

Gravity effects on Soret-induced nonequilibrium fluctuations in ternary mixtures

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Abstract. We discuss the gravity effects on the dynamics of composition fluctuations in a ternary mixture around the non-equilibrium quiescent state induced by thermodiffusion when subjected to a stationary temperature gradient. We found that the autocorrelation matrix of concentration fluctuations can be expressed as the sum of two exponentially decaying concentration modes. Without accounting for confinement, we obtained exact analytical expressions for the two decay rates which, as a consequence of gravity, display a wave number dependent mixing. The stability of the quiescent solution is also examined, as a function of the two solutal Rayleigh numbers used to express the decay rates. After having discussed the dynamics of the two concentration modes, we calculate the corresponding amplitudes. Consequences for optical experiments are discussed.

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1 Introduction

The present paper represents one further step in the development of the theory of spontaneous thermodynamic fluctuations in a ternary liquid mixture subjected to a stationary temperature gradient in the terrestrial gravity field. Fluctuations in equilibrium ternary mixtures (homogeneous temperature, concentrations and pressure) has been the topic of several investigations over the years. A first analysis was presented by Lekkerkerker and Laidlaw [1] who considered the generic case of a compressible fluid in which fluctuations in five independent variables are coupled. This pioneering study was focused on the dynamics of the fluctuations, and an explicit discussion of the equal-time correlation functions was not considered. Later, van der Elsken and Bot [2] considered the intensity of fluctuations in multicomponent mixtures in equilibrium, deriving an expression for the ratio of the intensities of Rayleigh and Brillouin lines of the scattering spectrum. More recently, Ivanov and Winkelmann [3] re-derived the expressions of Lekkerkerker and Laidlaw [1] for the Rayleigh peak of a ternary mixture, and studied the slowing-down of the concentration fluctuations close

to a critical consolute point but without including a discussion of the statics of the fluctuations. Finally we should mention Bardow [4] who combined previous works, considering both the statics and the dynamics of fluctuations in equilibrium ternary systems, while adopting some approximations adequate for mixtures in the liquid state, in particular the fact that concentration fluctuations in liquids relax much slower than temperature fluctuations. This approach is equivalent to the large Lewis number approximation, introduced by Velarde and Schechter [5], to simplify the calculation of the convection threshold in binary fluids.

All these works on equilibrium fluctuations in ternary mixtures [1–4] evaluated the correlation functions on the basis of the Mountain method of arbitrary initial conditions [6,7], an approach often adopted by books dealing with thermodynamic fluctuations [8–10]. There exists an alternative method, namely, fluctuating hydrodynamics (FHD) originally developed by Landau and Lifshitz [11] (with relevant subsequent contributions by Fox and Uhlenbeck [12]) for one-component fluid systems. FHD has been later extended, among other developments, to equilibrium binary mixtures [13]. Both theoretical approaches are equivalent for systems in equilibrium, but FHD can be extended for dealing with fluctuations in non-equilibrium (NE) systems [14–17], while the Mountain method of ar-

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bitrary initial conditions cannot. Indeed, it has been the systematic application of FHD that allowed the investigation of fluctuations in systems out of (global) equilibrium. The validity of this non-equilibrium extension of FHD, in the case of binary liquid mixtures, has been confirmed by a series of pioneering experiments [18–22]. One other notable example of FHD success is the prediction of the influence of gravity on the fluctuations [23], an effect initially considered to be not accessible to experiments, and later confirmed by novel optical techniques [24]. Similarly, detailed FHD predictions about finite size effects on non-equilibrium fluctuations [25–27] have been later experimentally verified, by Gradflex [28] in microgravity and by ground-based measurements [27, 29] in the presence of buoyancy force. Hence, as a preliminary step in developing the theory of thermodynamic fluctuations in NE ternary mixtures, it was necessary to re-derive [30] the equilibrium results for ternary mixtures on the basis of FHD, for which the simplifications of Bardow [4] were adopted.

As a second step [31], we evaluated in the absence of gravity the spectrum of thermodynamic fluctuations when a ternary mixture is subjected to a stationary temperature gradient, so that a composition gradient is induced by the Soret effect. As previous investigations in binary mixtures have shown [23], gravity has no influence in the spatial spectrum of NE fluctuations for large wave numbers $q \rightarrow \infty$ so that, in addition to microgravity conditions, the results of Ref. [31] are applicable to ground conditions as an asymptotic limit, as experimentally verified by Bataller et al. [32].

In the present paper, we consider the effects of gravity (buoyancy) on the problem. This question is not only relevant on theoretical grounds. The experimental investigation of the dynamics of NE concentration fluctuations has been used as a method to simultaneously measure diffusion and thermal diffusion coefficients in a binary mixture [33, 34]. To extend such a method to multi-component mixtures, it is needed to understand the effects of buoyancy on NE fluctuations, starting with ternary mixtures. For these reasons, our current results are also part of the SCCO (Soret Coefficients for Crude Oil) project [35, 36], currently being jointly developed by the European Space Agency (ESA) and the Chinese Space Agency (CSA), aimed at obtaining reference quantitative values of thermodynamic coefficients in multi-component fluid mixtures, a goal of interest also for the oil industry.

We shall proceed by first presenting in Sect. 2 the equations of FHD for a ternary system subjected to a stationary temperature gradient, in an approximation suitable for liquid mixtures, and accounting for buoyancy effects. In Sect. 3 we then explain how a solution to the fluctuating hydrodynamic equations can be obtained in ‘bulk’, without accounting for boundary conditions in the fluctuating fields. For this purpose we found highly advantageous to adopt linear combination of concentrations that diagonalize the diffusion matrix, as considered in detail in Sect. 3.1. Next, in Sect. 4, we obtain explicit expressions for the decay times of the NE composition fluctuations

and analyze the related issue of the appearance of convection in Sect. 4.2. Next, in Sect. 4.3, we turn our attention to the amplitudes of the two diffusion modes presented in the correlation matrix of the composition fluctuations. Finally, our main conclusions are summarized in Sect. 5.

2 Fluctuating hydrodynamics

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, \mathbf{J}_1 and \mathbf{J}_2 , and Fick’s law in isotropic systems is expressed by a 2×2 diffusion matrix \underline{D} . Similarly, there exist two thermodynamic coefficients, \bar{D}_{T1} and \bar{D}_{T2} , so that in the simultaneous presence of temperature and concentrations gradients, diffusion fluxes are expressed as:

$$\begin{aligned} \mathbf{J}_1 &= -\rho (D_{11} \nabla c_1 + D_{12} \nabla c_2 + D_{T1} \nabla T), \\ \mathbf{J}_2 &= -\rho (D_{21} \nabla c_1 + D_{22} \nabla c_2 + D_{T2} \nabla T), \end{aligned} \quad (1)$$

where D_{nm} are the components of the diffusion matrix

$$\underline{D} = \begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix}. \quad (2)$$

SI units of $\text{m}^2 \text{s}^{-1}$, and ρ is the mass density of the mixture. Here, differently from [37], we consider a completely general diffusion matrix, the D_{nm} values being restricted only by generic symmetry properties [38]. Congruent with the appearance of the barycentric velocity \mathbf{v} in the hydrodynamic equations (see below), here we use diffusion fluxes and diffusion matrix defined in the center of mass frame of reference.

