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Analysis of non-equilibrium fluctuations during thermodiffusion in a binary mixture by two-wavelength shadowgraphy

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Introduction

Non-equilibrium fluctuations (NEFs) are a model for investigating the diffusion processes in complex fluids. Shadowgraphy is a robust near-field scattering technique with a simple configuration and is highly sensitive to NEFs. Besides allowing the measurement of the transport properties in complex fluids (Croccolo et al. 2006a, Croccolo et al. 2012), shadowgraphy allows probing the effect of diffusion, gravity (Croccolo et al. 2006b) and confinement (Giraudet et al. 2015) on the dynamics of NEFs and the presence of propagating waves due to the coupling of the different relaxation modes (Croccolo et al. 2019; García-Fernández et al. 2019). The need for developing the two-wavelength shadowgraphy is dictated by the impossibility of separating the two solutal relaxation modes in a ternary molecular mixture with a classical one-wavelength shadowgraph (Bataller et al. 2016). Indeed, in such mixture, the eigenvalues of the diffusion matrix are almost identical, implying that the relaxation times of the NEFs of the two independent concentration fields cannot be distinguished. In such case, it is impossible to differentiate the two eigenvalues of the diffusion matrix. Using the same approach as the one implemented in the two-wavelength selectable optical digital interferometry (SODI) of the DCMIX project (Mialdun et al. 2020) to separate the two independent concentration fields of a ternary mixture, a two-wavelength shadowgraph would allow, in principle, to separate the contributions of the two concentration fields to the shadowgraph signal. Indeed, the same approach can be used to separate NEFs of temperature and concentration fields in a binary mixture subjected to a temperature gradient. The binary system is a simple and effective test for the two-wavelength shadowgraphy technique. In this case, the relaxation modes of temperature and concentration are well distinct in time and can therefore be also separated with a classical shadowgraph by fitting the structure function of the NEFs with two exponential decays. In this work, we present the principles of two-wavelength shadowgraphy and demonstrate the technique working principle by performing a thermodiffusion experiment on an equimassic binary mixture of toluene/n-hexane subjected to a temperature difference of 20 K.

Working principle of two-wavelength shadowgraphy

The shadowgraph consists of two superluminescent diodes ($\lambda = 675 \pm 13$ nm or $\lambda = 405 \pm 13$ nm) connected to a single-mode optical fiber that delivers a weakly coherent beam collimated by an achromatic lens. The intensity of the light scattered strikes the CCD sensor of an s-CMOS camera placed in the near field of the thermodiffusion cell containing the sample. Owing to their random nature, NEFs are characterized by an autocorrelation function and static structure factor. These quantities can be calculated theoretically by fluctuating hydrodynamics (Ortiz De Zárate et al. 2006) and are directly

related to the static structure factor and autocorrelation function of the refractive index fluctuations measured by shadowgraphy. The case of an ordinary binary mixture (with a large Lewis number) subjected to a temperature gradient in the Boussineq approximation (pressure fluctuations are neglected) is considered here. With a large Lewis number, all couplings between the temperature and concentration fluctuations are neglected, at least for large enough wave numbers, and the autocorrelation function of the refractive index fluctuations for a given wavelength λ can be written as:

$$S_{\lambda}(q, \Delta t) = \left(\frac{\partial n}{\partial c}\right)_{\lambda}^2 S_{cc}(q, \Delta t) + \left(\frac{\partial n}{\partial T}\right)_{\lambda}^2 S_{TT}(q, \Delta t) \quad (1)$$

where q is the wave number, i.e. the modulus of the wave vector. The derivatives of the refractive index with respect to the temperature and concentration depend on the wavelength of the probe beam. Using shadowgraphy, the wave vector at which the structure factor or autocorrelation function is measured does not depend on the wavelength of the probe beam or scattering angle, as is the case in far-field scattering. Therefore, for the same wave number q , the autocorrelation function of NEFs with probe beams of different wavelengths can be easily measured. At large wave numbers, any coupling between different modes, which is responsible for the appearance of the propagating modes, disappears. The concentration and temperature signals can be easily separated if the optical contrast factor matrix is known:

$$\begin{pmatrix} S_{cc}(q, \Delta t) \\ S_{TT}(q, \Delta t) \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial n}{\partial c}\right)_{\lambda_1}^2 & \left(\frac{\partial n}{\partial T}\right)_{\lambda_1}^2 \\ \left(\frac{\partial n}{\partial c}\right)_{\lambda_2}^2 & \left(\frac{\partial n}{\partial T}\right)_{\lambda_2}^2 \end{pmatrix}^{-1} \cdot \begin{pmatrix} S_{\lambda_1}(q, \Delta t) \\ S_{\lambda_2}(q, \Delta t) \end{pmatrix} \quad (2)$$

