluids.

Usually, diffusion coefficient in freely suspended liquid films is measured by FRAP (fluorescence recovery after photobleaching); in a FRAP experiment, a spot is bleached on a film that contains a fluorescent dye, by a strong laser radiation: then, the diffusion of the bleached fluorophores is observed as a progressive smearing of the bleached spot. In this paper, I present the calculation of the power spectrum expected for the fluctuations arising during the diffusion of a component, that starts with a gaussian distribution, similar to what happens in FRAP experiments. The results should be valid for completely liquid films; I propose that the measurement of deviations from the expected spectrum could be used to study the effect of rigid structures in the film, or the interaction with surrounding media.

2 Root mean square amplitude of the fluctuations.

The time evolution of the concentration $c(\vec{x}, t)$ is given by convection and diffusion:

$$\frac{\partial}{\partial t} c(\vec{x}, t) = -\vec{u}(\vec{x}, t) \cdot \vec{\nabla} c(\vec{x}, t) + D \nabla^2 c(\vec{x}, t)$$

(1)

where $\vec{u}(\vec{x}, t)$ is the velocity field and $D$ is the diffusion constant. I assume that the concentration gradient is a constant, since it is always much more than the fluctuations. In Fourier space:

$$-i\omega c(\vec{q}, \omega) = -\vec{u}(\vec{q}, \omega) \cdot \vec{\nabla} c_0 - q^2 D c(\vec{q}, \omega)$$

(2)

By solving with respect to the concentration, I obtain the correlation functions:

$$\langle c(\vec{q}, \omega) c^*(\vec{q}', \omega') \rangle = \nabla^2 \frac{\delta \langle \bar{u}(\vec{q}, \omega) \cdot \vec{z} \bar{u}^*(\vec{q}', \omega') \cdot \vec{z} \rangle}{D^2 q^4 + \omega^2}$$

(3)

where $\vec{z}$ is the versor of the concentration gradient. The velocity correlation function for a liquid is:

$$\langle \bar{u}(\vec{q}, \omega) \cdot \vec{z} \bar{u}^*(\vec{q}', \omega') \cdot \vec{z} \rangle = \delta \langle \vec{q} - \vec{q}' \rangle \delta (\omega - \omega') \frac{K_B T \nu q^2 - (\vec{q} \cdot \vec{z})^2}{8\pi^2 \rho}$$

(4)

In both 3 and 2 dimensions [2, 5, 8]:

$$\langle c(\vec{q}, \omega) c^*(\vec{q}', \omega') \rangle = \delta \langle \vec{q} - \vec{q}' \rangle \delta (\omega - \omega') \frac{K_B T \nu q^2 - (\vec{q} \cdot \vec{z})^2}{8\pi^2 \rho \nabla^2} \frac{q^2 - (\vec{q} \cdot \vec{z})^2}{(\omega^2 + D^2 q^4) (\omega^2 + \nu^2 q^4)}$$

(5)
It should be noticed that, in 2d, $\rho$ is the superficial mass density.

The static power spectrum of the fluctuations can be derived, by integrating over $\omega$. The diffusion time is much longer than the viscous time, since $D \ll \nu$. 

$$
\langle c(\vec{q}, t) c(\vec{q}', t) \rangle = \delta (\vec{q} + \vec{q}') \frac{K_B T}{8\pi^3 \rho} \nabla c^2 \frac{1}{\nu D} q^1 \frac{1}{q^4} \left( \frac{q^2 - (\vec{q} \cdot \vec{z})^2}{q^2} \right) ^2 \tag{6}
$$

Root mean square value of the fluctuations of concentration, in 3d, by using polar coordinates:

$$
c_{\text{rms}}^2 = \frac{K_B T}{8\pi^3 \rho} \nabla c^2 \frac{1}{\nu D} \int_0^{2\pi} d\varphi \int_0^{\pi} \sin (\theta) d\theta \int_Q^\infty q^2 dq \frac{\sin^2 (\theta)}{q^4} \tag{7}
$$

$$
c_{\text{rms}}^2 = \frac{K_B T}{3\pi^2 \rho} \nabla c^2 \frac{1}{\nu D} Q \tag{8}
$$

where $Q$ is the wavevector of the longest wavelength fluctuations. At the beginning, the concentration of the solution increases by $\Delta c$ along a length $L$. The gradient is thus $\nabla c = \Delta c / L$. The time needed for the fluctuations in order to fully develop is their diffusive time. The most intense fluctuations will be found approximately at the diffusive time of the macroscopic concentration profile; at that time $Q \approx \pi / L$.

