Eur. Phys. J. E (2014) **37**: 77
DOI 10.1140/epje/i2014-14077-2

THE EUROPEAN PHYSICAL JOURNAL E

Regular Article

Non-equilibrium fluctuations induced by the Soret effect in a ternary mixture*

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Received 20 June 2014
Published online: 28 August 2014 – © EDP Sciences / Società Italiana di Fisica / Springer-Verlag 2014

Abstract. We present, based on fluctuating hydrodynamics, the theory of concentration fluctuations in a ternary mixture subjected to a stationary temperature gradient, so that composition gradients are present due to thermal diffusion (Soret effect). We neglect gravity and confinement (boundary conditions) but consider a completely generic diffusion matrix, including cross-diffusion effects. We find, as in the case of binary mixtures, an important non-equilibrium enhancement of the concentration fluctuations, which is proportional to the square of the gradient and inversely proportional to the fourth power of the fluctuations wave number, q^{-4}. The results of this paper are expected to be asymptotically correct for fluctuations of large q, while for shorter q gravity and confinement effects need to be incorporated. Comparison with previous work in the topic is included.

1 Introduction

Transport processes are theoretically studied in the framework of non-equilibrium thermodynamics [1–3]. Non-equilibrium thermodynamics is not only a theory of fluxes, it also includes a theory of thermal fluctuations [4,5]. Therefore, a complete understanding of thermodynamic transport phenomena has to include an analysis of the associated fluctuations of the relevant thermodynamic properties. For binary mixtures transport by diffusion and thermal diffusion, and their associated fluctuations, are nowadays relatively well understood, a large amount of reliable experimental data being available for many binary systems [5]. Hence, in the last few years the focus has been shifted to transport phenomena in ternary systems [6–15].

In contrast to binary fluid mixtures, the study of transport phenomena in ternary mixtures still presents some challenges both experimentally and theoretically. Many of these are related to the difficulty of performing accurate measurements of diffusion matrices, in particular of cross-diffusion coefficients. In this context, it is worth mentioning that the European Space Agency (ESA) is currently performing the DCMIX series of experiments onboard the International Space Station (ISS) [16,17], where microgravity conditions allow to perform measurements that otherwise are not possible on Earth due to convective phenomena.

These current efforts suggest that concentrations fluctuations induced by the Soret effect in ternary mixtures will become a topic of interest in the coming years, leading us to embark on some further theoretical analysis of the nature of these fluctuations. Indeed, in a first publication [18] the theory of concentration fluctuations in a ternary mixture in equilibrium was reviewed, and expressions for the correlation matrix based on fluctuating hydrodynamics [19,20] were presented.

We note that previous works on equilibrium fluctuations in ternaries [21–24] evaluated these correlation functions on the basis of the Mountain method of arbitrary initial conditions [25,26], that is the most popular in books dealing with thermodynamic fluctuations [27–29]. Expressions obtained by following any of these two alternative paths fully agree for equilibrium systems, including ternary mixtures [18]. However, although not generally known, only fluctuating hydrodynamics can be extended to deal with fluctuations in systems that are out of global equilibrium [5]. The dynamics of equilibrium and non-equilibrium fluctuations is the same at large wave numbers (see a more complete discussion below), while important differences appear in the fluctuations intensity. Fluctuating hydrodynamics include a natural way of evaluating the intensity of fluctuations (a local fluctuation-dissipation theorem), while the arbitrary initial condition method relies on some external input. For equilibrium

* Contribution to the Topical Issue "Thermal non-equilibrium phenomena in multi-component fluids" edited by Fabrizio Croccolo and Henri Bataller.

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systems, statistical physics and equilibrium thermodynamic potentials naturally provide such an input [25, 26]. However, there are not out-of-equilibrium thermodynamic potentials that everybody agrees on, and the Mountain method [25,26] cannot be readily extended to out-of-equilibrium situations.

Consequently, as a first step, we reworked the theory of equilibrium fluctuations in ternaries, but based on fluctuating hydrodynamics [18]. We are now in the position of taking a second step, and consider how thermal fluctuations spectra are affected by the presence of a stationary composition gradient. This same problem has been addressed recently by Balakrishnan *et al.* [30], but they only consider a particular diffusion matrix, adequate for the gas mixture they were performing computer simulations on. Here we shall consider a generic diffusion matrix, and adopt approximations satisfactory for the liquid state.

We proceed by first presenting in sect. 2 the equations of fluctuating hydrodynamics for a ternary system subjected to a stationary temperature gradient, in an approximation valid for liquid mixtures. In sect. 3 we then explain how a solution to the fluctuating hydrodynamic equations can be obtained in "bulk", without accounting for boundary conditions of the fields. In sect. 4 we present the main results of the paper, giving explicit expressions for the time correlation matrix of the composition fluctuations. Our main conclusions are summarized in sect. 5.