In this paper we consider a ternary liquid mixture subjected to a uniform stationary temperature gradient ∇T , of magnitude ∇T , in the direction of the z -axis, *i.e.*, parallel to gravity. If one assumes diffusion and thermodynamic coefficients to be constants, the system may evolve to a stationary state characterized by vanishing diffusion fluxes. Hence, thermodiffusion induces the appearance of a steady composition gradient that for isotropic mixtures is in the same direction as gravity and the temperature gradient, and whose magnitude can be obtained from Eq. (1) as:

$$\begin{bmatrix} \nabla c_1 \\ \nabla c_2 \end{bmatrix} = -\underline{D}^{-1} \begin{bmatrix} D_{T1} \\ D_{T2} \end{bmatrix} \nabla T. \quad (3)$$

Borrowing nomenclature from one-component fluids, we refer to this state as the “conductive” state. Buoyancy effects may lead to convection, *i.e.*, the conductive state described by Eq. (3) may be unstable and non-existent in practice. For the time being we shall assume stability of the conductive solution leaving for later, in Sect. 4, a discussion of convection in this system. We mention that to realize in practice the conductive state of Eq. (3) the system must be confined between two plates, separated by a distance L and maintained at different temperatures. However, for the rest of this paper we shall neglect the

presence of boundaries. Previous studies show that confinement affects both the amplitude [25,26] and the dynamics [27] of NE fluctuations at lateral wave numbers $q \lesssim L^{-1}$. Hence, our current results are expected to be valid only for fluctuations with q large enough, while we leave for future publications a thorough investigation of confinement effects on NE fluctuations in ternary mixtures.

Hence, our purpose here is to study composition fluctuations around the NE steady conductive state of Eq. (3), including buoyancy but neglecting confinement effects. Initially, this is a complicated problem for which one has to consider coupling between velocity, density, temperature and two concentration fluctuations. To simplify the problem, as elucidated by other researchers in the field [4,37] and by us in previous publications [30,31], it is convenient to adopt a series of approximations, adequate for ternary liquid mixtures, before attempting any detailed calculation. Here, we shall consider the same approximations used in our previous publications [30,31], to which we refer for a detailed discussion. In summary, they amount to incompressible (divergence-free) flow, large values of the Lewis and the Schmidt numbers and use of average thermophysical properties. In the case of multi-component systems large Lewis and Schmidt numbers means that both thermal diffusivity a and kinematic viscosity ν of the mixture are much larger than *all* eigenvalues of the diffusion matrix [4]. Under these simplifications, fluctuations in the concentrations (δc_1 and δc_2 for a ternary mixture) are only coupled with fluctuations in the fluid velocity component parallel to the gradients (δv_z), explicitly reading [31]:

$$0 = \nu \nabla^4 \delta v_z - \beta_1 g \nabla_{\parallel}^2 \delta c_1 - \beta_2 g \nabla_{\parallel}^2 \delta c_2 - \frac{1}{\rho} \left[\nabla \times \nabla \times (\nabla \delta \Pi) \right]_z, \quad (4)$$

$$\begin{aligned} \partial_t \delta c_1 &= D_{11} \nabla^2 \delta c_1 + D_{12} \nabla^2 \delta c_2 - \delta v_z \nabla c_1 - \frac{1}{\rho} \nabla \cdot \delta \mathbf{J}_1, \\ \partial_t \delta c_2 &= D_{21} \nabla^2 \delta c_1 + D_{22} \nabla^2 \delta c_2 - \delta v_z \nabla c_2 - \frac{1}{\rho} \nabla \cdot \delta \mathbf{J}_2, \end{aligned}$$

where g is the gravity acceleration, ρ the average density and

$$\beta_i = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial c_i} \right)_{p,T} \quad (5)$$

the solutal expansion coefficients. In addition, and in accordance with the rules of FHD, the linear phenomenological laws for the dissipative fluxes have to be supplemented with random contributions reflecting the stochastic nature of molecular motion [16,11]. Hence, Eqs. (4) contain a stochastic stress tensor $\delta \Pi(\mathbf{r}, t)$, and two stochastic diffusive fluxes, $\delta \mathbf{J}_1(\mathbf{r}, t)$ and $\delta \mathbf{J}_2(\mathbf{r}, t)$. Subscript z in the first of Eqs. (4) refers to the z -component of the vector between brackets. Similarly, symbol $\nabla_{\parallel}^2 = \partial_x^2 + \partial_y^2$ represents the component of the Laplacian perpendicular to gravity and the gradients, thus, parallel to the bounding surfaces.

We note that Eqs. (4) are exactly the same working equations of our most recent publication on the topic [31],

with the only difference that we incorporate here the effects of buoyancy through the terms containing g and the solutal expansion coefficients. In particular, and as a consequence of the large Lewis numbers approximation [5], temperature fluctuations are neglected. Alternatively, at the time scale defined by the magnitude of the diffusion matrix and used in Eqs. (4), temperature (and velocity) fluctuations are assumed to be fully decayed and only couple statically (the velocity) to composition fluctuations. However, recent experiments with fast cameras [32] have observed the decay of temperature fluctuations in shadowgraph signals; a complete analysis of these results would require further development of the theory including the coupling with temperature fluctuations, even for binary mixtures. Nevertheless, we note that temperature fluctuations are indeed observed [32] only for wave numbers $a q^2 t_e \lesssim 1$ (where a is the thermal diffusivity of the mixture and t_e the 'experimental' time delay, *i.e.*, the time difference between consecutive images in a shadowgraph machine) and that, in most cases, this limitation is not more stringent than the condition $q \lesssim L^{-1}$ coming from having neglected confinement.

After discussing the limitations of the various approximations adopted, to complete the setting of the problem, one has to specify the statistical properties of the random dissipative fluxes in Eqs. (4). They are: zero average, $\langle \delta \Pi_{ij}(\mathbf{r}, t) \rangle = \langle \delta J_{1,i}(\mathbf{r}, t) \rangle = \langle \delta J_{2,i}(\mathbf{r}, t) \rangle = 0$; and correlation functions given by the fluctuation-dissipation theorem (FDT) [16,30,11], which for incompressible flows reads:

$$\begin{aligned} \langle \delta \Pi_{ij}(\mathbf{r}, t) \cdot \delta \Pi_{kl}(\mathbf{r}', t') \rangle &= 2k_B T \eta (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \\ &\times \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \end{aligned} \quad (6)$$

for the random stress tensor, and [30]

$$\langle \delta J_{n,i}^*(\mathbf{r}, t) \delta J_{m,j}(\mathbf{r}', t') \rangle = 2k_B L_{nm} \delta_{ij} \delta(t - t') \delta(\mathbf{r} - \mathbf{r}'), \quad (7)$$

for the random diffusive fluxes, while in accordance with the Curie principle, the random stress is uncorrelated with $\delta \mathbf{J}_i$. In Eqs. (6)-(7) k_B is Boltzmann constant, η the shear viscosity, L_{nm} the elements of the Onsager matrix (with $L_{12} = L_{21}$). Here and elsewhere in this paper, the indices n, m span the two independent mixture components $n, m \in \{1, 2\}$, while the indices i, j, k, l span the three spatial coordinates $i, j, k, l \in \{x, y, z\}$ (we are implicitly assuming that the system is isotropic).