$$
c_{\text{rms}}^2 = \frac{K_B T}{3\pi^2 \rho} \frac{\Delta c^2}{L} \frac{1}{\nu D} \tag{9}
$$

Using Stokes-Einstein relation [9]:

$$
D = \frac{K_B T}{6\pi \eta a} \tag{10}
$$

for writing $D$ in terms of the shear viscosity $\eta$ and the radius $a$ of the diffusing particles, I obtain:

$$
c_{\text{rms}} = \Delta c \sqrt{\frac{2\eta}{\pi \nu D a}} \tag{11}
$$

This equation shows that fluctuations are essentially a molecular effect in 3D: as the size $L$ of the sample increase with respect to the molecular size $a$, the fluctuation amplitude decrease.

Root mean square value of the fluctuations of concentration, in 2d:

$$
c_{\text{rms}}^2 = \frac{K_B T}{8\pi^3 \rho} \nabla c^2 \frac{1}{\nu D} \int_0^{2\pi} d\theta \int_Q^\infty q dq \frac{\sin^2 (\theta)}{q^4} \tag{12}
$$

$$
c_{\text{rms}}^2 = \frac{K_B T}{4\pi^2 \rho} \nabla c^2 \frac{1}{\nu D} Q^2 \tag{13}
$$

Following the previous calculation:

$$
c_{\text{rms}}^2 = \frac{K_B T}{4\pi^4 \rho} \Delta c^2 \frac{1}{\nu D} \tag{14}
$$
The term $1/Q$ multiplied by the gradient of $c$ gives the total concentration difference.

This equation shows that, for an ideal 2D fluid, the relative fluctuation amplitude does not vanish as the size $L$ of the system increases. Fluctuations are not a molecular effect in 2D. Moreover, it can be noticed that the fluctuations, as expected from Eq. (14), can be of the same order as the macroscopic concentration difference. We could also consider cases in which Eq. (14) gives unreal result $c_{rms} > \Delta c$: this means that linearization is not allowed.

In the case of a free-standing liquid film, the diffusion coefficient $D$ must be evaluated by using Saffmann equation, that holds for a thin sheet of liquid, surrounded by a less viscous fluid [7, 10, 11]:

$$D = \frac{K_B T}{4\pi \eta_0 h} \ln \left( \frac{l}{aq_C} \right) \quad (15)$$

where $q_C = 2 \eta_1 / (h\eta_0)$, $\eta_0$ is the shear viscosity of the fluid film, $\eta_1$ is the shear viscosity of the surrounding fluid, $h$ is the thickness of the fluid sheet, $a$ is the radius of the molecules, and $l \approx 1.12294$ is an adimensional constant, close to 1. Since we are dealing with a two dimensional fluid, the mass density of the liquid composing it is $\rho/h$, and thus $\eta_0 h = \rho \nu$. The meaning of the critical wavelength $q_C$ will be discussed in more depth later. I obtain:

$$c_{rms} = \Delta c \sqrt{\frac{1}{\pi^3 \ln \left( \frac{l}{aq_C} \right)}} \quad (16)$$

For a soap film $c_{rms} \approx 0.07 \Delta c$.

Comparing eq. (11) and eq. (16) we can notice that the greatest root mean square amplitude reached by the fluctuations in three dimensions decreases as the initial concentration distribution becomes macroscopic, with the square root of the size of the region where the gradient is present. In two dimensions the process is completely independent on the size of the region where the gradient is present. There is indeed a macroscopic characteristic size, that is $1/q_C$, but the dependence of the fluctuation amplitude on this characteristic size is only logarithmic.