2 Fluctuating hydrodynamics of a ternary mixture

In a ternary mixture, there are two independent concentrations c_1 and c_2 that we take as mass fractions. Hence, there are two independent diffusion fluxes, $\boldsymbol{J}_1$ and $\boldsymbol{J}_2$, and Fick's law in isotropic systems is expressed by a 2×2 diffusion matrix $\underline{\underline{\mathrm{D}}}$. Similarly, there exist two thermodiffusion coefficients, D'_{T1} and D'_{T2}, so that in the simultaneous presence of temperature and concentrations gradients, diffusion fluxes are expressed as

$$\begin{aligned}\boldsymbol{J}_1 &= -\rho\left(D_{11}\boldsymbol{\nabla}c_1 + D_{12}\boldsymbol{\nabla}c_2 + D'_{T1}\boldsymbol{\nabla}T\right),\\ \boldsymbol{J}_2 &= -\rho\left(D_{21}\boldsymbol{\nabla}c_1 + D_{22}\boldsymbol{\nabla}c_2 + D'_{T2}\boldsymbol{\nabla}T\right),\end{aligned} \tag{1}$$

with D_{ij} the components of the diffusion matrix

$$\underline{\underline{\mathrm{D}}} = \begin{bmatrix} D_{11} & D_{12}\\ D_{21} & D_{22}\end{bmatrix}, \tag{2}$$

where SI units of $\mathrm{m}^2\ \mathrm{s}^{-1}$ are used, and ρ is the mass density of the mixture. Here we consider a completely general diffusion matrix, the D_{ij} values being restricted only by generic symmetry properties [2].

In this paper we consider a ternary liquid mixture subjected to a uniform stationary temperature gradient $\boldsymbol{\nabla}T$, of magnitude ∇T, in the direction of the z-axis. If one assumes the various diffusion and thermodiffusion coefficients to be constant, the system evolves to a stationary state characterized by vanishing diffusion fluxes. Hence, Soret effect induces the appearance of steady concentration gradients that for isotropic mixtures are parallel (or antiparallel) to the temperature gradient, and whose magnitudes can be obtained from eq. (1) as

$$\begin{bmatrix}\nabla c_1\\ \nabla c_2\end{bmatrix} = -\underline{\underline{\mathrm{D}}}^{-1}\begin{bmatrix}D'_{T1}\\ D'_{T2}\end{bmatrix}\nabla T. \tag{3}$$

Borrowing nomenclature from one-component fluids, we refer to this state as the "conductive" state. Since we neglect here the effects of gravity, the conductive state is stable.

The purpose of this paper is to study concentration fluctuations around the non-equilibrium steady conductive state given by eq. (3). Initially, this is a complicated problem for which one has to consider velocity, density, temperature and two concentration fluctuations, leading to a system of seven coupled partial differential equations. However, not all the couplings are equally strong and, in the end, we are interested only in the fluctuations of the two concentrations. Thus, it is quite advantageous to adopt a series of approximations from the beginning, before attempting any detailed calculation. This approach, already adopted by other researchers in the field [18,24, 30], greatly simplifies the problem while emphasizing the physically most relevant terms. Hence, we adopt the following approximations:

1. Neglect Dufour effect, that is only relevant for gas mixtures.
2. Assume incompressible flow.
3. Linearize the equations on the fluctuating fields.
4. Take mass density and all other thermophysical properties to be constant, evaluated at temperature and concentrations representative of the full layer.
5. Adopt a large Lewis number approximation [31–33], or a large Schmidt number approximation [30] as alternatively referred to by other authors.

In the case of ternary mixtures, the large Lewis number approximation means that both the thermal diffusivity a and the kinematic viscosity ν are much larger than the two eigenvalues of the diffusion matrix [18,24]. Similarly to the case of binary mixtures [31–33], in the limit of large Lewis (and Schmidt) numbers any coupling between the concentration fluctuations (δc_1 and δc_2 for a ternary mixture) and the temperature fluctuations vanishes [18,24]. Only if concentration gradients exist, there is a coupling with the component of the velocity fluctuations parallel to the gradient. Then, after all the simplifications mentioned above, the fluctuating hydrodynamics equations for the fluctuations around the conductive state of eq. (3) become

$$\begin{aligned}0 &= \nu\nabla^4\delta v_z + \frac{1}{\rho}\left[\boldsymbol{\nabla}\times\boldsymbol{\nabla}\times(\boldsymbol{\nabla}\underline{\underline{\delta\Pi}})\right]_z,\\ \frac{\partial\delta c_1}{\partial t} &= D_{11}\nabla^2\delta c_1 + D_{12}\nabla^2\delta c_2 - \delta v_z\ \nabla c_1 - \frac{1}{\rho}\boldsymbol{\nabla}\cdot\boldsymbol{\delta J}_1,\\ \frac{\partial\delta c_2}{\partial t} &= D_{21}\nabla^2\delta c_1 + D_{22}\nabla^2\delta c_2 - \delta v_z\ \nabla c_2 - \frac{1}{\rho}\boldsymbol{\nabla}\cdot\boldsymbol{\delta J}_2.\end{aligned} \tag{4}$$

