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Asymmetric time cross-correlation of non-equilibrium concentration fluctuations in a ternary liquid mixture

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Equilibrium phenomena are characterized by time symmetry. Thermodynamic fluctuations are also time-symmetric at equilibrium. Conversely, diffusion of a solute in a liquid in the presence of a gradient is a non-equilibrium phenomenon, which gives rise to long-range fluctuations with amplitude much larger than the equilibrium one for small enough wave number. In the case of diffusion in binary mixtures such fluctuations are time-symmetric, notwithstanding the fact that they are generated by a non-equilibrium condition. In this paper, we investigate diffusion of two solutes in a ternary liquid mixture by means of fluctuating hydrodynamics theory. We show that the time cross-correlation function of the concentrations is not time-symmetric, hence showing that time-symmetry is violated for such non-equilibrium fluctuations. We discuss the feasibility of experiments aimed at the detection of the asymmetry of the cross correlation function of non-equilibrium concentration fluctuations in ternary mixtures, as envisaged in the Giant Fluctuations (NEUF-DIX) microgravity project of the European Space Agency.

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I. INTRODUCTION

One of the features of systems at equilibrium is time symmetry: given a sequence of observations, it is not possible to say if they are presented in the forward or backward time direction [1]. Considering, in particular, a binary liquid mixture, thermodynamic fluctuations of the concentration are always present. Basically, they represent the Poisson noise arising when molecules are counted inside a given volume. The process describing molecules entering and exiting a volume is time-symmetric at the macroscopic scale. From the mesoscopic point of view the equilibrium fluctuations of the concentration of a solute can be described by using fluctuating hydrodynamics [2]: a fluctuation arises because of a random source, and is dissipated by diffusion. Although the two processes are not time-symmetric, they are however connected by the fluctuation-dissipation and linear response theorems, which safeguard the time-symmetry of the outcoming phenomena.

Under such circumstances, time-symmetry is a consequence of the fact that the process is isoentropic, and this feature prevents the identification of a preferential direction for time. In the presence of a non-equilibrium condition dissipative processes determine a progressive increase of entropy. If one takes into account the degrees of freedom of all the molecules, however, the system still exhibits microscopic time-symmetry. This is due to the fact that the equations of motion of the molecules are of second order in time, without any term containing time derivatives of odd order. Conversely, the evolution of the macroscopic degrees of freedom of the system is not time-symmetric, because the averaged microscopic degrees of freedom determine the presence of derivatives of odd order in the equations for the evolution of the macroscopic system [1]. A typical example of such system is a Brownian particle under the action of a constant external force like gravity or a thermophoretic force [3]. A reconciliation of time symmetry at the microscopic scale and time asymmetry at the macroscopic scale requires a thorough comparison of the probability distribution of finding a certain time evolution for the position of the particle in the presence of a forward non-equilibrium driving force and the probability distribution in the presence of a backward driving force. The presence of a non-equilibrium condition breaks the time-symmetry of these probability distributions, giving rise to a production of entropy proportional to the unbalance between the probability distributions [4].

A signature of the presence of time-symmetry is provided by the behavior of the time correlation functions of fluctuations upon inversion of time. With this respect, the understanding of time-cross-correlations in a stochastic system is of wide general relevance, because an asymmetric behavior can underlie the presence of a causal relationship between the correlated variables. A meaningful example of a stochastic system which exhibits a time-asymmetry is represented by the fluctuations in returns of stocks in financial markets. In this case, the time cross-correlation function between fluctuations is asymmetric whenever a causal relationship exists between the returns of different stocks [5, 6].

A model system suitable for the understanding of time-symmetry in non-equilibrium systems is represented by a binary mixture where a macroscopic concentration gradient determines a non-equilibrium diffusion process. In the last 20 years it has been shown that a non-equilibrium diffusion process is accompanied by long-range large-

amplitude fluctuations of concentration. These fluctuations have been predicted theoretically [7–13], reported experimentally [14–18] and in numerical simulations [19–22]. Since the origin of such fluctuations is a non-equilibrium phenomenon determined by the presence of a macroscopic gradient [23], the fluctuations are not compelled to follow the fluctuation-dissipation and linear response theorems. In the presence of a non-equilibrium steady state the fluctuation-dissipation theorem can be generalized by taking into account the total entropy production [24–26], but so far we are not aware of attempts of application of the theorem to the case of non-equilibrium fluctuations in liquid mixtures.

In this paper, we investigate the time cross-correlations of the concentration fluctuations of two solutes in a ternary mixture. We show that a violation of time-symmetry is observable at the mesoscopic scale for fluctuations in this system, as evidenced by the asymmetry of the time cross-correlation function. In Sect. II we outline how non-equilibrium fluctuations in binary mixtures are time-symmetric. In Sect. III A, we show that the time cross-correlation between the concentrations of the two solutes is indeed not time-symmetric, its center of mass being displaced from $\Delta t = 0$. In Sect. III B we give a qualitative account of the observed behavior. In Sect. IV, we discuss the feasibility of experiments showing the violation of the time-symmetry. Finally, in Sect. V we perform a critical comparison of our results with those of previous work in the field [27].

II. NON-EQUILIBRIUM FLUCTUATIONS IN BINARY LIQUID MIXTURES

Theoretical, experimental and numerical work performed in the last 25 years [12, 13] showed that Fluctuating Hydrodynamics [2] represents a reliable quantitative model to describe non-equilibrium fluctuations generated by small gradients. Fluctuating Hydrodynamics relies on a linearization of the Navier-Stokes equations to obtain a set of equations that, once supplemented with stochastic white noise terms, act as Langevin equations for the fluctuations of the relevant thermophysical variables. In this work we are interested mainly in modeling the non-equilibrium concentration fluctuations generated by a concentration gradient and we will assume that the system is isothermal, so that the non-equilibrium temperature fluctuations can be neglected. We will also neglect the contribution of temperature and concentration equilibrium fluctuations and the gravitational force.