The Onsager matrix \underline{L} in Eq. (7) is related to the experimentally accessible diffusion matrix \underline{D} by [1,4,38]

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

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 in Eq. (8) are specific (per unit mass), while in other works [4] chemical potentials per mole have been used.

3 Bulk solution

The goal of FHD is to solve the system of stochastic differential equations (4) and, from Eqs. (6) and (7), obtain expressions for the correlation functions of the two fluctuating concentrations. In general, such a procedure must include boundary conditions for the fluctuating fields which, as elucidated elsewhere [16, 25–27], modify the spatial and dynamical spectrum of NE fluctuations at small q . These confinement effects are a direct consequence of the nonequilibrium fluctuations having, generically, long spatial range [39]. In any case, it is also known that a bulk calculation, that does not take into account boundary conditions, gives the correct behavior for $q \gtrsim L^{-1}$ of both the decay rates and the intensity of the fluctuations [16]. Hence, we proceed next with such a bulk calculation, that will be highly useful as a comparison reference for future work incorporating boundary conditions and for comparing experimental data on ternary mixtures [32, 40].

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

$$\underline{\underline{M}}(\omega, \mathbf{q}) \begin{bmatrix} \delta v_z(\omega, \mathbf{q}) \\ \delta c_1(\omega, \mathbf{q}) \\ \delta c_2(\omega, \mathbf{q}) \end{bmatrix} = \begin{bmatrix} F_z(\omega, \mathbf{q}) \\ F_1(\omega, \mathbf{q}) \\ F_2(\omega, \mathbf{q}) \end{bmatrix}, \quad (9)$$

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

$$\begin{aligned} F_z(\omega, \mathbf{q}) &= i \epsilon_{zik} \epsilon_{kjl} \frac{q_i}{\rho} q_j q_p \delta \Pi_{pl}(\omega, \mathbf{q}) \\ F_1(\omega, \mathbf{q}) &= -i \frac{q_i}{\rho} \delta J_{1,i}(\omega, \mathbf{q}) \\ F_2(\omega, \mathbf{q}) &= -i \frac{q_i}{\rho} \delta J_{2,i}(\omega, \mathbf{q}), \end{aligned} \quad (10)$$

where ϵ_{ijk} is the Levi-Civita permutation tensor, subscript $p \in \{x, y, z\}$ and sum over repeated indices is understood. Finally, in Eq. (9), the linear response matrix $\underline{\underline{M}}(\omega, \mathbf{q})$ is given by:

$$\underline{\underline{M}}(\omega, \mathbf{q}) = \begin{bmatrix} \nu q^4 & \beta_1 g q_{\parallel}^2 & \beta_2 g q_{\parallel}^2 \\ \nabla c_1 i\omega + D_{11} q^2 & & D_{12} q^2 \\ \nabla c_2 & D_{21} q^2 & i\omega + D_{22} q^2 \end{bmatrix}, \quad (11)$$

where $q_{\parallel}^2 = q_x^2 + q_y^2$ is the component of the wave vector in the plane parallel to the system boundaries.

3.1 Diagonal concentrations

The solution for the fluctuating fields in Eq. (9) is obtained by inverting the matrix $\underline{\underline{M}}(\omega, \mathbf{q})$ defined by Eq. (11). For such a calculation we have found convenient, following previous authors [4, 41–43], to use as independent variables the concentrations $\delta c'_1$ and $\delta c'_2$ making diagonal the diffusion matrix. Then, we switch to diagonal variables by

$$\begin{bmatrix} \delta v_z(\omega, \mathbf{q}) \\ \delta c'_1(\omega, \mathbf{q}) \\ \delta c'_2(\omega, \mathbf{q}) \end{bmatrix} = \underline{\underline{U}} \cdot \begin{bmatrix} \delta v_z(\omega, \mathbf{q}) \\ \delta c_1(\omega, \mathbf{q}) \\ \delta c_2(\omega, \mathbf{q}) \end{bmatrix}, \quad (12)$$

with the transformation matrix [4]

$$\underline{\underline{U}} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & \frac{D_{22} - \hat{D}_2}{D_{21}} \\ 0 & \frac{D_{11} - \hat{D}_1}{D_{12}} & 1 \end{bmatrix}, \quad (13)$$

where we introduce the eigenvalues of the diffusion matrix [30, 4, 44–46]

$$\hat{D}_{1,2} = \frac{1}{2} \left[D_{11} + D_{22} \mp \sqrt{(D_{11} - D_{22})^2 - 4D_{12}D_{21}} \right]. \quad (14)$$

Of course, since $\underline{\underline{D}}$ is a diffusion matrix, it will always have two real and positive eigenvalues. Here, and in the rest of this paper, the plus and the minus sign are applied in Eq. (14) in such a way that $\hat{D}_1 < \hat{D}_2$. Hence, \hat{D}_1 will always represent the slowest diffusion mode and \hat{D}_2 the fastest one. It is also implicitly assumed, here and in the rest of this paper, that $\hat{D}_1 \neq \hat{D}_2$. The particular case $\hat{D}_1 = \hat{D}_2$ will be considered in the Appendix A. With these definitions, the equations in the new ‘diagonal’ variables will be expressed as:

$$\underline{\underline{U}} \cdot \underline{\underline{M}}(\omega, \mathbf{q}) \cdot \underline{\underline{U}}^{-1} \begin{bmatrix} \delta v_z(\omega, \mathbf{q}) \\ \delta c'_1(\omega, \mathbf{q}) \\ \delta c'_2(\omega, \mathbf{q}) \end{bmatrix} = \underline{\underline{U}} \cdot \begin{bmatrix} F_z(\omega, \mathbf{q}) \\ F_1(\omega, \mathbf{q}) \\ F_2(\omega, \mathbf{q}) \end{bmatrix}, \quad (15)$$

where it is convenient to make a linear combination of the two last equations, equivalent to multiply by the matrix $\underline{\underline{U}}$. Indeed, the matrix

$$\underline{\underline{M}}'(\omega, \mathbf{q}) = \underline{\underline{U}} \cdot \underline{\underline{M}}(\omega, \mathbf{q}) \cdot \underline{\underline{U}}^{-1} \quad (16)$$

is semi-diagonal. Simple algebra from Eqs. (11) and (13) gives

$$\underline{\underline{M}}'(\omega, \mathbf{q}) = \begin{bmatrix} \nu q^4 & \beta_1' g q_{\parallel}^2 & \beta_2' g q_{\parallel}^2 \\ \nabla c'_1 i\omega + \hat{D}_1 q^2 & 0 & 0 \\ \nabla c'_2 & 0 & i\omega + \hat{D}_2 q^2 \end{bmatrix}, \quad (17)$$

where, to express the various quantities it is useful to introduce the minor $\underline{\underline{U}}_{\text{m}}$ of the matrix $\underline{\underline{U}}$ representing the concentrations change, namely

$$\underline{\underline{U}}_{\text{m}} = \begin{bmatrix} 1 & \frac{D_{22} - \hat{D}_2}{D_{21}} \\ \frac{D_{11} - \hat{D}_1}{D_{12}} & 1 \end{bmatrix}. \quad (18)$$