### 3 Non-equilibrium fluctuations with a non-constant gradient

In experiments on free-standing liquid films, the gradient is limited to a small region of the sample. For example, we can use fluorescent molecules, and mark a part of the molecules by photo-bleaching, and then we can follow the diffusion and formation of fluctuations in fluorescence. In order to evaluate the results of such an experiment, we must know what happens in the case of a non-constant, time-dependent gradient. Here are the calculations.
\[
\frac{\partial}{\partial t} c(\vec{x}, t) = -\vec{u}(\vec{x}, t) \cdot \vec{\nabla} c(\vec{x}, t) + D \nabla^2 c(\vec{x}, t) \quad (17)
\]

Approximation: \( c(\vec{x}, t) = \delta c(\vec{x}, t) + c_0(\vec{x}, t) \)

At zeroth-order:
\[
\frac{\partial}{\partial t} c_0(\vec{x}, t) = D \nabla^2 c_0(\vec{x}, t) \quad (18)
\]

At the first order in the fluctuations:
\[
\frac{\partial}{\partial t} \delta c(\vec{x}, t) = -\vec{u}(\vec{x}, t) \cdot \vec{\nabla} c_0(\vec{x}, t) + D \nabla^2 \delta c(\vec{x}, t) \quad (19)
\]

Ansatz: \( \delta c(\vec{x}, t) = \vec{\xi}(\vec{x}, t) \cdot \vec{\nabla} c_0(\vec{x}, t) \).

\[
\frac{\partial}{\partial t} \vec{\xi}(\vec{x}, t) = -\vec{u}(\vec{x}, t) + D \nabla^2 \vec{\xi}(\vec{x}, t) \cdot \vec{\nabla} c_0(\vec{x}, t) \quad (20)
\]

There are also other mixed terms, \( \partial/\partial x \nabla c_0 \times \partial/\partial x \xi \), which are negligible if the fluctuations are on spatial scales smaller than the macroscopic concentration profile. Moreover, we are interested only in the component of \( \xi \) along \( \vec{\nabla} c \), so we can arbitrarily add a second equation, thus obtaining the following vector equation:
\[
\frac{\partial}{\partial t} \vec{\xi}(\vec{x}, t) = -\vec{u}(\vec{x}, t) + D \nabla^2 \vec{\xi}(\vec{x}, t) \quad (21)
\]

In the Fourier space:
\[
\frac{\partial}{\partial t} \vec{\xi}(\vec{q}, t) = -\vec{u}(\vec{q}, t) - Dq^2 \vec{\xi}(\vec{q}, t) \quad (22)
\]

Solving we get:
\[
\vec{\xi}(\vec{q}, t) = \int_0^t \vec{u}(\vec{q}, t') e^{-Dq^2(t-t')} dt' \quad (23)
\]

Now, we calculate the correlation matrix of \( \xi \):
\[
\langle \vec{\xi}(\vec{q}, t) \cdot \vec{\xi}^T(\vec{q}', t) \rangle = \int_0^t dt' dt'' \langle \vec{u}(\vec{q}, t') \cdot \vec{u}^T(\vec{q}', t'') \rangle e^{-D|\vec{q}|^2(2t-t')e^{-D|\vec{q}|^2(2t-t'')}} \quad (24)
\]

The velocity correlation is a Dirac delta, whence \( q = q' \); moreover, since \( u(q) \) is orthogonal to \( q \), the matrix is the operator which projects orthogonally to \( q \):  
\[
\langle \vec{\xi}(\vec{q}, t) \cdot \vec{\xi}^T(\vec{q}', t) \rangle = \delta(\vec{q} - \vec{q}') S_\xi(\vec{q}, t) \quad (25)
\]

\[
S_\xi(\vec{q}, t) = \left[ 1 - \frac{\vec{q} \cdot \vec{q}'}{|\vec{q}|^2} \right] S_\xi(\vec{q}, t) \quad (26)
\]

\[
S_\xi(\vec{q}, t) = \int_0^t dt' dt'' \langle \vec{u}(\vec{q}, t') \cdot \vec{u}^*(\vec{q}', t'') \rangle e^{-D|\vec{q}|^2(2t-t'') e^{-D|\vec{q}|^2(2t-t'')}} \quad (27)
\]
By using the definition of spectrum in $\omega$ we get:

$$S_\xi (\vec{q}, t) = \int d\omega \left| \int_0^t e^{-Dq^2(t-t')} - i\omega t' dt' \right|^2 S_\vec{u} (\vec{q}, \omega)$$