According to fluctuating hydrodynamics, the linear phenomenological laws for the dissipative fluxes are supplemented with random contributions reflecting the stochastic nature of molecular motion [5,19]. Hence, eqs. (4) contain a stochastic stress tensor $\underline{\underline{\delta\Pi}}(\boldsymbol{r},t)$, and two stochastic diffusive fluxes, $\boldsymbol{\delta J}_1(\boldsymbol{r},t)$ and $\boldsymbol{\delta J}_2(\boldsymbol{r},t)$. Subscript z in the first of eqs. (4) refers to the z-component of the vector between brackets.

We note that eqs. (4) are the same working equations of Balakrishnan *et al.* [30], with several differences: First, here we include the random diffusive fluxes, $\boldsymbol{\delta J}_1$ and $\boldsymbol{\delta J}_2$, that were neglected elsewhere [30]. Second, on the left-hand side (LHS) of the first of eqs. (4) we neglect the temporal derivative of the velocity fluctuations. This is congruent with the large Lewis number approximation [31–33] and valid for liquids, while for the gases considered by ref. [30] this derivative must be retained. Of course, an additional difference with Balakrishnan *et al.* [30] is that eqs. (4) are for a generic diffusion matrix, see eq. (2), and not just for the particularly restrictive case considered by them [30]. We finally note in eqs. (4) that the stationary composition gradient couples the spatiotemporal evolution of the concentration fluctuations with the fluctuations in the velocity component parallel to the gradient. Hence, in contrast to equilibrium, the three equations must be solved simultaneously. As further discussed below, this coupling, that does not exist in equilibrium, will be responsible of a giant enhancement of the concentration fluctuations.

To complete the setting of the problem, one has to specify the statistical properties of the random dissipative fluxes. They are: zero average, $\langle\delta\Pi_{nm}(\boldsymbol{r},t)\rangle = \langle\delta J_{1,n}(\boldsymbol{r},t)\rangle = \langle\delta J_{2,m}(\boldsymbol{r},t)\rangle = 0$; and correlation functions given by the fluctuation-dissipation theorem [5,18,19], which for incompressible flows reads

$$\langle\delta\Pi_{nm}(\boldsymbol{r},t)\cdot\delta\Pi_{kl}(\boldsymbol{r}',t')\rangle = 2k_{\mathrm{B}}T\eta\left(\delta_{nk}\delta_{ml}+\delta_{nl}\delta_{mk}\right) \times\delta(\boldsymbol{r}-\boldsymbol{r}')\;\delta(t-t') \tag{5}$$

for the random stress tensor, and [18]

$$\langle\delta J^*_{i,n}(\boldsymbol{r},t)\;\delta J_{j,m}(\boldsymbol{r}',t')\rangle = 2k_{\mathrm{B}}L_{ij}\;\delta_{nm}\;\delta(t-t')\;\delta(\boldsymbol{r}-\boldsymbol{r}') \tag{6}$$

for the random diffusive forces. In accordance with the Curie principle, the random stress is uncorrelated with the random diffusion fluxes. In eqs. (5), (6) k_{B} is Boltzmann constant, η the shear viscosity, L_{ij} the elements of the Onsager matrix $\underline{\underline{\mathrm{L}}}$ (with $L_{12}=L_{21}$). Here and elsewhere in this paper, the indices i,j span the two independent mixture components $i,j\in\{1,2\}$, while the indices n,m,k,l span the three spatial coordinates $n,m,k,l\in\{x,y,z\}$ (we are implicitly assuming that the system is isotropic).

Initially, in a state out of global equilibrium, temperature and thermophysical properties appearing as prefactors in eqs. (5), (6) are locally dependent. This has some effect on the fluctuations, as theoretically analyzed for some simple cases [34–38] and also experimentally investigated [39]. However when, like in eqs. (4) coupling(s) between fluctuating fields are present at linear order, the effects of the locally dependent prefactors are fully negligible [38], being of the same order as, for instance, those from a locally dependent diffusion coefficient. Hence, we assume the prefactors in the fluctuation-dissipation theorem (5), (6) to be constants, as evaluated at a single point representative of the full layer.