Then, as expected, one has

$$\begin{bmatrix} \nabla c'_1 \\ \nabla c'_2 \end{bmatrix} = \underline{\underline{U}}_m \cdot \begin{bmatrix} \nabla c_1 \\ \nabla c_2 \end{bmatrix}, \quad (19)$$

and

$$\begin{bmatrix} \beta_1 \\ \beta_2 \end{bmatrix} = \underline{\underline{U}}_m^\top \cdot \begin{bmatrix} \beta'_1 \\ \beta'_2 \end{bmatrix}. \quad (20)$$

The latter equation means that the β'_i are the derivatives of the density with respect to the ‘diagonal’ concentrations c'_i . The rows of $\underline{\underline{U}}_m^{-1}$ contain the components of the eigenvectors of the diffusion matrix $\underline{\underline{D}}$, which are specified except by a normalization factor. This freedom in the choice of $\underline{\underline{U}}_m$ has been used by some authors [41–43] to slightly simplify the problem making $\beta'_i = \beta_i$, at the cost of introducing explicitly the solutal expansion coefficients in $\underline{\underline{U}}_m$. We have preferred not to do so here, and only the components of the diffusion matrix appear in Eq. (18). Obviously, the physics of the problem does not depend on the normalization selected for the eigenvectors of $\underline{\underline{D}}$.

As a conclusion of this section, to solve the problem in the new ‘diagonal’ variables, one has to invert the matrix $\underline{\underline{M}}'(\omega, \mathbf{q})$ defined by Eq. (16). Due to the presence of two zeros in Eq. (17) it results simpler than the original problem of inverting the matrix $\underline{\underline{M}}(\omega, \mathbf{q})$ of Eq. (11). In addition, the new problem also results physically more transparent and the role of the eigenvalues of the mass diffusion matrix is highlighted.

3.2 Random forcing terms

Next, to obtain from Eq. (15) the correlation functions among the fluctuating concentrations, we need the correlation function among the random forcing terms at its RHS. The first of these forcing terms coincides with $F_z(\omega, \mathbf{q})$ in Eq. (10). Its autocorrelation $\langle F_z^*(\omega, \mathbf{q}) F_z(\omega', \mathbf{q}') \rangle$ can be computed from Eq. (10) itself and the corresponding FDT in real space, Eq. (6). Such a calculation has been presented several times in the literature [16, 47, 23] and here we display only the final result:

$$\begin{aligned} \langle F_z^*(\omega, \mathbf{q}) F_z(\omega', \mathbf{q}') \rangle &= 2k_B T \frac{\nu}{\rho} q_\parallel^2 q^4 \\ &\times (2\pi)^4 \delta(\omega - \omega') \delta(\mathbf{q} - \mathbf{q}'). \end{aligned} \quad (21)$$

The random force $F_z(\omega, \mathbf{q})$ is uncorrelated with the other two random forcing terms at the RHS of Eq. (15). Indeed, if one defines ‘diagonal’ random forces by

$$\begin{bmatrix} F'_1(\omega, \mathbf{q}) \\ F'_2(\omega, \mathbf{q}) \end{bmatrix} = \underline{\underline{U}}_m \cdot \begin{bmatrix} F_1(\omega, \mathbf{q}) \\ F_2(\omega, \mathbf{q}) \end{bmatrix}, \quad (22)$$

one sees that the forcing terms, $F'_i(\omega, \mathbf{q})$, appearing in the diagonal concentration equations of Eq. (15) are linear combinations of the random forces $F_i(\omega, \mathbf{q})$ in Eq. (10). Since the latter are uncorrelated with $F_z(\omega, \mathbf{q})$, the $F'_i(\omega, \mathbf{q})$ will be uncorrelated with $F_z(\omega, \mathbf{q})$ too.

The final ingredient one needs for the calculation of the autocorrelation of NE composition fluctuations (cNEFs), is the correlation matrix $\langle F_i^*(\omega, \mathbf{q}) F_j(\omega', \mathbf{q}') \rangle$ of random forcing terms for the diagonal concentrations. This can be obtained combining Eq. (22) with Eq. (10) and the Fourier-transformed version of the FDT for the diffusion fluxes, Eq. (7). Such a calculation is long but straightforward and one important result, already anticipated by Bardow [4], is the vanishing of the cross correlation

$$\langle F_1^*(\omega, \mathbf{q}) F_2(\omega', \mathbf{q}') \rangle = 0, \quad (23)$$

while the autocorrelation of these random forces results proportional to delta function in frequency and wave number, namely

$$\begin{aligned} \langle F_i^*(\omega, \mathbf{q}) F_i(\omega', \mathbf{q}') \rangle &= 2\hat{S}_i \hat{D}_i q^2 \\ &\times (2\pi)^4 \delta(\omega - \omega') \delta(\mathbf{q} - \mathbf{q}'). \end{aligned} \quad (24)$$

By following the procedure described above, we have computed the elements \hat{S}_i . The corresponding expressions are rather long, and we are not displaying it here since, as further discussed below in Sect. 4.3, they will be actually used only for the computation of the equilibrium correlation matrix, resulting in expressions that have been previously presented in the literature [4, 30]. As discussed in more detail by Bardow [4], the coefficients \hat{S}_i are, essentially, the derivatives of the entropy with respect to the ‘diagonal’ concentrations c'_i .

4 Nonequilibrium concentration fluctuations

In the previous section, we set the problem in a mathematically convenient way to be solved by adopting diagonal concentrations that somehow simplify the linear response matrix and, most importantly, have uncorrelated random forcing terms, see Eq. (23). In this section we proceed with the solution, discussing first the decay rates of the fluctuations.