(28)

Now we calculate the integral in $dt'$:

$$S_\xi (\vec{q}, t) = \int d\omega \frac{e^{-2Dq^2t} + 1 - 2 \cos (\omega t) e^{-Dq^2t}}{\omega^2 + D^2q^4} S_\vec{u} (\vec{q}, \omega)$$

(29)

In the limit of $t \gg 1/(Dq^2)$:

$$S_\xi (\vec{q}, t \to +\infty) \to \int d\omega \frac{1}{\omega^2 + D^2q^4} S_\vec{u} (\vec{q}, \omega)$$

(30)

Anyhow, the width of the Maxwellian curve is $Dq^2$, which is much less than the width in $\omega$ of the velocity correlation; for this reason we can approximate as follows:

$$S_\xi (\vec{q}, t) = S_\vec{u} (\vec{q}, \omega = 0) \int d\omega \frac{e^{-2Dq^2t} + 1 - 2 \cos (\omega t) e^{-Dq^2t}}{\omega^2 + D^2q^4}$$

(31)

By integrating:

$$S_\xi (\vec{q}, t) = \frac{\pi}{Dq^2} \frac{1 - e^{-2Dq^2t}}{Dq^2} S_\vec{u} (\vec{q}, \omega = 0)$$

(32)

From Ref. [12], we can evaluate the velocity fluctuation:

$$S_\xi (\vec{q}, t) = \frac{1 - e^{-2Dq^2t}}{Dq^2} \frac{K_B T}{4\pi^3 q_0 h} \frac{1}{q (q_C + q)}$$

(33)

Here we can also write $\eta_0 h = \rho_0 \nu$, with the superficial density. Now we apply the Saffman formula for the diffusion coefficient in 2D:

$$S_\xi (\vec{q}, t) = \frac{1}{\pi \ln \left( \frac{1}{aq_C} \right)} \frac{1 - e^{-2Dq^2t}}{q^3 (q_C + q)}$$

(34)

Ritorniamo a delta $c$, e scriviamo la trasformata del prodotto come convoluzione delle trasformate:

$$\delta c (\vec{q}, t) = -i \int d\vec{q}' c_0 (\vec{q}', t) \vec{q}' \cdot \hat{\xi} (\vec{q} - \vec{q}', t)$$

(35)

Calcoliamo lo spettro; in questo caso non si ha $<dc(q)dc(q')>$, perché’ di fatto c’e’ una correlazione anche se $q \neq q'$.

$$\langle |\delta c (\vec{q}, t)|^2 \rangle = \int d\vec{q}' |c_0 (\vec{q}', t)|^2 \vec{q}' \cdot \hat{S}_\xi (\vec{q} - \vec{q}', t) \cdot \vec{q}'$$

(36)
Ora usiamo ancora la approssimazione su $c$: che il suo modulo sia diverso da 0 solo per valori di $q'$ piccoli, molto più piccoli dei $q$ a cui siamo interessati.

$$\left\langle |\delta c(q', t)|^2 \right\rangle = C_0^2(q', t) S_\xi(q', t)$$  \hspace{1cm} (37)

dove

$$C_0^2(q', t) = \int dq' |c_0(q', t)|^2 \frac{|q'|^2 - (q' \cdot q')^2}{|q' - q|^4}$$  \hspace{1cm} (38)

rappresenta una misura della quantità di gradiente macroscopico. Si noti che dipende solo dalla direzione di $q$, e non dal modulo. Una volta fatto lo spettro di potenza dell’immagine, che è la somma degli spettri di potenza da $c_0$ e $\delta c$, possiamo valutare $C_0^2$ integrando per valori di $q$ piccoli, e poi dividere lo spettro risultante per $C_0^2$.