The Onsager matrix $\underline{\underline{\mathrm{L}}}$ of phenomenological coefficients in eq. (6) is the same that, in the general context of non-equilibrium thermodynamics, linearly relates the dissipative fluxes ($\boldsymbol{J}_1$ and $\boldsymbol{J}_2$) with the thermodynamic "forces" associated to these fluxes in the expression of the entropy production. For the case of diffusion, these thermodynamic forces are $\boldsymbol{\nabla}(\hat{\mu}_1/T)$ and $\boldsymbol{\nabla}(\hat{\mu}_2/T)$ [1], with $\hat{\mu}_1=\mu_1-\mu_3$ being the chemical potential difference between component 1 of the mixture and component 3, and the same for $\hat{\mu}_2=\mu_2-\mu_3$. Component 3 is the one whose mass fraction concentration is taken as a dependent variable, *i.e.*, $c_3=1-c_1-c_2$. Consistent with the use of concentrations in terms of mass fractions, the chemical potentials are expressed here per unit mass, while in other works [24] chemical potentials per mole have been used.

As is well known [2,21,24], the experimentally accesible diffusion matrix $\underline{\underline{\mathrm{D}}}$ is proportional to the product of the Onsager matrix $\underline{\underline{\mathrm{L}}}$ by the equation of state (EOS) matrix $\underline{\underline{\mathrm{G}}}$ of derivatives of chemical potential differences

$$G_{ij}=\left(\frac{\partial\hat{\mu}_i}{\partial c_j}\right)_T. \tag{7}$$

In particular, we have

$$\begin{bmatrix}D_{11}\;D_{12}\\D_{21}\;D_{22}\end{bmatrix}=\frac{1}{\rho T}\begin{bmatrix}L_{11}\;L_{12}\\L_{21}\;L_{22}\end{bmatrix}\begin{bmatrix}\left(\frac{\partial\hat{\mu}_1}{\partial c_1}\right)_T & \left(\frac{\partial\hat{\mu}_1}{\partial c_2}\right)_T\\ \left(\frac{\partial\hat{\mu}_2}{\partial c_1}\right)_T & \left(\frac{\partial\hat{\mu}_2}{\partial c_2}\right)_T\end{bmatrix}. \tag{8}$$

Note that we follow the nomenclature of de Groot and Mazur [1] instead of the nomenclature of Taylor and Krishna [2], and that the Onsager matrix $\underline{\underline{\mathrm{L}}}$ as defined here is ρT times the inverse of the Onsager matrix $\underline{\underline{\mathrm{H}}}$ as used by others [24]: $\underline{\underline{\mathrm{H}}}=\rho T\underline{\underline{\mathrm{L}}}^{-1}$.

Because of a Maxwell thermodynamic relation, the EOS matrix is symmetric [2,24]. From the symmetry of $\underline{\underline{\mathrm{G}}}$ the following relation between Onsager and diffusion coefficients can be derived:

$$L_{12}(D_{11}-D_{22})-D_{21}L_{11}+D_{12}L_{22}=0. \tag{9}$$

In addition, the symmetry of the Onsager matrix implies the following relation between diffusion coefficients and chemical potential derivatives [2,21,24]:

$$-D_{12}G_{11}+G_{12}D_{11}=-D_{21}G_{22}+G_{12}D_{22}, \tag{10}$$

that is independent of whether one uses the convention of de Groot and Mazur [1] or of Taylor and Krishna [2] for the Onsager matrix.

3 Bulk solution

The goal of fluctuating hydrodynamics is to solve the system of stochastic differential equations (4), and to obtain expressions for the correlation functions of the two fluctuating concentrations from the correlation functions of the random dissipative fluxes, eqs. (5) and (6). In general, such a procedure must include boundary conditions for the fluctuating fields which, as discussed elsewhere at length [5], strongly modify the spectrum of the fluctuations at small q. Furthermore, as further discussed elsewhere [40], the presence of gravity also affects the fluctuations at intermediate values of q. These effects are a direct consequence of the non-equilibrium fluctuations having, generically, long spatial range [38]. In any case, it is also known that a bulk calculation, that does not take into account boundary conditions nor gravity, gives the correct asymptotic large q behavior of both the decay rate and the intensity of the fluctuations [5]. Hence, we proceed next with such a bulk calculation, that will be highly useful as a comparison reference for future work incorporating both gravity and boundary conditions.