4.1 Decay rates

The bulk solution for the fluctuating concentrations requires the inversion of the linear response matrix $\underline{\underline{M}}'(\omega, \mathbf{q})$ in Eq. (15), that depends critically on its determinant. As it will become clear below, the ω -roots of the determinant are the decay rates of the fluctuations. Here, as we neglected the temporal derivative of the velocity fluctuations in the LHS of Eq. (4), there are only two decay rates that, for convenience, we express in terms of wave vector dependent mass transport coefficients, $\Gamma_i(\mathbf{q}) = \gamma_i(\mathbf{q}) q^2$ in such a way that:

$$|\underline{\underline{M}}'(\omega, \mathbf{q})| = -\nu q^4 [i\omega + \gamma_1(\mathbf{q}) q^2] [i\omega + \gamma_2(\mathbf{q}) q^2], \quad (25)$$

with $|\underline{\underline{M}}'(\omega, \mathbf{q})|$ representing the determinant of the linear response matrix. Some algebra shows that the γ_i associated to the linear response matrix of Eq. (17) are conveniently expressed as:

$$\gamma_{1,2}(\mathbf{q}) = \frac{1}{2} \left(\hat{D}_2 + \hat{D}_1 - \frac{\tilde{q}_{\parallel}^2}{\tilde{q}^6} Ra_i \hat{D}_i \right) \left[1 \mp \sqrt{1 - \frac{\frac{4\hat{D}_1\hat{D}_2}{(\hat{D}_1 + \hat{D}_2)^2} \left[1 - \frac{\tilde{q}_{\parallel}^2}{\tilde{q}^6} Ra_s \right]}{\left[1 - \frac{\tilde{q}_{\parallel}^2}{\tilde{q}^6} \frac{Ra_i \hat{D}_i}{\hat{D}_1 + \hat{D}_2} \right]^2}} \right], \quad (26)$$

where $\tilde{q} = qL$ is a dimensionless wave number, and we introduce two solutal Rayleigh numbers [43] defined by:

$$\begin{aligned} Ra_1 &= \frac{gL^4}{\nu \hat{D}_1} \beta'_1 \nabla c'_1, \\ Ra_2 &= \frac{gL^4}{\nu \hat{D}_2} \beta'_2 \nabla c'_2. \end{aligned} \quad (27)$$

In Eq. (26) the minus sign applies to γ_1 and the plus sign to γ_2 . Furthermore, to simplify notation, we adopt in Eq. (26) the repeated subscript summation convention,

$$Ra_i \hat{D}_i = Ra_1 \hat{D}_1 + Ra_2 \hat{D}_2, \quad (28)$$

while $Ra_s = Ra_1 + Ra_2$.

It is important to note that the decay rates of the ‘diagonal’ prime concentrations, $\delta c'_i$ are the same as the decay rates of the actual concentrations, δc_i ; since the transformation among them, matrices \underline{U} or \underline{U}_m in Eqs. (12)-(13), does not involve the frequency or wave number of the fluctuations. It is also interesting to note that the decay rates of the fluctuations depend only on the eigenvalues \hat{D}_i and not on the whole diffusion matrix. Further notice that the density gradient associated to the composition gradients results invariant under the concentrations transformation:

$$\frac{\nabla_s \rho}{\rho} = \beta_1 \nabla c_1 + \beta_2 \nabla c_2 = \beta'_1 \nabla c'_1 + \beta'_2 \nabla c'_2, \quad (29)$$

as readily deduced from Eqs. (19) and (20). The quantity $Ra_i \hat{D}_i$ is proportional to this mass density gradient. We shall turn back to these issues in Sect. 4.5, particularly at Eq. (46).

Equation (26) is one of the current main results, it represents the two mass diffusivities for a generic wave vector \mathbf{q} , and includes the effects of buoyancy through the two solutal Rayleigh numbers. For a discussion of its consequences, we note that in most practical situations, like in shadowgraphy or small-angle light-scattering experiments, probed wave vectors are restricted to a plane parallel to the bounding walls, so that the approximation $q_{\parallel} \simeq q$ applies [16,48]. In what follows, we continue our discussion adopting such an assumption.

In this paper we order the diffusion eigenvalues in such a way that $\hat{D}_1 < \hat{D}_2$, hence, in the absence of gravity ($Ra_1 = Ra_2 = 0$), it can be readily verified from Eq. (26) that the two $\gamma_i(q)$ reduce to the two eigenvalues of the diffusion matrix, $\gamma_i = \hat{D}_i$ independent of the wave number, a result already obtained in a previous publication [31]. We note that the same ($\gamma_i = \hat{D}_i$) is true in the limit $q \rightarrow \infty$ even in the presence of buoyancy, as also anticipated in

the same publication [31]. Hence, we associate γ_1 with the slowest concentration mode and γ_2 with the fastest one.

However, in the limit of extremely small wave numbers, $q \rightarrow 0$, the two $\gamma_i(q)$ given by Eq. (26) exhibit qualitatively different behaviors as a function of the wave number. A simple series expansion gives:

$$\begin{aligned} \gamma_1(q) &\xrightarrow{q \rightarrow 0} \frac{\hat{D}_1 \hat{D}_2 Ra_s}{Ra_i \hat{D}_i} + \mathcal{O}(q^4), \\ \gamma_2(q) &\xrightarrow{q \rightarrow 0} -\frac{Ra_i \hat{D}_i}{q^4} + \frac{Ra_i \hat{D}_i^2}{Ra_i \hat{D}_i} + \mathcal{O}(q^4). \end{aligned} \quad (30)$$

Hence, in the $q \rightarrow 0$ limit, the fastest decay rate (the one approaching at $q \rightarrow \infty$ the product of the larger diffusion eigenvalue by q^2) diverges as q^{-2} , as it is the case for the single composition decay rate of a binary mixture [23]. Thus, the fastest decay rate $\Gamma_2(q) = \gamma_2(q) q^2$ exhibits a minimum for a certain q , a feature that (for binary mixtures) has been proposed to measure the Soret effect [33, 34]. However, one important consequence of Eq. (30), is that the slowest decay rate, $\Gamma_1(q) = \gamma_1(q) q^2$, even under the influence of gravity, continues to decrease diffusively proportional to q^2 when $q \rightarrow 0$. Note that this decay rate corresponds to the one identifying, at large q , with the smallest diffusion eigenvalue, $\hat{D}_1 q^2$.

The two different behaviors at small wave numbers implied by Eq. (30) are graphically illustrated in Fig. 1, where the two decay times of cNEFs, *i.e.*, the inverse decay rates $\Gamma_i(q)^{-1} = \gamma_i(q)^{-1} q^{-2}$, are plotted as a function of the wave number \tilde{q} . Data shown in the figure are conveniently normalized by the smaller diffusion eigenvalue, and are intended to represent a small amount of a polymer dissolved in a mixture of two hydrocarbons at 50% weight fraction [40]. In that case, cross diffusion is almost negligible and one can use for estimations the solutal expansions, diffusion and Soret coefficients typical of a binary hydrocarbon mixture (for Ra_2) and of a small amount of polymer in a liquid hydrocarbon (for Ra_1). Combining this information with a temperature gradient of 50 Kcm⁻¹ we obtain the numbers used to plot Fig. 1, namely $\hat{D}_2 = 10\hat{D}_1$, $Ra_1 = -3 \times 10^6$ and $Ra_2 = -3 \times 10^5$. The two qualitatively different asymptotic behaviors of Eq. (30) are evident in Fig. 1, in particular the local maximum in $\Gamma_1(q)$. It is worth mentioning here that preliminary experiments [40] seem to confirm this qualitative different behavior at small q of the two diffusion decay rates of the composition fluctuations in a ternary mixture.