Amplitude of the fluctuations:

$$c_{\text{rms}}^2(\vec{x}, t) = \vec{\nabla} c_0^T(\vec{x}, t) \cdot \left\langle \vec{\xi}(\vec{x}, t) \cdot \vec{\xi}^T(\vec{x}, t) \right\rangle \cdot \vec{\nabla} c_0(\vec{x}, t)$$  \hspace{1cm} (39)

From the definition of the Fourier transform:

$$c_{\text{rms}}^2(\vec{x}, t) = \vec{\nabla} c_0^T(\vec{x}, t) \cdot \int S_\xi(q, t) dq \cdot \vec{\nabla} c_0(\vec{x}, t)$$  \hspace{1cm} (40)

Now we rewrite the equations in polar coordinates; we use the definition of $S_\xi$ and we add a low-frequency cut-off, representing the macroscopic length scale on which $c_0$ is present.

$$c_{\text{rms}}^2(\vec{x}, t) = \left| \vec{\nabla} c_0(\vec{x}, t) \right|^2 \int_0^{2\pi} d\vartheta \cos^2(\vartheta) \int_0^{+\infty} dq S_\xi(q, t)$$  \hspace{1cm} (41)

Now we put the expression of $S$:

$$c_{\text{rms}}^2(\vec{x}, t) = \left| \vec{\nabla} c_0(\vec{x}, t) \right|^2 \frac{1}{\pi \ln \left( \frac{l}{aqc} \right)} \int_0^{+\infty} dq \frac{1 - e^{-2Dq^2t}}{q^2(qc + q)}$$  \hspace{1cm} (42)

We change the integration variable:

$$c_{\text{rms}}^2(\vec{x}, t) = \left| \vec{\nabla} c_0(\vec{x}, t) \right|^2 \frac{1}{\pi \ln \left( \frac{l}{aqc} \right)} 2Dt f^2(qc^22Dt)$$  \hspace{1cm} (43)

where:

$$f(x) = \sqrt{\frac{1}{x} \int_0^{+\infty} 1 - e^{-xy^2} \frac{dy}{y^2(y + 1)}}$$  \hspace{1cm} (44)

The integral can be solved in terms of special functions.

$$f(x) = \frac{1}{\sqrt{2\pi}} \sqrt{e^{-x} \left[ -\pi \text{Erfi}\sqrt{x} + \text{Eir} \right] - \gamma + 2\sqrt{\pi x} - \log x}$$  \hspace{1cm} (45)
Figure 1: Function $f(x)$ of Eq. (45), and asymptotic approximations.
where \( E_i \) is the integral exponential function, \( \text{Erfi} \) is \( \text{erf}(ix)/i \), and \( \gamma \) is the Euler gamma function. The function \( f(x) \) is shown in Fig. 1. Limits: for \( x \to 0 \) \( f(x) \approx \sqrt{-\log(x)/2} \); for \( x \to +\infty \) \( f(x) \approx 1/\sqrt{x/\pi} \).

Root mean square:

\[
c_{rms}(\vec{x},t) = \left| \nabla c_0(\vec{x},t) \right| \sqrt{\frac{1}{Dt}} \frac{1}{\sqrt{\pi \ln \left( \frac{1}{q_{2C}} \right)}} f(q_{2C}^2Dt) \tag{46}
\]

The numeric factor (the root), is about 1/3. The term \( \nabla c 2Dt \) is the difference of concentration over a distance equal to the diffusion length.

4 Non-equilibrium fluctuations in a FRAP experiment on a freely-suspended liquid film

In the previous section, a two-dimensional fluid was analyzed, in which a constant concentration gradient was present. In this section, I analyze an actual system, that could be experimented. In the real world, a thin, freely suspended liquid layer is considered a system that follows two-dimensional hydrodynamics, on length scales longer than the layer thickness. Many experiments have been performed on soap films, that consist of two monolayers of amphiphilic molecules around a layer of water. The layer thickness ranges from the 4nm of the Newton black film to many micrometers; features down to a fraction of a millimeter should be considered two dimensional \[13\]. Also smectic A liquid crystals can form films, by a different effect. It spontaneously form a layered structure, with the elongated molecules alligned to the surface normal. When a film is drawn from this kind of liquid crystal, it is formed by a set of monolayers, ranging from two to many hundreds \[11\]; the thickness can be selected with extreme accuracy. Because of the absence of translational order in the monolayers, the film behaves as a two dimensional system.