A. Time-symmetry in binary mixtures

In binary mixtures of liquids, the composition is defined univocally by the concentration of one component. Therefore the only time-correlation function that can be calculated is the self correlation $< \delta c^*(t,\mathbf{q})\delta c(t+\Delta t,\mathbf{q}) >$. Here the brackets indicate a time average and δc is the displacement of the local concentration c from the macroscopic average. By definition, this function is time-symmetric under stationary conditions:

$$\langle \delta c^*(t,\mathbf{q})\delta c(t-\Delta t,\mathbf{q})\rangle = \langle \delta c^*(t'+\Delta t,\mathbf{q})\delta c(t',\mathbf{q})\rangle = \langle \delta c^*(t+\Delta t,\mathbf{q})\delta c(t,\mathbf{q})\rangle \quad (1)$$

where the first equality is obtained by substituting $t = t' + \Delta t$ and the second equality holds due to the time invariance of the process.

It is important to notice that this time-symmetry is simply a mathematical consequence of the definition of time correlation, and would hold also in the case of an apparently time-asymmetric signal. In principle, higher-order correlations could show a time-asymmetry. However, concentration fluctuations have a Gaussian statistics, as a consequence of the central limit theorem. Therefore, by means of Wick's theorem, we can relate any n-point correlation to the 2-point correlation, which is, as previously shown, time-symmetric. It follows that every n-point correlation of the concentration fluctuations shows a symmetric behaviour, and, more generally, we can conclude that all of them are actually time-symmetric.

B. Fluctuating hydrodynamics in binary mixtures

The Fluctuating Hydrodynamics equations for the concentration fluctuations in binary mixtures can be written as:

$$\frac{\partial \delta c}{\partial t} = D\nabla^2\delta c - \delta v_z \nabla c - \frac{1}{\rho}\nabla\cdot\delta\mathbf{J} \quad (2)$$

where δc is the fluctuation of the concentration, δv_z is the fluctuation of the vertical component of the velocity, D is the mass diffusion coefficient, ∇c is the macroscopic concentration gradient, ρ is the density, and δJ is a stochastic source term for concentration fluctuations. This equation describes the variation of concentration due to diffusion, advection and the source of fluctuations.

We will neglect the source term δJ, which gives rise to the equilibrium fluctuations only; it is negligible under all the practical conditions where the amplitude of non-equilibrium fluctuations is much larger than that of equilibrium ones, i.e. small wave numbers.

Under non-equilibrium conditions concentration fluctuations are generated by the coupling of velocity fluctuations to the macroscopic concentration gradient, which gives rise to non-equilibrium concentration fluctuations [12]. The relevant component of the velocity is δv_z, the component perpendicular to the macroscopic concentration gradient. The correlation of the velocity

fluctuations is [27, 28]:

$$\langle \delta v_z^* (\omega, \mathbf{q}) \, \delta v_z (\omega', \mathbf{q}') \rangle = 2 \frac{k_B T \nu}{\rho} \frac{q_\parallel^2}{\omega^2 + \nu^2 q^4} (2\pi)^4 \, \delta (\omega - \omega') \, \delta (\mathbf{q} - \mathbf{q}') \quad (3)$$

where $q_\parallel^2 = q^2 - (\mathbf{q} \cdot \nabla c)^2$ is the square of the component of the wave vector q perpendicular to the macroscopic concentration gradient.

C. Concentration-velocity cross-correlation in binary mixtures

The investigation of non-equilibrium fluctuations relies on linearized hydrodynamics, where second order fluctuations are neglected. However, it can be shown that second order fluctuations in concentration δc and velocity δv_z give rise to mesoscopic mass currents $\delta j = \delta v_z \delta c$. Quite interestingly, the cumulative contribution of the microscopic mass currents determined by non-equilibrium fluctuations accounts for the whole Fick's flux [29–31]. This term violates time-symmetry. However, it is not present unless renormalization is performed. Therefore, the investigation of cross-correlations between velocity fluctuations and concentration fluctuations is particularly meaningful, because it is strictly connected to the microscopic flux δj.

In the case of a binary liquid mixture the equation governing the evolution on non-equilibrium fluctuations is Eq. 2. Rewriting it in Fourier space we get:

$$\mathrm{i}\omega \delta c = -q^2 D \delta c - \delta v_z \nabla c \quad (4)$$

By solving with respect to the concentration fluctuations, we get:

$$\delta c = -\frac{\delta v_z \nabla c}{i\omega + q^2 D} \quad (5)$$

The cross-correlation function of velocity (along ∇c_0) and concentration is expressed by:

$$\langle \delta c (\mathbf{q}, \omega) \, \delta v_z (\mathbf{q}', \omega') \cdot \nabla c \rangle = - \frac{\langle \delta v_z (\mathbf{q}, \omega) \, \delta v_z (\mathbf{q}', \omega') \rangle}{-i\omega + q^2 D}, \quad (6)$$

By substituting the expression of the velocity correlation, Eq. 3, into Eq. 6:

$$\langle \delta c (\mathbf{q}, \omega) \, \delta v_z (\mathbf{q}', \omega') \rangle = -\delta (\mathbf{q} - \mathbf{q}') \, \delta (\omega - \omega') \, \nabla c \, \frac{K_B T \nu}{8\pi^4 \rho} \frac{q_\parallel^2}{(\omega^2 + \nu^2 q^4)(-i\omega + q^2 D)}. \quad (7)$$

We carry on the calculation by assuming that the diffusion time is much longer than the viscous time. this approximation holds true for $Sc = \nu / D \gg 1$, the so-called large Schmidt number approximation, a condition fulfilled by most binary liquid mixtures (more details about the validity of such approximation are discussed in Ref. [11]). We obtain the approximated expression:

$$\langle \delta c (\mathbf{q}, \omega) \, \delta v_z (\mathbf{q}', \omega') \rangle = -\delta (\mathbf{q} - \mathbf{q}') \, \delta (\omega - \omega') \, \nabla c \, \frac{K_B T \nu}{8\pi^4 \rho} \frac{q_\parallel^2}{\nu^2 q^4 (-i\omega + q^2 D)}. \quad (8)$$

The time correlation is obtained by Fourier transforming. The integrand has one pole at the positive imaginary part of ω, hence we get a correlation only for $\Delta t > 0$:

$$\langle \delta c (\mathbf{q}, t) \, \delta v_z (\mathbf{q}', t + \Delta t) \rangle = -\delta (\mathbf{q} - \mathbf{q}') \, \nabla c \, \frac{K_B T \nu}{8\pi^4 \rho} \frac{q_\parallel^2}{\nu^2 q^4} \exp \left(-\Delta t D q^2 \right) H (\Delta t). \quad (9)$$

This result has a clear physical interpretation: the concentration fluctuations in non-equilibrium conditions are generated by the coupling of velocity fluctuations with the macroscopic concentration gradient, hence the concentration fluctuation takes place only after the velocity fluctuation. Therefore, under such circumstances the causal relation between velocity fluctuations and concentration fluctuations determines the presence of a correlation between the two quantities.