We wish to finalize this section by noting that the conclusion of the two decay rates of cNEFs having different qualitative behaviors at small q must be taken with caution. The experience with binary mixtures [27] shows that

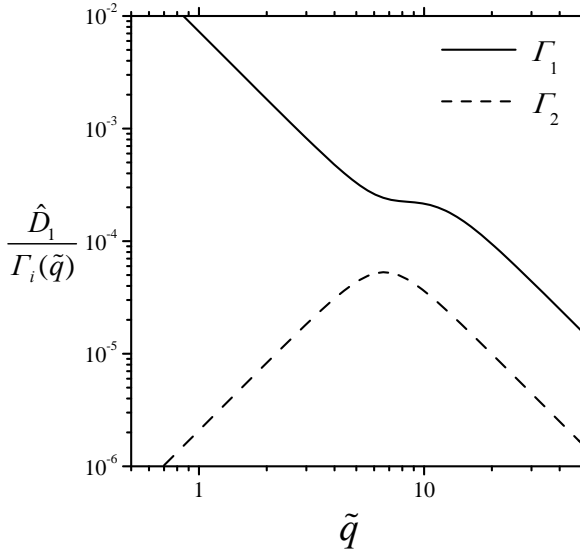


Fig. 1. The two mass diffusion decay times of cNEFs, as given by Eq. (26), normalized by the smaller diffusion eigenvalue, as a function of \tilde{q} the (dimensionless) wave number, $\hat{D}_1 / [\gamma_i(\tilde{q}) \tilde{q}^2] = \hat{D}_1 / \Gamma_i(\tilde{q})$. At large $q \rightarrow \infty$ both decay proportionally to q^{-2} . At small $q \rightarrow 0$ the two qualitatively different asymptotic behaviors of Eq. (26) are evident. Data are calculated for $\hat{D}_2 = 10\hat{D}_1$, $Ra_1 = -3 \times 10^6$ and $Ra_2 = -3 \times 10^5$, which are reasonable numbers (see main text and [40]).

1 confinement effects, neglected in the current publication,
2 may affect the dynamics of the fluctuations at very small
3 wave numbers. One initially expects that, when bound-
4 ary conditions are considered, the two decay rates recover
5 diffusive behavior at $q \rightarrow 0$, although with renormalized
6 diffusion coefficient.

7 4.2 Stability of the quiescent state

8 Equation (26) for the decay rates allows us to perform a
9 study of the stability of the quiescent solution of Sect. 2,
10 about which fluctuations are studied. Indeed, for the qui-
11 escent state to be stable, the real part of the decay rates
12 of fluctuations around it must be positive. Some analysis
13 with Eq. (26) shows that the most dangerous situation
14 (*i.e.*, when the decay rates become lower) is for $q \rightarrow 0$,
15 meaning that within the approximations adopted in this
16 work, the appearance of convection is a long-wavelength
17 instability. It is known that when temperature fluctua-
18 tions are incorporated, and for realistic perfectly conduct-
19 ing walls, the instability can be short-wavelength (at finite
20 q) [42], depending on the parameter values. The fact that
21 we obtain here always a long-wavelength instability is a
22 shortcoming of the large Lewis numbers approximation
23 adopted in this paper, that neglects temperature fluctua-
24 tions, and of not having considered boundary conditions.

25 In any case, within the several approximations adopted
26 in this paper, convection is at $q = 0$ and the key to the
27 stability analysis is given by the small q expansions of

28 Eqs. (30). Consequently, one readily concludes

if $Ra_i \hat{D}_i > 0 \Rightarrow$ always unstable

$$\text{if } Ra_i \hat{D}_i < 0 \Rightarrow \begin{cases} Ra_s > 0, \text{ unstable} \\ Ra_s < 0, \text{ stable.} \end{cases} \quad (31)$$

29 It is also interesting to note that, when the system is sta-
30 ble, the diffusion modes may be propagating, *i.e.*, their
31 imaginary parts may be non-zero. We have found that
32 propagating modes only exists for $Ra_1 < 0$ and posi-
33 tive Ra_2 or, accounting for the stability, for $Ra_1 < 0$ and
34 $-(\hat{D}_1 / \hat{D}_2) Ra_1 > Ra_2 > 0$. Adopting the Cross and Ho-
35 henberg [49] classification of instabilities, under the ap-
36 proximations adopted in this paper, we conclude that the
37 convection transition in a ternary mixture is a station-
38 ary I_s -instability for positive Ra_1 and an oscillatory I_o -
39 instability for negative Ra_1 .

40 As a summary of these findings we represent in Fig. 2
41 a stability diagram for convection in a ternary mixture,
42 where the stable region in the space of solutal Rayleigh
43 numbers is shadowed, while the region where propagating
44 modes do exist is also indicated. As stressed above, all the
45 calculations presented in this paper are only valid when
46 the quiescent state is stable, *i.e.*, inside the shadowed re-
47 gion of Fig. 2.

48 It is worth noticing that the instability condition (31)
49 depends only on the eigenvalues \hat{D}_i , and not on the com-
50 plete diffusion matrix $\underline{\underline{D}}$, which is an expected result. On
51 physical grounds, the appearance of convection should be
52 independent of the frame of reference used to describe dif-
53 fusion and, hence, it is unsurprising that Eq. (31) contains
54 only frame-invariant quantities, such as the eigenvalues of
55 $\underline{\underline{D}}$ [38].

56 We finalize this section by stressing that Fig. 2 and
57 the associated stability conditions are obtained here with-
58 out accounting for boundary conditions in the fluctuat-
59 ing fields (concentrations and vertical velocity). Inclusion
60 of confinement effects is expected to modify the stabil-
61 ity diagram. However, experience with convection in one-
62 component fluids or binary mixtures suggests that consid-
63 eration of boundary conditions leads to an increase of the
64 stability region in plots equivalent to Fig. 2. Hence, we
65 can safely assume that the shadowed region in Fig. 2 rep-
66 resents a *minimum* region of stability. Current literature
67 on convection thresholds in ternary mixtures [43] seems
68 to support this conclusion.