Many papers \[13, 14, 15, 16, 17\] describe experiments in which turbulent flows have been detected, and discuss the agreement with two dimensional hydrodynamics. One result is that the role of the air surrounding the film cannot be neglected. In turbulent flows, it damps the turbulent vortices. From a theoretical point of view, an exact evaluation of this effect is extremely difficult; for example, Rivera et al. \[18\] modeled this damping as a linear drag term in the two dimensional Navier-Stokes equations, in order to describe velocity fluctuations observed in a turbulent flow. They evaluated the amplitude of the drag term from experimental data; from this value, they found the dissipation due to air friction to be a significant energy dissipation mechanism in their experimental system.

Another well known effect of air friction on thin liquid films can be found in diffusion of particles, whose diameter is about the thickness of the layer. Neglecting air friction, the mobility of a particle in a two dimensional system should be infinite, that is, a particle subjected to a steady force should accelerate
indefinitely. This would result in an infinite diffusion coefficient. Saffman \[7\] found that air friction reduces the mobility to a finite value: the author evaluated the diffusion coefficient and found that it strongly depends on the viscosity of the surrounding fluid, and diverges as the viscosity vanishes. Saffman formula has been tested both in soap films \[10\] and in liquid crystal films \[11\].

Diffusion has been measured in liquid crystal films, by FRAP experiments. The observation of the diffusion of the bleached spots should show strong fluctuations. In the following, I describe an algorithm for evaluating the fluctuations, arising during the diffusion of a gaussian-shaped spot; I also include the effect of drag of the surrounding fluids.

Now we evaluate \( C_0^2 \) for a Gaussian spot. First of all, we use the circular symmetry:

\[
C_0^2 (t) = \int q' dq' d\vartheta |c_0 (q', t)|^2 q'^2 \sin^2 (\vartheta) = \int_0^{+\infty} \frac{dq'}{2} q'^3 |c_0 (q', t)|^2
\]

and we put an explicit solution of the diffusion equations:

\[
c_0 (q, t) = c_0 e^{-q^2/2\sigma^2(t)}
\]

where \( \sigma^2(t) = \sigma_0^2/(1 + 2D\sigma_0^2 t) \)

\[
C_0^2 (t) = \frac{c_0^2}{2} \int_0^{+\infty} dq q^3 e^{-q^2/\sigma^2(t)} = \frac{c_0^2}{4} \sigma^4(t)
\]

Now we evaluate the whole spectrum:

\[
S_c (q) = c_0^2 e^{-q^2/\sigma^2(t)} + \left| \delta c (\vec{q}, t) \right|^2 = c_0^2 e^{-q^2/\sigma^2(t)} + \frac{c_0^2}{4} \sigma^4(t) \frac{1}{\pi^2 \ln \left( \frac{l_{\alpha q_C}}{\alpha q_C} \right)} \frac{1 - e^{-2Dq^2 t}}{q^3 (q_C + q)}
\]

We rescale the variables, by placing \( x = q/\sigma(t) \) and \( s_c (x) = S_c (x) / c_0^2 \):

\[
s_c (x) = e^{-x^2} + \frac{1}{4\pi^2 \ln \left( \frac{l_{\alpha q_C}}{\alpha q_C} \right)} \frac{1 - e^{-x^2} 2D\sigma^2(t) t}{x^3 (q_C/\sigma(t) + x)}
\]

For \( 2D\sigma_0^2 (t) t \gg 1 \), i.e. asymptotically for long times:

\[
s_c (x) \approx e^{-x^2} + \frac{1}{4\pi^2 \ln \left( \frac{l_{\alpha q_C}}{\alpha q_C} \right)} \frac{1 - e^{-x^2}}{x^3 (q_C/\sigma(t) + x)}
\]

The result is shown in Fig. 2.

References

[1] A. Vailati and M. Giglio. Giant fluctuations in diffusion processes. Nature, 390:262–, 1997.
Figure 2: Function $s_c(x)$, expressed in Eq. (52).
[2] A. Vailati and M. Giglio. Nonequilibrium fluctuations in time-dependent diffusion processes. *Phys. Rev. E*, 58(4):4361–4371, October 1998.