In the next section we show that, at variance with the binary mixtures, mixtures of three or more components show an asymmetry of the time-correlations.

III. NON-EQUILIBRIUM FLUCTUATIONS IN TERNARY MIXTURES

We now consider the case of non-equilibrium fluctuations in a ternary liquid mixture. The determination of the time auto-correlations of non-equilibrium fluctuations in ternary mixtures has been dealt with in detail in a previous work [27]. A similar approach can be used to determine the time cross-correlation functions. In the Appendix we will present the results of this approach. In the following we will present a more direct determination of the time cross-correlation function of concentration fluctuations in a ternary mixture, which relies directly on the diagonalization of the hydrodynamic equations describing the non-equilibrium concentration fluctuations.

A. Correlation and cross-correlation of the concentration fluctuations

In analogy to Eq. 2, the Fluctuating Hydrodynamics equations for the concentration fluctuations in ternary mixtures can be written as:

$$\begin{aligned} \frac{\partial \delta c_1}{\partial t} &= D_{11} \nabla^2 \delta c_1 + D_{12} \nabla^2 \delta c_2 - \delta v_z \nabla c_1 - \frac{1}{\rho} \nabla \cdot \delta \mathbf{J_1} \\ \frac{\partial \delta c_2}{\partial t} &= D_{21} \nabla^2 \delta c_1 + D_{22} \nabla^2 \delta c_2 - \delta v_z \nabla c_2 - \frac{1}{\rho} \nabla \cdot \delta \mathbf{J_2} \end{aligned} \quad (10)$$

where δc_i is the concentration fluctuations of the component $i \in [1,2]$, δv_z is the fluctuation of the vertical component of the velocity, $D_{i,j}$ is the mass diffusion matrix, ∇c_i is the macroscopic concentration gradient of component i, ρ is the density, and δJ_i is a stochastic source term for concentration fluctuations. This equation describes the variation of concentration due to diffusion, advection and to the fluctuation source.

As we have done above for the binary mixture, we will neglect the source terms δJ_i, because it gives rise to the equilibrium fluctuations only.

We diagonalize the matrix $\mathbf{D}$, i.e. we find a transformation matrix T such that:

$$\mathbf{T}^{-1} \cdot \begin{bmatrix} D_{1,1} & D_{1,2} \\ D_{2,1} & D_{2,2} \end{bmatrix} \cdot \mathbf{T} = \begin{bmatrix} \hat{D}_1 & 0 \\ 0 & \hat{D}_2 \end{bmatrix} \tag{11}$$

The diagonal elements $\hat{D}_1$ and $\hat{D}_2$ are the eigenvalues of the matrix $\mathbf{D}$. Since the cross-diffusion terms are usually smaller than the self-diffusion terms, T is usually close to an identity and the eigenvalues $\hat{D}_1$ and $\hat{D}_2$ are close to the self-diffusion coefficients D_1 and D_2.

By using this transformation, we define the diagonalized concentration fluctuations $\hat{\delta c}_i$

$$\mathbf{T}^{-1} \cdot \begin{bmatrix} \delta c_1 \\ \delta c_2 \end{bmatrix} = \begin{bmatrix} \hat{\delta c}_1 \\ \hat{\delta c}_2 \end{bmatrix} \tag{12}$$

and diagonalized macroscopic concentration gradients $\hat{\nabla} c_i$

$$\mathbf{T}^{-1} \cdot \begin{bmatrix} \nabla c_1 \\ \nabla c_2 \end{bmatrix} = \begin{bmatrix} \hat{\nabla} c_1 \\ \hat{\nabla} c_2 \end{bmatrix} \tag{13}$$

We thus rewrite Eqs. 10 as:

$$\begin{aligned} \frac{\partial \hat{\delta c}_1}{\partial t} &= \hat{D}_1 \nabla^2 \hat{\delta c}_1 - \delta v_z \hat{\nabla} c_1 \\ \frac{\partial \hat{\delta c}_2}{\partial t} &= \hat{D}_2 \nabla^2 \hat{\delta c}_2 - \delta v_z \hat{\nabla} c_2 \end{aligned} \tag{14}$$

The two equations are now decoupled and can be solved separately, similarly to what we have done in Sect. II for the fluctuations in a binary mixture. First we rewrite the equations in Fourier space:

$$\mathrm{i}\omega \hat{\delta c}_i = -\hat{D}_1 q^2 \hat{\delta c}_i - \delta v_z \hat{\nabla} c_i \tag{15}$$

By solving with respect to the concentration fluctuations, we get:

$$\hat{\delta c}_i = -\frac{\delta v_z \hat{\nabla} c_i}{i\omega + q^2 \hat{D}_i} \tag{16}$$

From this expression, we calculate the self and cross correlations:

$$\left\langle \hat{\delta c}_i^{\,*}(\mathbf{q},\omega) \quad \hat{\delta c}_j(\mathbf{q}',\omega') \right\rangle = \hat{\nabla} c_i \hat{\nabla} c_j \frac{\langle \delta v_z(\mathbf{q},\omega) \quad \delta v_z(\mathbf{q}',\omega') \rangle}{\left(\hat{D}_i q^2 + i\omega\right)\left(\hat{D}_j q^2 - i\omega\right)} \tag{17}$$

By using Eq. 3:

$$\left\langle \hat{\delta c}_i^{\,*}(\mathbf{q},\omega) \quad \hat{\delta c}_j(\mathbf{q}',\omega') \right\rangle = 2\frac{k_B T \nu}{\rho} \hat{\nabla} c_i \hat{\nabla} c_j \frac{q_\parallel^2}{(\omega^2 + \nu^2 q^4)\left(\hat{D}_i q^2 + i\omega\right)\left(\hat{D}_j q^2 - i\omega\right)} (2\pi)^4 \delta(\omega - \omega')\, \delta(\mathbf{q} - \mathbf{q}') \tag{18}$$

and by using the definition of correlation:

$$\left\langle \hat{\delta c}_i^{\,*}(\mathbf{q},\omega)\, \hat{\delta c}_j(\mathbf{q}',\omega')^T \right\rangle = \hat{C}_{i,j}(\mathbf{q},\omega)\, (2\pi)^4 \delta(\omega - \omega')\, \delta(\mathbf{q} - \mathbf{q}') \tag{19}$$

we determine the correlation function C from Eq. 18:

$$\hat{C}_{i,j}(\mathbf{q},\omega) = 2\frac{k_B T \nu}{\rho} \hat{\nabla} c_i \hat{\nabla} c_j \frac{q_\parallel^2}{(\omega^2 + \nu^2 q^4)\left(\hat{D}_i q^2 + i\omega\right)\left(\hat{D}_j q^2 - i\omega\right)} \tag{20}$$