If one does not consider boundary conditions, fluctuations of any length or time scales are allowed in the system. Then, to solve eqs. (4) one performs full spatiotemporal Fourier transforms, so as to obtain

$$\underline{\underline{\mathrm{M}}}(\omega,\boldsymbol{q})\begin{bmatrix}\delta v_z(\omega,\boldsymbol{q})\\ \delta c_1(\omega,\boldsymbol{q})\\ \delta c_2(\omega,\boldsymbol{q})\end{bmatrix}=\begin{bmatrix}F_z(\omega,\boldsymbol{q})\\ F_1(\omega,\boldsymbol{q})\\ F_2(\omega,\boldsymbol{q})\end{bmatrix}, \tag{11}$$

where ω is the frequency and $\boldsymbol{q}$ the wave vector of the fluctuations, and $F_\alpha(\omega,\boldsymbol{q})$ represents the (Fourier transformed) random forcing terms on the right-hand side (RHS) of eqs. (4), namely

$$\begin{aligned}F_z(\omega,\boldsymbol{q}) &= -\mathrm{i}\ \epsilon_{znk}\epsilon_{kml}\frac{q_n}{\rho}q_m q_p\ \delta\Pi_{pl}(\omega,\boldsymbol{q}),\\ F_1(\omega,\boldsymbol{q}) &= -\mathrm{i}\ \frac{q_n}{\rho}\ \delta J_{1,n}(\omega,\boldsymbol{q}),\\ F_2(\omega,\boldsymbol{q}) &= -\mathrm{i}\ \frac{q_n}{\rho}\ \delta J_{2,n}(\omega,\boldsymbol{q}),\end{aligned} \tag{12}$$

where ϵ_{nmk} is the Levi-Civita permutation tensor, subscript $p\in\{x,y,z\}$ and sum over repeated indices is understood. Finally, in eq. (11), the linear response matrix $\underline{\underline{\mathrm{M}}}(\omega,\boldsymbol{q})$ is given by

$$\underline{\underline{\mathrm{M}}}(\omega,\boldsymbol{q})=\begin{bmatrix}-\nu q^4 & 0 & 0\\ \nabla c_{1,0} & \mathrm{i}\omega+D_{11}q^2 & D_{12}q^2\\ \nabla c_{2,0} & D_{21}q^2 & \mathrm{i}\omega+D_{22}q^2\end{bmatrix}. \tag{13}$$

Next, the solution for the fluctuating fields in eq. (11) is obtained by inverting the matrix $\underline{\underline{\mathrm{M}}}(\omega,\boldsymbol{q})$ defined by eq. (13). To express the solution it is convenient to separate the random forcing on the RHS of eq. (11) into two parts, namely:

$$\begin{bmatrix}F_z(\omega,\boldsymbol{q})\\ F_1(\omega,\boldsymbol{q})\\ F_2(\omega,\boldsymbol{q})\end{bmatrix}=\begin{bmatrix}0\\ F_1(\omega,\boldsymbol{q})\\ F_2(\omega,\boldsymbol{q})\end{bmatrix}+\begin{bmatrix}F_z(\omega,\boldsymbol{q})\\ 0\\ 0\end{bmatrix}, \tag{14}$$

noticing that, since the random stress is uncorrelated with the random diffusion fluxes, the first random forcing vector on the RHS of eq. (14) will also be uncorrelated with the second. The decomposition (14) also splits the solution to eq. (11) into two additive components, namely

$$\begin{aligned}\delta c_1(\omega,\boldsymbol{q}) &= \delta c_1^{\mathrm{E}}(\omega,\boldsymbol{q})+\delta c_1^{\mathrm{NE}}(\omega,\boldsymbol{q}),\\ \delta c_2(\omega,\boldsymbol{q}) &= \delta c_2^{\mathrm{E}}(\omega,\boldsymbol{q})+\delta c_2^{\mathrm{NE}}(\omega,\boldsymbol{q}),\end{aligned} \tag{15}$$

where the superscripts "E" and "NE" stand for Equilibrium and Non-Equilibrium, respectively. Indeed, it turns out that the "E" components in eq. (15) are exactly the same as if the system were at equilibrium at temperature and composition representative of the full layer, the same temperature and composition at which density and other transport properties are evaluated in eqs. (4) and in the prefactors of eqs. (5), (6). Moreover, because the two random forces in eq. (14) are uncorrelated, the "E" and "NE" components in eq. (15) will be uncorrelated too. Hence, we conclude that the correlation functions between fluctuating concentrations split additively into equilibrium and non-equilibrium contributions. The equilibrium part is exactly the same investigated in a previous publication [18] (evaluated at representative temperature and composition), so that we skip it here and from now on we investigate the non-equilibrium part only.

But, before focusing on the non-equilibrium part, we should note that a similar decomposition to that of eqs. (14) and (15) can be done for binary mixtures. In that case, a more complete investigation that includes gravity [40], shows that the simultaneous presence of gravity and a gradient affects the decay rate of the concentration fluctuations, even of what is called the equilibrium component. The gravity-induced decay rate modification is particularly important at small wave numbers q [40], being negligible at large q. This has been experimentally checked in a number of experiments in normal gravity [39, 41–45] and in micro-gravity [46,47]. We expect something similar in ternaries, although a more comprehensive investigation is left for future work. In any case, as already commented, the theory presented here shall give the correct asymptotic large q behavior of a more complete development that would include gravity, and even confinement. Actually the effect of confinement on the dynamics for a binary mixture has not been investigated until now.