[3] D. Brogioli, A. Vailati, and M. Giglio. Universal behaviour of nonequilibrium fluctuations in free diffusion processes. *Phys. Rev. E Rapid Communications*, 61:R1–R4, January 2000.

[4] D. Brogioli, A. Vailati, and M. Giglio. Giant fluctuations in diffusion processes. *J. Phys.*, 12:39–46, February 2000.

[5] Doriano Brogioli and Alberto Vailati. Diffusive mass transfer by nonequilibrium fluctuations: Fick’s law revisited. *Phys. Rev. E*, 63, 2001.

[6] A. Vailati and M. Giglio. Prog. Colloid Polym. Sci., 104:76–, 1997.

[7] P. G. Saffman. Brownian motion in thin sheets of viscous fluid. *J. Fluid Mech.*, 73(4):593–602, 1976.

[8] L. D. Landau and E. M. Lifshitz. *Fluid Mechanics*. Pergamon, New York, 1959.

[9] C. Tanford. *Physical Chemistry of Macromolecules*. Wiley, New York, 1961.

[10] C. Cheung, Y. H. Hwang, X. L. Wu, and H. J. Choi. Diffusion of particles in free-standing liquid films. *Phys. Rev. Lett.*, 76(14):2531–2534, 1996.

[11] J. Bechhoefer, J. C. Géminard, L. Bocquet, and P. Oswald. Experiments on tracer diffusion in thin free-standing liquid-crystal films. *Phys. Rev. Lett.*, 79(24):4922–4925, 1997.

[12] Doriano Brogioli. Correlation function of velocity fluctuations in a freely suspended liquid film. http://arxiv.org/abs/1103.4760v1.

[13] H. Kellay, X. L. Wu, and W. I. Goldburg. Experiments with turbulent soap films. *Phys. Rev. Lett.*, 74:3875–, 1995.

[14] X. L. Wu, B. K. Martin, H. Kellay, and W. I. Goldburg. Hydrodynamic convection in a two-dimensional couette cell. *Phys. Rev. Lett.*, 75:236–, 1995.

[15] M. A. Rutgers, X. L. Wu, R. Bhagavatula, A. A. Petersen, and W. I. Goldburg. Two-dimensional velocity profiles and laminar boundary layers in flowing soap film. *Phys. Fluids*, 8(11):2847–2854, November 1996.

[16] Y. Couder. Two-dimensional grid turbulence in a thin liquid film. *J. Phys. Lett.*, 45:353–, 1984.

[17] Y. Couder, J. M. Chomaz, and M. Rabaud. On the hydrodynamics of soap films. *Physica D*, 37:384–, 1989.

[18] M. Rivera and X. L. Wu. External dissipation in driven two-dimensional turbulence. *Phys. Rev. Lett.*, 85(5):976–979, July 2000.
[19] A. A. Trapeznikov. In Butterworths, editor, Proceedings of the Second International Congress on Surface Activity, page 242, London, 1957.

[20] David R. Lide. Handbook of Chemistry and Physics. CRC Press, Boston, 1992.
5 Other notes...

Theoretical evaluation of diffusion coefficient in thin sheets of viscous fluid, surrounded by a less viscous fluid \cite{7}.

Diffusion in free-standing liquid films: soap films \cite{10}, liquid crystal films \cite{11}.

Effect of viscosity of air in flows; modeled as a linear drag term, with 2D Navier-Stokes equations \cite{18}.

6 Fluctuations as the origin of Fick’s flow

and

\[
\langle e(\vec{q}, \omega) \, u^* (\vec{q'}, \omega') \rangle = \nabla c_0 \frac{\langle \vec{u}(\vec{q}, \omega) \cdot \vec{z} \, u^* (\vec{q'}, \omega') \cdot \vec{z} \rangle}{D q^2 - i \omega},
\]

(53)

The power spectrum of the velocity fluctuations has been evaluated for a film surrounded by a fluid \cite{12}. In particular, for \( \omega = 0 \):

\[
S_u (\vec{q}, \omega = 0) = \frac{K_B T}{4 \pi \eta_0 h} \frac{1}{q (q_C + q)},
\]

(54)

where:

\[
q_C = \frac{2 \eta_1}{h \eta_0},
\]

(55)

\( K_B \) is the Boltzmann constant, \( T \) the temperature, \( \eta_0 \) and \( \eta_1 \) are the shear viscosity of the film and the surrounding fluid, and \( h \) is the thickness of the film.