Result and discussion

From the shadowgraph images, one can thus calculate the structure function (figure 1. a), and the static structure factor (figure 1. b), from which the autocorrelation functions (figure 1.c) of the NEFs at the two wavelengths are calculated. Having previously measured the optical contrast factors by means of a refractometer, the autocorrelation functions of the temperature and concentration NEFs can be separated (figure 1. d). On the one hand, the individual analysis of the structure functions makes it possible to determine the relaxation times of the NEFs of temperature and concentration, as well as their intensities. On the other hand, the analysis of the autocorrelation functions of the NEFs of concentration and temperature, separated optically, makes it possible to determine the relaxation times distribution of the fluctuations as well as their intensities. Preliminary analysis shows that the results obtained by the two procedures correspond for the majority of the wavenumbers. Further analysis is in progress, and the results will be presented at the IMT15.

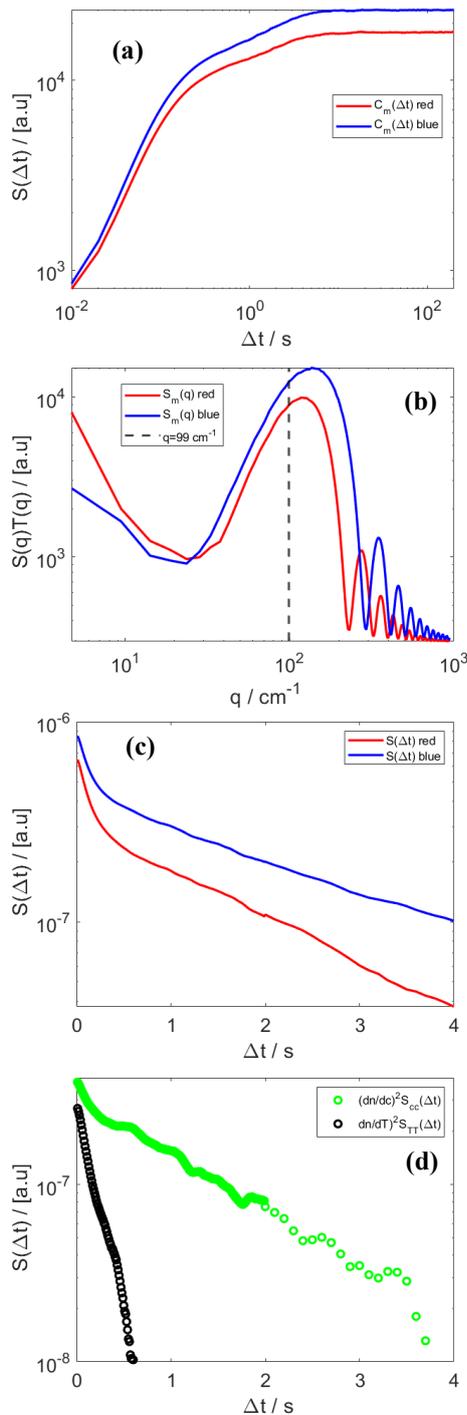


Figure 1 (a) Structure functions for both wavelengths and for $q = 118 \text{ cm}^{-1}$. (b) Static structure factor for both wavelengths. The vertical dashed line stands for $q = 118 \text{ cm}^{-1}$ (c) Autocorrelation functions extracted from (a) and (b) and for $q = 118 \text{ cm}^{-1}$. (d) Extracted autocorrelation functions of the temperature and concentration NEFs as obtained by applying Eq. 2 to the data of panel (c). The distributions of the relaxation times of the temperature and concentration fluctuations are determined from the separate signals. Analysis of the distribution of the relaxation times makes it possible to determine the thermal and mass diffusion coefficients.

The procedure for separating the temperature and concentration modes in a binary system is robust enough despite a large value of the condition number of the contrast factors matrix (>400). While the analysis involved in SODI is based on fitting through a series of exponential decays, the Fourier-based analysis of Shadowgraphy is based on simple exponential decays. This actually increases the applicability

of the Shadowgraph technique to a larger range of condition numbers. The large condition number obtained here, is due to the fact that the thermal contrast factor varies very little with the wavelength. This result validates the technique and promises even better results when separating solutal modes in a ternary mixture.

Conclusions

In this work, we make a first demonstration of the feasibility of the two-wavelength shadowgraphy technique to separate the signals of uncoupled fluctuating fields in a binary or ternary liquid mixture. First, we tested the ability of the technique in separating the temperature and concentration fields in a binary mixture subjected to a temperature gradient. The results obtained make it possible to validate the technique and demonstrate its robustness. The next step of our work will be to test the technique on a ternary polymer mixture and then on a ternary molecular mixture.

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