Again, we make use of the large Schmidt number approximation [11] in its straightforward extension to ternary mixtures: $Sc_i = \nu / D_i \gg 1$, so that the result is:

$$\hat{C}_{i,j}(\mathbf{q},\omega) = 2\frac{k_B T}{\rho \nu q^4} \hat{\nabla} c_i \hat{\nabla} c_j \frac{q_\parallel^2}{\left(\hat{D}_i q^2 + i\omega\right)\left(\hat{D}_j q^2 - i\omega\right)} \tag{21}$$

The time-correlation is then obtained by Fourier transforming in ω:

$$\hat{C}_{i,j}(\mathbf{q},\Delta t) = 2\frac{k_B T}{\rho \nu q^4} \hat{\nabla} c_i \hat{\nabla} c_j \int \frac{q_\parallel^2}{\left(\hat{D}_i q^2 + i\omega\right)\left(\hat{D}_j q^2 - i\omega\right)} e^{i\omega \Delta t} \mathrm{d}\omega \tag{22}$$

In the case of the autocorrelation, the two decay times (forward and backward) equal the diffusion decay time of the component under consideration.

The integration can be easily performed by means of the method of the residues (see Fig. 1). The integrand has two poles on the imaginary axis of ω, one at positive and one at negative imaginary part, with residues R_+ and R_-:

$$\begin{aligned} R_+ &= i\frac{e^{-\hat{D}_1 q^2 \Delta t}}{\left(\hat{D}_1 + \hat{D}_2\right) q^2} \\ R_- &= i\frac{e^{\hat{D}_2 q^2 \Delta t}}{\left(\hat{D}_1 + \hat{D}_2\right) q^2}. \end{aligned} \tag{23}$$

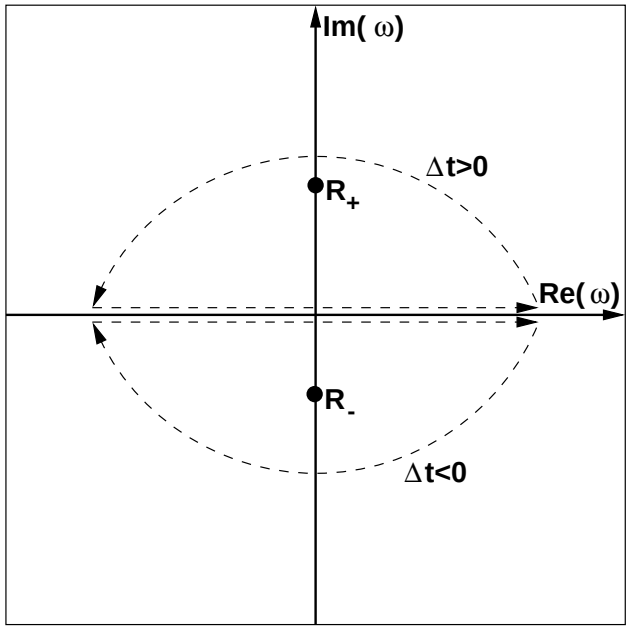

FIG. 1. Residues of the integrand in Eq. 22 and integration paths.

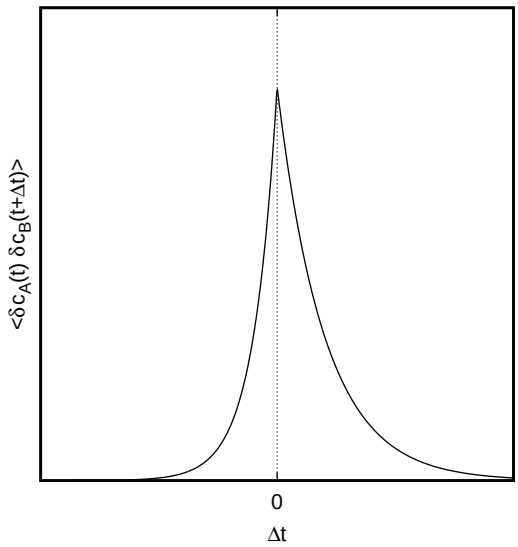

FIG. 2. Example of correlation function. The axis are arbitrary. The ratio between the two diffusion coefficients is 3.

The integration is performed along different paths in the case of $\Delta t > 0$ and $\Delta t < 0$, as shown in Fig. 1. In the two different cases, a different pole is enclosed by the path, and the corresponding residue (with either $\hat{D}_1$ or $\hat{D}_2$) appears in the result. By using the Heaviside step function H the correlation function can be expressed as:

$$\hat{C}_{i,j}\left(\mathbf{q},\Delta t\right) = 2\frac{k_B T}{\rho\nu q^4}\hat{\nabla}c_i\hat{\nabla}c_j \left[H\left(\Delta t\right)e^{-\Delta t\hat{D}_1 q^2} + H\left(-\Delta t\right)e^{\Delta t\hat{D}_2 q^2}\right] \quad (24)$$

Therefore, the correlation function is composed by two exponential decays, with different characteristic decay times forward and backward in time, as shown in Fig. 2.

B. Origin of the time-asymmetry

In this section, we discuss the qualitative reason why the cross-correlation is time-asymmetric, and in particular, why it shows an exponential decay with different time constants forward and backward in time.

In our system, the observable quantities (δc_1 and δc_2) are fully determined by the liquid velocity v_z. In particular, the concentration fluctuation at time t_0 is determined by the values of v_z at times $t < t_0$; this can be seen as a consequence of the cause-effect relation between liquid velocity and concentration fluctuations discussed in Sect. II C. We can thus write $\delta c\left(v_z^{(-\infty,t]},t,\mathbf{q}\right)$, evaluated at time t and wave vector $\mathbf{q}$, as deterministically given as a function of v_z in the interval $(-\infty,t]$.