69 4.3 Correlation matrix

70 After having discussed the decay rates of the two con-
71 centration modes, we proceed now with the calculation of
72 the corresponding amplitudes. They will be determined
73 by the product of the matrix $\underline{\underline{M}}'^{-1}(\omega, \mathbf{q})$ by the vector of
74 random forces in Eq. (15). First of all, we note that, as
75 in previous publications [30,31], and in view of Eqs. (21)
76 and (24) for the random forcing terms, the correlation

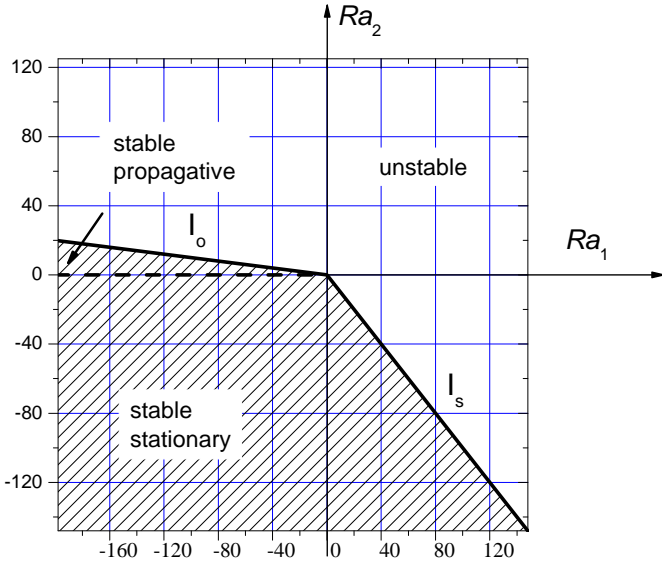


Fig. 2. Stability diagram for convection in a ternary mixture, represented on the basis of Eq. (31) in the plane $\{Ra_1, Ra_2\}$ of solutal Rayleigh numbers. The data are, as in Fig. 1, for $\hat{D}_2 = 10\hat{D}_1$. The convective instability is stationary for positive Ra_1 and oscillatory for negative Ra_1 . Recall that Ra_1 is associated to the slowest concentration mode by Eq. (27). The current diagram corresponds to absence of boundary conditions, its incorporation is expected to modify the limits of the stability regions [43].

functions among fluctuations in the diagonal concentrations are conveniently expressed in terms of a correlation matrix $\underline{\underline{C}}'(\omega, q)$, with components $C'_{nm}(\omega, q)$ defined by [30, 31]:

$$\langle \delta c_n^*(\omega, \mathbf{q}) \delta c_m(\omega', \mathbf{q}') \rangle = C'_{nm}(\omega, q) \times (2\pi)^4 \delta(\omega - \omega') \delta(\mathbf{q} - \mathbf{q}'). \quad (32)$$

Combining the explicit expression of $\underline{\underline{M}}'^{-1}(\omega, \mathbf{q})$ with Eqs. (21) and (24) for the correlation of the random forces, it is relatively straightforward to obtain the complete correlation matrix $\underline{\underline{C}}'(\omega, q)$. As already anticipated, the resulting expression for $\underline{\underline{C}}'(\omega, q)$ can be written as the sum of two lorentzians, meaning that (when Fourier anti-transformed in the frequency ω) the time correlation function will be the sum of two exponential decays¹, with the two decay rates discussed in Sect. 4.1. However, in the most general case, the corresponding amplitudes have a quite long and complicated expression, not easy for physical interpretation. For these reasons we have preferred here to perform one further approximation before proceeding with the calculation of the amplitudes, and we shall only consider the effect of the random force $F_z(\omega, \mathbf{q})$ coming from the random stress tensor, this means to approximate the

RHS of Eq. (15) as

$$\underline{\underline{U}} \cdot \begin{bmatrix} F_z(\omega, \mathbf{q}) \\ F_1(\omega, \mathbf{q}) \\ F_2(\omega, \mathbf{q}) \end{bmatrix} \simeq \begin{bmatrix} F_z(\omega, \mathbf{q}) \\ 0 \\ 0 \end{bmatrix}. \quad (33)$$

As further elucidated below, the random force $F_z(\omega, \mathbf{q})$ gives terms in the amplitudes of cNEFs proportional to the square of the gradients, $(\nabla c'_i)^2$, while the terms associated to the $F'_i(\omega, \mathbf{q})$ are linear in the gradients. In practice, for realistic experimental situations, the contribution of $F'_i(\omega, \mathbf{q})$ associated to the random diffusion fluxes is unobservable, except for situations so close to $\nabla c'_i \simeq 0$ that the correlation matrix $\underline{\underline{C}}'(\omega, q)$ can be actually substituted by its equilibrium value. The same approximation of Eq. (33) was adopted by some of us in a previous publication [31] where gravity effects on cNEFs were not considered. It is also worth noting that a similar situation occurs for cNEFs in binary mixtures [23], where the contribution from the random diffusion flux gives a linear (in the gradient) correction to the quadratic term arising from the random stress tensor. We shall return to this issue later, in Sect. 4.5. In summary, we shall express here the correlation matrix of Eq. (33) as:

$$\underline{\underline{C}}'(\omega, q) = \underline{\underline{C}}'_E(\omega, q) + \underline{\underline{C}}'_{NE}(\omega, q), \quad (34)$$

where, on the one hand, the amplitude of $\underline{\underline{C}}'_E(\omega, q)$ is evaluated at $\nabla T = 0$ and, consequently, with both $\nabla c'_1 = \nabla c'_2 = 0$. On the other hand, the amplitude of $\underline{\underline{C}}'_{NE}(\omega, q)$ will be explicitly presented here under the approximation of Eq. (33), accounting only for the effect of the random stress tensor and neglecting the contribution from the random diffusion fluxes represented by $F'_i(\omega, \mathbf{q})$. The equilibrium matrix is easily calculated and it is diagonal:

$$C'^E_{nm}(\omega, q) = \delta_{nm} \hat{S}_n \frac{2\hat{D}_n q^2}{\omega^2 + \hat{D}_n^2 q^4} \quad (35)$$

as already obtained by Bardow [4, 30]. Since the equilibrium contribution has been already the subject of several publications, we shall not further extend here on it.

Regarding the nonequilibrium contribution in Eq. (34), with the approximation (33) and for the most common case of non-propagating modes, some algebra allows to conveniently display it as the sum of two purely diffusive modes, namely:

$$\underline{\underline{C}}'_{NE}(\omega, q) = \frac{k_B T}{\rho \nu (\hat{D}_1 + \hat{D}_2)} \frac{q_{\parallel}^2}{q^6 \left[1 + \frac{q_{RO}^4 q_{\parallel}^2}{q^6} \right]} \times \left[\underline{\underline{A}}^{(1)} \frac{2\gamma_1 q^2}{\omega^2 + \gamma_1^2 q^4} + \underline{\underline{A}}^{(2)} \frac{2\gamma_2 q^2}{\omega^2 + \gamma_2^2 q^4} \right], \quad (36)$$

where, similar to the case of binary mixtures, we introduce a ‘roll-off’ wave number:

$$q_{RO}^4 = \frac{-Ra_i \hat{D}_i}{L^4 (\hat{D}_1 + \hat{D}_2)} = \frac{-g(\beta_1 \nabla c_1 + \beta_2 \nabla c_2)}{\nu (\hat{D}_1 + \hat{D}_2)}. \quad (37)$$