Hence, we concentrate next in our goal of obtaining the non-equilibrium part of the correlations among the fluctuating concentrations. For that we need the correlation function $\langle F_z^*(\omega,\boldsymbol{q})\ F_z(\omega',\boldsymbol{q}')\rangle$ of the random forcing, which can be obtained from its definition (12) and the corresponding fluctuation-dissipation theorem in real space, eq. (5). Such a calculation has been presented several times in the literature [5,32,40], hence, we display here only the final result

$$\begin{aligned}\langle F_z^*(\omega,\boldsymbol{q})\ F_z(\omega',\boldsymbol{q}')\rangle &= 2k_{\mathrm{B}}T\frac{\nu}{\rho}q_\parallel^2 q^4\\ &\quad\times(2\pi)^4\delta(\omega-\omega')\ \delta(\boldsymbol{q}-\boldsymbol{q}'),\end{aligned} \tag{16}$$

where $q_\parallel^2 = q_x^2 + q_y^2$ is the component of the fluctuations wave vector $\boldsymbol{q}$ in the plane parallel to the walls (perpendicular to the gradient).

4 Non-equilibrium concentration fluctuations

4.1 Decay rates

The bulk solution for the non-equilibrium part of the fluctuating concentrations requires the inversion of the linear response matrix $\underline{\underline{\mathrm{M}}}(\omega, \boldsymbol{q})$ in eq. (11), that depends critically on its determinant. The ω-roots of the determinant are the decay rates of the fluctuations. Here, as we neglected the temporal derivative of the velocity fluctuations on the LHS of eq. (4), there are only two decay rates, $\hat{D}_1 q^2$ and $\hat{D}_2 q^2$, defined by

$$|\underline{\underline{\mathrm{M}}}(\omega, \boldsymbol{q})| = -\nu q^4 \; [\mathrm{i}\omega + \hat{D}_1 q^2] \; [\mathrm{i}\omega + \hat{D}_2 q^2], \tag{17}$$

where $|\underline{\underline{\mathrm{M}}}(\omega, \boldsymbol{q})|$ represents the determinant of the linear response matrix. Simple algebra shows that the decay rates calculated from eq. (13) are exactly the same as in equilibrium. That is, the two eigenvalues of the diffusion matrix [10,11,15,18,24], namely

$$\hat{D}_{1,2} = \tfrac{1}{2}\left[D_{11} + D_{22} \pm \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}}\right], \tag{18}$$

with the plus sign applying to $\hat{D}_1$ and the minus to $\hat{D}_2$. Hence, with the approximations adopted in this paper the decay rates of the non-equilibrium composition fluctuations are the same as if the system were at equilibrium at representative temperature and composition. This confirms the comments in the Introduction that most relevant differences between equilibrium and non-equilibrium fluctuations are in the statics (intensity) and not in the dynamics.

We do not want to be too repetitive, but if gravity and/or confinement are included in the theory, one expects differences with eq. (18), in particular a mixing between the two diffusive modes (18) and the viscous mode that will depend on the wave number q [40]. Such differences will be more pronounced at small q, while at larger q, eq. (18) will still give the correct asymptotic behavior of the decay rates.

4.2 Correlation matrix

The non-equilibrium part of the composition fluctuations is conveniently expressed in terms of a correlation matrix $\underline{\underline{\mathrm{C}}}^{\mathrm{NE}}(\omega, q)$, with components $C_{ij}^{\mathrm{NE}}(\omega, q)$ that we define by [18]

$$\langle \delta c_i^*(\omega, \boldsymbol{q}) \; \delta c_j(\omega', \boldsymbol{q}')\rangle^{\mathrm{NE}} = C_{ij}^{\mathrm{NE}}(\omega, q) \; (2\pi)^4 \; \delta(\omega - \omega') \; \delta(\boldsymbol{q} - \boldsymbol{q}'). \tag{19}$$

Some straightforward but long calculations show that the correlation matrix can be expressed as the sum of two diffusion modes

$$\underline{\underline{\mathrm{C}}}^{\mathrm{NE}}(\omega, q) = \frac{\rho k_{\mathrm{B}} T}{\nu} \frac{q_\parallel^2}{q^6} \left[\underline{\underline{\mathrm{A}}}_1^{\mathrm{NE}} \frac{2\hat{D}_1 q^2}{\omega^2 + \hat{D}_1^2 q^4} + \underline{\underline{\mathrm{A}}}_2^{\mathrm{NE}} \frac{2\hat{D}_2 q^2}{\omega^2 + \hat{D}_2^2 q^4}\right]. \tag{20}$$