The correlation function becomes:

$$\left\langle\delta c_1\left(t,\mathbf{q}\right)^*\delta c_2\left(t+\Delta t,\mathbf{q}\right)\right\rangle = \int\delta c_1\left(v_z^{(-\infty,t]},t,\mathbf{q}\right)^*\delta c_2\left(v_z^{(-\infty,t+\Delta t]},t+\Delta t,\mathbf{q}\right) \mathcal{P}\left[v_z^{(-\infty,t+\Delta t]}\right]\mathcal{D}\left[v_z^{(-\infty,t+\Delta t]}\right] \quad (25)$$

where $\mathcal{P}$ represents the probability of a given v_z and $\int\cdot\mathcal{D}\left[v_z\right]$ is the functional integral over the function v_z. In the case $\Delta t > 0$, we can separate the interval $(-\infty,t+\Delta t]$ into the two separate intervals $(-\infty,t]$ and $(t,t+\Delta t]$:

$$\left\langle\delta c_1\left(t,\mathbf{q}\right)^*\delta c_2\left(t+\Delta t,\mathbf{q}\right)\right\rangle = \int\delta c_1\left(v_z^{(-\infty,t]},t,\mathbf{q}\right)^*\delta c_2\left(v_z^{(-\infty,t]},v_z^{(t,t+\Delta t]},t+\Delta t,\mathbf{q}\right) \mathcal{P}\left[v_z^{(-\infty,t]}\right]\mathcal{P}\left[v_z^{(t,t+\Delta t]}|v_z^{(-\infty,t]}\right]\mathcal{D}\left[v_z^{(-\infty,t]}\right]\mathcal{D}\left[v_z^{(t,t+\Delta t]}\right] \quad (26)$$

where the symbol $\mathcal{P}\left[A|B\right]$ represents the conditional probability. By multiplying and dividing by $\delta c_2\left(t,\mathbf{q}\right)$:

$$\left\langle\delta c_1\left(t,\mathbf{q}\right)^*\delta c_2\left(t+\Delta t,\mathbf{q}\right)\right\rangle = \int\delta c_1\left(v_z^{(-\infty,t]},t,\mathbf{q}\right)^*\delta c_2\left(v_z^{(-\infty,t]},t,\mathbf{q}\right) \frac{\delta c_2\left(v_z^{(-\infty,t]},v_z^{(t,t+\Delta t]},t+\Delta t,\mathbf{q}\right)}{\delta c_2\left(v_z^{(-\infty,t]},t,\mathbf{q}\right)} \mathcal{P}\left[v_z^{(-\infty,t]}\right]\mathcal{P}\left[v_z^{(t,t+\Delta t]}|v_z^{(-\infty,t]}\right]\mathcal{D}\left[v_z^{(-\infty,t]}\right]\mathcal{D}\left[v_z^{(t,t+\Delta t]}\right] \quad (27)$$

This can be rewritten as:

$$\left\langle \delta c_1\left(t,\mathbf{q}\right)^* \delta c_2\left(t+\Delta t,\mathbf{q}\right)\right\rangle = \int g\left(v_z^{(-\infty,t]},t,\mathbf{q}\right) f_2\left(v_z^{(-\infty,t]},t,\Delta t,\mathbf{q}\right) \mathcal{P}\left[v_z^{(-\infty,t]}\right] \mathcal{D}\left[v_z^{(-\infty,t]}\right] \quad (28)$$

where

$$g\left(v_z^{(-\infty,t]},t,\mathbf{q}\right) = \delta c_1\left(v_z^{(-\infty,t]},t,\mathbf{q}\right)^* \delta c_2\left(v_z^{(-\infty,t]},t,\mathbf{q}\right) f_2\left(v_z^{(-\infty,t]},t,\Delta t,\mathbf{q}\right) = \int \frac{\delta c_2\left(v_z^{(-\infty,t]},v_z^{(t,t+\Delta t]},t+\Delta t,\mathbf{q}\right)}{\delta c_2\left(v_z^{(-\infty,t]},t,\mathbf{q}\right)} \mathcal{P}\left[v_z^{(t,t+\Delta t]}|v_z^{(-\infty,t]}\right] \mathcal{D}\left[v_z^{(t,t+\Delta t]}\right] \quad (29)$$

We thus see that, for $\Delta t > 0$, the correlation function reflects the behavior of δc_2 with time. An analogous calculation with $\Delta t < 0$ gives an analogous expression, with δc_1 playing the same role.

Therefore, the time-asymmetry is a consequence of the cause-effect relation: both δc_1 and δc_2 are determined by v_z, and the effect of v_z at a given time can be seen only at subsequent times.

The center of mass of the cross-correlation function, Eq. 24, is not at $\Delta t = 0$, as visible in Fig. 2. This is a violation of the time-symmetry. As mentioned above, the concentration fluctuations of the two solutes are generated simultaneously by a velocity fluctuation, but then they relax at different rate, depending on the diffusion coefficient. Obviously, the solute with larger diffusion coefficient relaxes faster than the other. The center of mass of the cross-correlation function is displaced accordingly.

IV. APPLICATIONS TO EXPERIMENTS

Non-equilibrium concentration fluctuations arise during diffusion processes in multi-component mixtures. In the presence of a macroscopic concentration gradient the coupling of spontaneous thermal velocity fluctuations gives rise to non-equilibrium concentration fluctuations. On Earth large-wavelength fluctuations are strongly influenced by the gravity force, which can give rise to their stabilization or destabilization, depending on whether the macroscopic density profile associated to the concentration gradient is gravitationally stable [10, 14] or not [32, 33].

In the case of binary liquid mixtures a stable configuration can be obtained by bringing two miscible fluids into contact, so that the denser fluid is below the less dense one [15, 16, 34]. Alternatively, one can use an external temperature gradient to induce the concentration gradient through the Soret effect [14, 18, 35, 36]. In the case of a sample with a positive Soret coefficient S_T, the imposition of a temperature gradient ∇T induces a steady-state concentration gradient $\nabla c = -S_T c(1-c)\nabla T$, where c is the concentration of the sample. Non-equilibrium fluctuations induce fluctuations in the index of refraction, which can be picked up by using either small angle light scattering techniques [15] or near field techniques such as quantitative shadowgraphy [37–39]. Both methods allow to determine the time autocorrelation function of the correlation fluctuations [34].

Per il quantitative shadowgraph ho aggiunto un riferimento al nostro articolo del 2000. Avete qualcosa in contrario?