The power spectrum has a \( q^{-2} \) dependence for \( q \gg q_C \); at smaller wavevectors, the divergence saturates to \( q^{-1} \), due to air damping. For a soap film in air, the values of densities are \( \rho_0 = 10^3 \text{Kg/m}^3 \) and \( \rho_1 = 1.3 \text{Kg/m}^3 \). The effective viscosity of the film is \( \nu_0 = 1.6 \cdot 10^{-6} \text{m}^2/\text{s} \), \cite{18}, evaluated by means of Trapeznikov relation \cite{19}. The viscosity of air is \( \nu_1 = 1.43 \cdot 10^{-5} \text{m}^2/\text{s} \). From these values, for a 2\( \mu \text{m} \) thick film, \( q_C \approx 1.2 \cdot 10^4 \text{m}^{-1} \), corresponding to a 0.5mm wavelength.

From the power spectrum of the velocity fluctuations, we can derive the diffusion coefficient\cite{5}:

\[
D \approx \pi \int_{\Lambda} S_u (q, \omega = 0) \, q^2 \, dq
\]

(56)

where the cut off wavevector \( \Lambda \) is of the order of the inverse of \( a \), the radius of the diffusing particle. By using the power spectrum of eq. (54), and using polar coordinates:

\[
D \approx \frac{K_B T}{2 \pi \eta_0 h} \int_{\Lambda} \frac{1}{q_C + q} \, dq,
\]

(57)

All the wave vectors less than \( q_C \) contribute equally to concentration diffusion; shorter wave lengths, down to the molecular scale, give a decreasing contribution. Integrating:

\[
D = \frac{K_B T}{2 \pi \eta_0 h} \left[ \ln \frac{h \eta_0}{a \eta_1} - \ln 2 \right]
\]

(58)
This is the well known Saffman formula for the diffusion coefficient of a particle on a liquid film \cite{7,10,11}.

Confronto con una teoria fenomenologica \cite{18}

7 Introduzione vecchia

The diffusion coefficient can be evaluated once we know the correlation function of the thermally excited velocity fluctuations; this means that the velocity correlation function must be strongly affected by air friction. In this paper, I evaluate the correlation function of the velocity field of a thin suspended liquid film, by solving the hydrodynamic equation of the whole system, including the liquid film and the fluid surrounding it.

Then I discuss the result, showing that both the temporal and the spatial statistical properties are the ones of a two dimensional, hypothetical fluid, only for temporal and spatial frequencies higher than critical values; at lower frequencies they show significative deviations due to the interactions of the liquid layer with the surrounding fluid.

Last, I derive approximately the value of diffusion coefficient, and I compare it with Saffman formula.

8 Definitions

Fourier transform:

\[
f (\vec{q}) = \frac{1}{(2\pi)^{D}} \int e^{i \vec{q} \cdot \vec{x}} f (\vec{x}) d\vec{x}
\]  

(59)

Fourier anti-transform:

\[
f (\vec{x}) = \int e^{-i \vec{q} \cdot \vec{x}} f (\vec{q}) d\vec{q}
\]  

(60)

Dirac delta:

\[
\delta (\vec{x}) = \frac{1}{(2\pi)^{D}} \int e^{i \vec{q} \cdot \vec{x}} d\vec{q}
\]  

(61)

Convolution:

\[
f (\vec{x}) \otimes g (\vec{x}) = \int f (\vec{x}') g^* (\vec{x}' - \vec{x}) d\vec{x}
\]  

(62)

Convolution / product:

\[
F \left[ f (\vec{x}) g^* (\vec{x}) \right] = f (\vec{q}) \otimes g (\vec{q})
\]  

(63)