Consequently, the corresponding time correlation matrix is expressed as the sum of two exponentials

$$\underline{\underline{\mathrm{C}}}^{\mathrm{NE}}(q, t) = \frac{\rho k_{\mathrm{B}} T}{\nu} \frac{q_\parallel^2}{q^6} \left[\underline{\underline{\mathrm{A}}}_1^{\mathrm{NE}} \; e^{-\hat{D}_1 t} + \underline{\underline{\mathrm{A}}}_2^{\mathrm{NE}} \; e^{-\hat{D}_2 t}\right]. \tag{21}$$

For an explicit and compact expression of the amplitude matrices, $\underline{\underline{\mathrm{A}}}_1^{\mathrm{NE}}$ and $\underline{\underline{\mathrm{A}}}_2^{\mathrm{NE}}$, we found convenient to introduce a "gradient" matrix defined in terms of the stationary concentration gradients as

$$\underline{\underline{\mathrm{X}}} = \begin{bmatrix} \nabla c_1 & \nabla c_1 \\ \nabla c_2 & \nabla c_2 \end{bmatrix}. \tag{22}$$

Then, the amplitude matrices in eq. (20) are simply given by

$$\underline{\underline{\mathrm{A}}}_1^{\mathrm{NE}} = \frac{\hat{D}_1 \; \underline{\underline{\mathrm{X}}}\underline{\underline{\mathrm{X}}}^\top - \hat{D}_2 |\underline{\underline{\mathrm{D}}}| \; \underline{\underline{\mathrm{D}}}^{-1} \underline{\underline{\mathrm{X}}}\underline{\underline{\mathrm{X}}}^\top (\underline{\underline{\mathrm{D}}}^{-1})^\top}{2(\hat{D}_1^2 - \hat{D}_2^2)}, \tag{23}$$

where $|\underline{\underline{\mathrm{D}}}|$ indicates the determinant of the diffusion matrix. The expression for $\underline{\underline{\mathrm{A}}}_2^{\mathrm{NE}}$ is obtained by exchanging the subscripts 1 and 2 in eq. (23) (not in the expressions of $\underline{\underline{\mathrm{X}}}$ or $\underline{\underline{\mathrm{D}}}$).

We note that, in general, one also obtains a nonzero imaginary part for the cross-correlation $\langle \delta c_1^*(\omega, \boldsymbol{q}) \;\; \delta c_2(\omega', \boldsymbol{q}')\rangle^{\mathrm{NE}}$ in the matrix $\underline{\underline{\mathrm{C}}}^{\mathrm{NE}}(\omega, q)$, which was not reported in eqs. (20)-(23). Such imaginary part, although mathematically present, is physically un-relevant. In a typical experiment one would observe the correlation function of refractive index fluctuations, $\delta n(\boldsymbol{r}, t)$, at a given wavelength, that is related to composition fluctuations by

$$\delta n(\boldsymbol{r}, t) = \left(\frac{\partial n}{\partial c_1}\right) \delta c_1(\boldsymbol{r}, t) + \left(\frac{\partial n}{\partial c_2}\right) \delta c_2(\boldsymbol{r}, t). \tag{24}$$

Hence, in the (Fourier transformed) autocorrelation function $\langle \delta n^*(\omega, \boldsymbol{q}) \; \delta n(\omega', \boldsymbol{q}')\rangle$, the concentrations cross correlation will appear as a term

$$[\langle \delta c_1^*(\omega, \boldsymbol{q}) \; \delta c_2(\omega', \boldsymbol{q}')\rangle + \langle \delta c_2^*(\omega, \boldsymbol{q}) \; \delta c_1(\omega', \boldsymbol{q}')\rangle]$$

so that any imaginary part does not contribute and is unobservable. Notice that if, hypothetically, index of refraction fluctuations at two different wavelengths were observed simultaneously, their cross-correlation cannot be measured, since light of different wavelengths does not interfere. For the case of observing the cross-correlation between two thermodynamic properties (that, in general, will be expressed as derivatives of some thermodynamic potential) a Jacobian appears, that cancels as a consequence of some Maxwell relation.

4.3 Statics

Application of double inverse Fourier transforms in the frequencies to eq. (20) defines an equal-time non-equilibrium correlation matrix, that gives the intensity of the fluctuations. Namely

$$\langle \delta c_i^*(\boldsymbol{q},t)\ \delta c_j(\boldsymbol{q}',t)\rangle^{\mathrm{NE}} = C_{ij}^{\mathrm{NE}}(q)\ (2\pi)^3\ \delta(\boldsymbol{q}-\boldsymbol{q}'), \quad (25)$$

with

$$\underline{\underline{\mathrm{C}}}^{\mathrm{NE}}(q) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \underline{\underline{\mathrm{C}}}^{\mathrm{NE}}(\omega,q)\ \mathrm{d}\omega = \underline{\underline{\mathrm{C}}}^{\mathrm{NE}}(q,t=0).$$