The experimental investigation of non-equilibrium fluctuations in ternary mixtures is problematic, because on Earth the presence of the gravity force gives rise to convective instabilities under rather generic conditions. This is due to the fact that, even in the configuration where the density profile is gravitationally stable, solutes diffuse at different rates and this can give rise to a local destabilization of the density profile. For this reason a systematic investigation of mass transfer in ternary liquid mixtures requires microgravity conditions. The mass transfer in ternary liquid mixtures has been investigated extensively in microgravity in the framework of the DCMIX project of the European Space Agency [40–42]. The DCMIX experiments were hosted inside the SODI facility of ESA, where a two color Mach-Zehnder interferometer allowed to recover the Soret coefficients and the eigenvalues of the diffusion matrix. Thermal gradient cells for the investigation on non-equilibrium fluctuations in ternary systems require a different geometry with respect to that adopted in DCMIX. Indeed, one wants to access the sample optically by looking in the direction parallel to the concentration gradient. This kind of configuration was used during the GRADFLEX experiment, which flew for two weeks aboard the FOTON M3 spacecraft [43–46]. GRADFLEX contained a thermal gradient cell and a shadowgraph diagnostics that allowed to grab images of the phase perturbations determined by non-equilibrium fluctuations. The experiments allowed to attain a first important confirmation of the fact that in the absence of gravity non-equilibrium fluctuations grow up to the size of the container hosting the sample. The Giant-Fluctuations (NEUF-DIX) project of ESA will adopt a configuration similar to GRADFLEX to investigate non-equilibrium fluctuations in multi-component complex liquids [47]. The facility will comprise 6 thermal gradient cells and shadowgraph diagnostics. The use of two light sources, one in the red and one in the blue region of the visible spectrum will allow to decouple the contributions to the fluctuations determined by the two independent components of the investigated mixtures. The cross-correlation of the shadowgraph images obtained with the two light sources will allow to perform an experimental check of the asymmetry

of the time cross-correlation function of non-equilibrium fluctuations in ternary mixtures. Suitable samples will include ternary mixtures including either a polymer or a colloid as a third component and ternary mixtures of biological relevance, such as protein solutions.

Qui e' necessaria una connessione con gli esperimenti

The various components of the mixtures have different refraction index and different disperions, thus the transfer function of the shadowgraph technique ... with a suitable procedure it is possible to calculate ...

Questa e' la frase di Jose'

The use of two-color shadowgraphy and light scattering for separating the contributions of the various compoments of the mixture requires to re-work the underlying physical optics theory, taking into account the presence of two wavelength. This study is beyond the scope of the present paper and will be performed as a part of the above-mentioned projects.

Qui inizia la parte banale di connessione tra indici di rifrazione e concentrazioni diagonali

In order to show the feasibility of the detection of the time-asimmetry of the fluctuations, here we use a simplified approach, i.e. we assume that the optical technique give access to the fluctuation of the refraction indices at the two wavelengths, $[\delta n_1, \delta n_2]$. We approximate with a linear relationship, as usually observed:

$$\begin{bmatrix} \delta c_1 \\ \delta c_2 \end{bmatrix} = \mathbf{R} \cdot \begin{bmatrix} \delta n_1 \\ \delta n_2 \end{bmatrix} \tag{30}$$

with a given matrix $\mathbf{R}$. Both $\mathbf{R}$ and $\mathbf{T}$ are experimentally measurable, thus, from the optically measured $[\delta n_1, \delta n_2]$ it is possible to calculate the diagonalized concentrations:

$$\begin{bmatrix} \hat{\delta c}_1 \\ \hat{\delta c}_2 \end{bmatrix} = \mathbf{T} \cdot \mathbf{R} \cdot \begin{bmatrix} \delta n_1 \\ \delta n_2 \end{bmatrix} \tag{31}$$

It is possible to first calculate the diagonalized concentrations $\left[\hat{\delta c}_1, \hat{\delta c}_1\right]$ and then calculate their correlation function $\hat{C}_{i,j}$, which shows the time-asymmetry. An alternative approach could be to calculate the correlation function of the refraction indices at the two wavelengths, $C^n_{i,j}$; it is connected to the correlation function of the diagonalized concentration by the following equation:

$$\left[C^n_{i,j}\right] = (\mathbf{T} \cdot \mathbf{R})^{-1} \left[\hat{C}_{i,j}\right] \left[(\mathbf{T} \cdot \mathbf{R})^{-1}\right]^T \tag{32}$$

From this equation, we see that the cross-correlation of the refraction index is a linear combination of the auto- and the cross-correlations of the diagonalized concentrations, hence it will appear more time-symmetric than the cross-correlation of the diagonalized concentration.

V. CONCLUSION

In this work we have analyzed the cross correlations of non-equilibrium concentration fluctuations of independent components in a multi-component mixture. In the trivial case of binary mixtures, the number of independent components is only one, so that one can only investigate auto-correlation, which is symmetric, notwithstanding the entropy production during the non-equilibrium process. In the case of a ternary mixture, the cross-correlations are investigated and they appear to be asymmetric in time. An experimental verification would require a measurement technique able to separate the contribution of different components. This is in principle possible with the two-wavelength shadowgraph apparatus that is being developed within the NEUFDIX project. An experimental verification of the time-asymmetry will then be performed in a near future.

Appendix

In this section we will derive the time cross-correlation function of non-equilibrium concentration fluctuations in a ternary mixture by using a procedure similar to that adopted in Ref. [27] to determine the auto-correlation function. At variance with Ref. [27] we will take into account the contribution of the imaginary part of the time correlation function. These contributions can be neglected when determining the auto-correlation function, but become significant in the case of the cross-correlation function. Following Ref. [27] the Fluctuations Hydrodynamics equations describing non-equilibrium concentration fluctuations in a ternary mixture are:

$$\begin{aligned} \frac{\partial \delta c_1}{\partial t} &= D_{11}\nabla^2 \delta c_1 + D_{12}\nabla^2 \delta c_2 - \delta v_z \nabla c_1 - \frac{1}{\rho}\nabla \cdot \delta \mathbf{J_1} \\ \frac{\partial \delta c_2}{\partial t} &= D_{21}\nabla^2 \delta c_1 + D_{22}\nabla^2 \delta c_2 - \delta v_z \nabla c_2 - \frac{1}{\rho}\nabla \cdot \delta \mathbf{J_2} \end{aligned} \tag{A.1}$$

In Fourier space:

$$\begin{aligned} \mathrm{i}\omega \delta c_1 &= -D_{11} q^2 \delta c_1 - D_{12} q^2 \delta c_2 - \delta v_z \nabla c_1 + F_1 \\ \mathrm{i}\omega \delta c_2 &= -D_{21} q^2 \delta c_1 + D_{22} q^2 \delta c_2 - \delta v_z \nabla c_2 + F_2 \end{aligned} \tag{A.2}$$

This expression can be rewritten as:

$$\mathrm{i}\omega \delta \mathbf{c} + q^2 \mathbf{D} \cdot \delta \mathbf{c} = -\delta v_z \nabla \mathbf{c} + \mathbf{F} \tag{A.3}$$

where $\delta c = (\delta c_1, \delta c_2)$, $\nabla \mathbf{c} = (\nabla c_1, \nabla c_2)$, $\mathbf{F} = (F_1, F_2)$, and $\mathbf{D}$ is the matrix of diffusion coefficients. We decompose the concentration fluctuation as the sum of an equilibrium and a non-equilibrium contribution:

$$\delta \mathbf{c} = \delta \mathbf{c}^E + \delta \mathbf{c}^{NE} \tag{A.4}$$

where

$$\mathrm{i}\omega \delta \mathbf{c}^E + q^2 \mathbf{D} \cdot \delta \mathbf{c}^E = \mathbf{F} \tag{A.5}$$

and

$$\mathrm{i}\omega \delta \mathbf{c}^{NE} + q^2 \mathbf{D} \cdot \delta \mathbf{c}^{NE} = -\delta v_z \nabla \mathbf{c} \tag{A.6}$$

Since $\mathbf{F}$ and δv_z are not correlated, we can evaluate separately the contributions of the two terms, and we now focus on the non-equilibrium part $\delta\mathbf{c}^{NE}$. By calculating $\delta\mathbf{c}^{NE}$:

$$\delta\mathbf{c}^{NE} = -\left(\mathrm{i}\omega + \mathbf{D}q^2\right)^{-1} \cdot \nabla\mathbf{c}\delta v_z \tag{A.7}$$

The correlation is:

$$\left\langle \delta\mathbf{c}^{NE}(\omega,\mathbf{q})^* \, \delta\mathbf{c}^{NE}(\omega',\mathbf{q}')^T \right\rangle = \left(-\mathrm{i}\omega\mathbb{I} + \mathbf{D}q^2\right)^{-1} \cdot \nabla\mathbf{c} \cdot \nabla\mathbf{c}^T \cdot \left(\mathrm{i}\omega\mathbb{I} + \mathbf{D}q^2\right)^{-1T} \langle \delta v_z^*(\omega,\mathbf{q})\, \delta v_z(\omega',\mathbf{q}')\rangle \tag{A.8}$$

The correlation of δv_z is:

$$\langle \delta v_z^*(\omega,\mathbf{q})\, \delta v_z(\omega',\mathbf{q}')\rangle = 2k_BT\frac{q_\parallel^2}{\nu\rho q^4}(2\pi)^4\,\delta(\omega-\omega')\,\delta(\mathbf{q}-\mathbf{q}') \tag{A.9}$$

Using this correlation, we get:

$$\left\langle \delta\mathbf{c}^{NE}(\omega,\mathbf{q})^* \, \delta\mathbf{c}^{NE}(\omega',\mathbf{q}')^T \right\rangle = \left(-\mathrm{i}\omega\mathbb{I} + \mathbf{D}q^2\right)^{-1} \cdot \nabla\mathbf{c} \cdot \nabla\mathbf{c}^T \cdot \left(\mathrm{i}\omega\mathbb{I} + \mathbf{D}q^2\right)^{-1T} 2k_BT\frac{q_\parallel^2}{\nu\rho q^4}(2\pi)^4\,\delta(\omega-\omega')\,\delta(\mathbf{q}-\mathbf{q}') \tag{A.10}$$

By using the definition of correlation:

$$\left\langle \delta\mathbf{c}^{NE}(\omega,\mathbf{q})^* \, \delta\mathbf{c}^{NE}(\omega',\mathbf{q}')^T \right\rangle = \mathbf{C}^{NE}(\omega,\mathbf{q})\,(2\pi)^4\,\delta(\omega-\omega')\,\delta(\mathbf{q}-\mathbf{q}') \tag{A.11}$$

we get:

$$\mathbf{C}^{NE}(\omega,\mathbf{q}) = 2k_BT\frac{q_\parallel^2}{\nu\rho q^4} \left(-\mathrm{i}\omega\mathbb{I} + \mathbf{D}q^2\right)^{-1} \cdot \nabla\mathbf{c} \cdot \nabla\mathbf{c}^T \cdot \left(\mathrm{i}\omega\mathbb{I} + \mathbf{D}q^2\right)^{-1T} \tag{A.12}$$

Now we diagonalize the matrix $\mathbf{D}$. We consider the case in which $\mathbf{D}$ has two real eigenvalues, although an imaginary part could be present. The eigenvalues can be calculated analytically (Eq. 18 of Ref. [27]):

$$\hat{D}_{1,2} = \frac{1}{2}\left[D_{11} + D_{22} \pm \sqrt{(D_{11}-D_{22})^2 + 4D_{12}D_{21}}\right] \tag{A.13}$$

The transformation $\mathbf{T}$ diagonalizes $\mathbf{D}$:

$$\mathbf{T}^{-1} \cdot \mathbf{D} \cdot \mathbf{T} = \hat{\mathbf{D}} \tag{A.14}$$

where $\hat{\mathbf{D}}$ is a diagonal matrix with elements $\hat{D}_1$ and $\hat{D}_2$. By using this transformation:

$$\mathbf{C}^{NE}(\omega,\mathbf{q}) = 2k_BT\frac{q_\parallel^2}{\nu\rho q^4} \left(-\mathrm{i}\omega\mathbb{I} + \mathbf{T}\cdot\hat{\mathbf{D}}\cdot\mathbf{T}^{-1}q^2\right)^{-1} \cdot \nabla\mathbf{c} \cdot \nabla\mathbf{c}^T \cdot \left(\mathrm{i}\omega\mathbb{I} + \mathbf{T}\cdot\hat{\mathbf{D}}\cdot\mathbf{T}^{-1}q^2\right)^{-1T} \tag{A.15}$$