Simple integration of eq. (20) and use of the explicit expressions for the amplitude matrices gives the relatively compact result

$$\underline{\underline{\mathrm{C}}}^{\mathrm{NE}}(q) = \frac{\rho k_{\mathrm{B}} T}{2\nu(D_{11}+D_{22})}\frac{q_{\parallel}^2}{q^6} \times \left[\underline{\underline{\mathrm{XX}}}^{\top} + |\underline{\underline{\mathrm{D}}}|\ \underline{\underline{\mathrm{D}}}^{-1}\underline{\underline{\mathrm{XX}}}^{\top}(\underline{\underline{\mathrm{D}}}^{-1})^{\top}\right]. \quad (26)$$

One observes in eq. (26) the q^{-4} dependence for wave vectors perpendicular to the gradient and large q. This q^{-4} dependence demonstrates the spatial long-range nature of non-equilibrium fluctuations and it is also found in one-component fluids [48,49] and binary mixtures [50]. Again, incorporation of gravity and confinement is expected to modify this dependence, particularly at intermediate and small wave numbers. However, even with gravity and boundary conditions, eq. (26) will still give the correct $q \to \infty$ asymptotic limit.

One also observes in eq. (26) that the amplitude of the correlation matrix, $\underline{\underline{\mathrm{C}}}^{\mathrm{NE}}(q)$, is proportional to the square of the gradients, namely to the product of matrices

$$\underline{\underline{\mathrm{XX}}}^{\top} = 2\begin{bmatrix} \nabla c_1^2 & \nabla c_1 \nabla c_2 \\ \nabla c_2 \nabla c_1 & \nabla c_2^2 \end{bmatrix}. \quad (27)$$

For the case of Soret-induced gradients one has to substitute eq. (3) into eq. (27). Unfortunately, this procedure does not lead to expressions more compact for $\underline{\underline{\mathrm{C}}}^{\mathrm{NE}}$ than eqs. (21) or (26), although it is obvious that for Soret-induced composition gradients one has an overall $\propto (\nabla T)^2$ dependence of $\underline{\underline{\mathrm{C}}}^{\mathrm{NE}}$. This gradient square proportionality is another typical feature of non-equilibrium fluctuations, as it is also found in one-component fluids [47] and binary mixtures [46].

5 Conclusions

In the present work fluctuating hydrodynamics has been utilized to develop the theory of concentration fluctuations in a ternary mixture subjected to a stationary temperature gradient. The most important result is the appearance of a non-equilibrium part, which must be added to the equilibrium contribution that would be obtained by simple substitution of average temperature and compositions in the expression of the correlation matrix of an isothermal ternary mixture. Although the local-equilibrium hypothesis is valid for the average values of the thermodynamic variables, that continue to be related by equilibrium EOS, it is no longer valid for their fluctuations, which contain terms that do not exist in equilibrium.

Equation (21) for the non-equilibrium time correlation matrix (dynamics of the fluctuations) and eq. (26) for the total intensity (statics) have been derived as the main results of this work. Since gravity and confinement have been neglected, the results of this paper are asymptotically correct for fluctuations of large wave vector q, while for smaller q other effects need to be incorporated. Overall, the obtained results appear to be comparable to the case of a binary mixture, and the amplitude of non-equilibrium concentration fluctuations is proportional to the square of the gradient and inversely proportional to the fourth power of the fluctuations wave number, q^{-4}. This last feature means that, depending on the value of q, the fluctuations of non-equilibrium origin can have an intensity much larger than the equilibrium fluctuations (giant fluctuations [30,41]).

Here a fully generic diffusion matrix has been considered, see eq. (2), while previous investigations by Balakrishnan *et al.* [30] considered a particularly restricted form for the diffusion matrix only. Although not fully evident, it can be shown that, for the particular diffusion matrix investigated elsewhere [30], the current eq. (26) reduces to the equation for $\langle(\delta\hat{\mathbf{Y}})(\delta\hat{\mathbf{Y}})^*\rangle_{\mathrm{neq}}$ (in their alternative notation) after Eq. (B4) in the second appendix of [30]. Hence, we generalize previous results, while expressing them in a more compact and convenient form.

Finally, we mention that the current growing interest in the measurement of thermal diffusion in ternary mixtures [6–15], including space experiments [16], means that it is reasonable to foresee for the coming years experiments measuring composition fluctuations in ternaries subjected to stationary temperature gradients, whether by dynamic light scattering [51] or by shadowgraphy [44]. The results presented in this paper are intended as a starting point for the analysis of these future experiments.

JMOZ wishes to acknowledge the hospitality of the *Université de Pau et des Pays de l 'Adour* during a sabbatical leave at Anglet, when most of the work presented here was developed. Also financial support from a UCM/Santander Research Grant (PR6/13-18867) is acknowledged.

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