We rewrite this last equation as:

$$\mathbf{C}^{NE}(\omega,\mathbf{q}) = 2k_BT\frac{q_\parallel^2}{\nu\rho q^4} \mathbf{T}\cdot\left(-\mathrm{i}\omega\mathbb{I} + \hat{\mathbf{D}}q^2\right)^{-1}\mathbf{T}^{-1}\cdot\nabla\mathbf{c} \cdot \nabla\mathbf{c}^T \cdot \mathbf{T}^{-1T} \cdot \left(\mathrm{i}\omega\mathbb{I} + \hat{\mathbf{D}}q^2\right)^{-1T} \cdot \mathbf{T}^T \tag{A.16}$$

By introducing the projectors P_i:

$$\mathbf{P}_1 = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \tag{A.17}$$

$$\mathbf{P}_2 = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \tag{A.18}$$

The correlation becomes:

$$\mathbf{C}^{NE}(\omega,\mathbf{q}) = 2k_BT\frac{q_\parallel^2}{\nu\rho q^4} \mathbf{T}\cdot\left[\frac{\mathbf{P}_1}{-\mathrm{i}\omega + \hat{D}_1q^2} + \frac{\mathbf{P}_2}{-\mathrm{i}\omega + \hat{D}_2q^2}\right]\mathbf{T}^{-1}\cdot\nabla\mathbf{c} \cdot \nabla\mathbf{c}^T \cdot \mathbf{T}^{-1T} \cdot \left[\frac{\mathbf{P}_1}{\mathrm{i}\omega + \hat{D}_1q^2} + \frac{\mathbf{P}_2}{\mathrm{i}\omega + \hat{D}_2q^2}\right] \cdot \mathbf{T}^T \tag{A.19}$$

By distributing the products on the sum:

$$\mathbf{C}^{NE}(\omega,\mathbf{q}) = 2k_BT\frac{q_\parallel^2}{\nu\rho q^6} \sum_{i,j}\mathbf{A}_{i,j}\frac{\left(\hat{D}_i + \hat{D}_j\right)q^2}{\left(-\mathrm{i}\omega + \hat{D}_iq^2\right)\left(\mathrm{i}\omega + \hat{D}_jq^2\right)} \tag{A.20}$$

where the matrices $\mathbf{A}_{i,j}$ are defined as:

$$\mathbf{A}_{i,j} = \frac{\mathbf{T}\cdot\mathbf{P}_i\mathbf{T}^{-1}\cdot\nabla\mathbf{c}\cdot\nabla\mathbf{c}^T\cdot\mathbf{T}^{-1T}\cdot\mathbf{P}_j\cdot\mathbf{T}^T}{\hat{D}_i + \hat{D}_j} \tag{A.21}$$

We now compare our results with those of Ref. [27]. The real part of $\mathbf{C}^{NE}$ can be written as:

$$\mathbf{C}^{NE}(\omega,\mathbf{q}) = 2k_BT\frac{q_\parallel^2}{\nu\rho q^6} \sum_{i,j}\mathbf{A}_{i,j}\left[\frac{\hat{D}_iq^2}{\omega^2 + \hat{D}_i^2q^4} + \frac{\hat{D}_jq^2}{\omega^2 + \hat{D}_j^2q^4}\right] \tag{A.22}$$

The sum can be rearranged as:

$$\mathbf{C}^{NE}(\omega,\mathbf{q}) = 2k_BT\frac{q_\parallel^2}{\nu\rho q^6} \mathbf{A}_1\frac{\hat{D}_iq^2}{\omega^2 + \hat{D}_i^2q^4} + \mathbf{A}_2\frac{\hat{D}_jq^2}{\omega^2 + \hat{D}_j^2q^4} \tag{A.23}$$

where

$$\mathbf{A}_1 = 2\mathbf{A}_{1,1} + \mathbf{A}_{1,2} + \mathbf{A}_{2,1} \tag{A.24}$$

$$\mathbf{A}_2 = 2\mathbf{A}_{2,2} + \mathbf{A}_{1,2} + \mathbf{A}_{2,1} \tag{A.25}$$

This expression corresponds to Eqs. 20-23 of Ref. [27]. The result given in Ref. [27] is thus correct for the auto-correlations, which are real, while it neglects a significant imaginary part in the calculation of the cross-correlation.

In practically relevant cases, $D_{1,2} = D_{2,1} = 0$; this means that the eigenvalues $\hat{D}$ correspond to the diffusion coefficients D_1 and D_2, and the transformation matrix T is the identity.

We calculate the correlations for this case:

$$\mathbf{C}^{NE}_{1,1}(\omega, \mathbf{q}) = 2k_B T \frac{q_\parallel^2}{\nu\rho q^6} \frac{\nabla c_1^2}{2D_1} \frac{2D_1 q^2}{\omega^2 + D_1 q^2} \tag{A.26}$$

$$\mathbf{C}^{NE}_{1,2}(\omega, \mathbf{q}) = 2k_B T \frac{q_\parallel^2}{\nu\rho q^6} \frac{\nabla c_1 \nabla c_2}{D_1 + D_2} \frac{(D_1 + D_2)\, q^2}{(-\mathrm{i}\omega + D_1 q^2)(\mathrm{i}\omega + D_2 q^2)} \tag{A.27}$$

$$\mathbf{C}^{NE}_{2,2}(\omega, \mathbf{q}) = 2k_B T \frac{q_\parallel^2}{\nu\rho q^6} \frac{\nabla c_1^2}{2D_2} \frac{2D_2 q^2}{\omega^2 + D_2 q^2} \tag{A.28}$$

$$\mathbf{C}^{NE}_{2,1}(\omega, \mathbf{q}) = 2k_B T \frac{q_\parallel^2}{\nu\rho q^6} \frac{\nabla c_1 \nabla c_2}{D_1 + D_2} \frac{(D_1 + D_2)\, q^2}{(\mathrm{i}\omega + D_1 q^2)(-\mathrm{i}\omega + D_2 q^2)} \tag{A.29}$$

We see that the self power-spectra of the concentration fluctuations are real with a Lorentzian shape. In this case the determination of the auto-correlation function is straightforward and yields a single exponential decay. Conversely, the cross-spectra exhibit two poles and the determination of the cross-correlation function requires the procedure outlined in Sect. III A.

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