¹ Or two exponentially damped oscillations in the region of propagative modes

Since we assume to be inside the region where the quiescent solution is stable (see Fig. 2) q_{RO} is indeed a real number. Further note that, to simplify Eq. (37), we have also used that: $\beta_1 \nabla c_1 + \beta_2 \nabla c_2 = \beta'_1 \nabla c'_1 + \beta'_2 \nabla c'_2$, so that q_{RO} can be computed from the real concentrations. The time correlation matrix corresponding to Eq. (36) will thus be expressed as the sum of two exponentials, with the decay rates $\Gamma_i = \gamma_i q^2$ discussed in Sect. 4.1. The amplitude matrices $\underline{\underline{A}}^{(k)}$ of Eq. (36) are proportional to the square of the concentration gradients and depend on the wave number q through $\gamma_i(q)$. Their components are conveniently expressed as:

$$A_{nm}^{(k)}(q) = \frac{(-1)^k \gamma_k}{\gamma_1 - \gamma_2} \nabla c'_n \nabla c'_m - \frac{(-1)^k \hat{D}_1^2 \hat{D}_2^2}{\gamma_k (\gamma_1 - \gamma_2)} \frac{\nabla c'_n \nabla c'_m}{\hat{D}_n \hat{D}_m}, \quad (38)$$

As noted by some of us in the absence of gravity [31], in general, one also obtains a nonzero imaginary part for the cross-correlation in the matrix $\underline{\underline{C}}'_{\text{NE}}(\omega, q)$. As discussed in detail elsewhere [31], such imaginary contribution for the cross correlation is physically unobservable, and we do not report it here.

4.4 Statics

Application of inverse Fourier transforms in the temporal frequencies to Eq. (32) defines an equal-time nonequilibrium correlation matrix, that gives the intensity (statics) of the fluctuations. Namely,

$$\langle \delta c_n^*(\mathbf{q}, t) \delta c_m(\mathbf{q}', t) \rangle_{\text{NE}} = C'_{nm}(q) (2\pi)^3 \delta(\mathbf{q} - \mathbf{q}'). \quad (39)$$

with

$$\underline{\underline{C}}'(q) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \underline{\underline{C}}'(\omega, q) d\omega = \underline{\underline{C}}'(q, t=0)$$

Integration of Eq. (34) allows to express the correlation matrix $\underline{\underline{C}}'(q)$ as the sum of an equilibrium and a non-equilibrium part. For the equilibrium part, making use of Eq. (35), we reproduce the isotropic result of Bardow [4, 30], i.e., $C'_{ij}^{\text{E}} = \delta_{ij} \hat{S}_i$ independent of the wave number.

The new results of this paper refer to the nonequilibrium part and include the effects of gravity. Simple integration of Eq. (36) gives

$$\underline{\underline{C}}'_{\text{NE}}(q) = \frac{k_B T}{\rho \nu (\hat{D}_1 + \hat{D}_2)} \frac{\underline{\underline{A}}(q)}{q^4 + q_{\text{RO}}^4}, \quad (40)$$

where we use the approximation $q_{\parallel} \simeq q$, mandatory for experiments, and the matrix $\underline{\underline{A}}(q) = \underline{\underline{A}}^{(1)}(q) + \underline{\underline{A}}^{(2)}(q)$. In the case of a ternary mixture the amplitude matrix $\underline{\underline{A}}(q)$ depends on the wave number. From Eq. (38), their elements are readily expressed as:

$$\begin{aligned} A_{nm}(q) &= \nabla c'_n \nabla c'_m + \frac{\hat{D}_1^2 \hat{D}_2^2}{\gamma_1 \gamma_2} \frac{\nabla c'_n \nabla c'_m}{\hat{D}_n \hat{D}_m}, \\ &= \nabla c'_n \nabla c'_m + \frac{\hat{D}_1 \hat{D}_2}{\hat{D}_n \hat{D}_m} \frac{\tilde{q}^4 \nabla c'_n \nabla c'_m}{\tilde{q}^4 - Ra_s}, \end{aligned} \quad (41)$$

with the wave vector dependence explicitly shown in the second line. As it was the case for the decay rates investigated in Sect. 4.1, Eqs. (40) and (41) for the amplitude of cNEFs will be used for vectors \mathbf{q} parallel to the bounding plates, in which case $q_{\parallel} \simeq q$. In that case the matrix $\underline{\underline{C}}'_{\text{NE}}(q)$ is isotropic and depends only on the wave number q . Some simple analysis shows that, essentially, $\underline{\underline{C}}'_{\text{NE}}(q)$ as a function of q displays a crossover from a $\propto q^{-4}$ dependence at large q to a constant limit at $q \rightarrow 0$. Indeed, some straightforward series expansions show that:

$$C'_{nm}{}^{\text{NE}}(q) \xrightarrow{q \rightarrow \infty} \frac{k_B T}{\rho \nu} \frac{\left[1 + \frac{\hat{D}_1 \hat{D}_2}{\hat{D}_n \hat{D}_m} \right] \nabla c'_n \nabla c'_m}{(\hat{D}_1 + \hat{D}_2) q^4}, \quad (42)$$

while

$$C'_{nm}{}^{\text{NE}}(q) \xrightarrow{q \rightarrow 0} \frac{k_B T}{\rho \nu} \frac{\nabla c'_n \nabla c'_m}{(\hat{D}_1 + \hat{D}_2) q_{\text{RO}}^4} \quad (43)$$

independent of q . Equation (42) does not depend on gravity g , and it reproduces exactly for the amplitude of cNEFs the results of a previous publication [31] where gravity was not considered². Equation (43) shows that buoyancy has a damping effect on the intensity of cNEFs. Indeed, the typical q^{-4} dependence of cNEFs given by Eq. (42) crosses over as $q \rightarrow 0$ to the constant limit of Eq. (43), quite similar to the behavior of binary mixtures. One difference though is the presence of the wave-number-dependent part in the amplitude $\underline{\underline{A}}(q)$ as given by Eq. (41), while in binary mixture the equivalent amplitude is wave number independent. Its effect amounts to a change of a global prefactor from unity to $1 + (\hat{D}_1 \hat{D}_2 / \hat{D}_n \hat{D}_m)$ at wave numbers around $\simeq (-Ra_s)^{(1/4)}$. Furthermore, depending on other parameter values (particularly if the two Rayleigh numbers are quite different) it may appear a local maximum in the correlation functions around this same wave number. We left for Sect. 5 further comments about Eq. (43), that is one of the main new results of the present publication.

4.5 Further considerations

Before concluding, we wish to add a couple of comments. First is about the approximation of Eq. (33) that, for simplicity, neglected the contribution of the random diffusion fluxes to the amplitude of cNEFs. We have also performed the full calculation, retaining all the terms in the random force of Eq. (33). The results are quite involved and not easily expressed as compact expressions, like those in Sect. 4.3 where only the contribution of the random stress is considered. Anyway, to give a quantitative idea of the approximation involved in Eq. (33), we quote here the expression replacing Eq. (42) in the limit of large q when all random forces are considered, namely

$$C'_{11}{}^{\text{NE}}(q) \simeq \frac{k_B T}{\rho \nu q^4} \left[\frac{(\nabla c'_1)^2}{\hat{D}_1} + \hat{S}_1 \frac{g \beta'_1 \nabla c'_1}{\hat{D}_1} \right], \quad (44)$$

² Note that there is a misprint in Eq. (20) of ref. [31], and the mass density ρ appearing in the numerator should be in the denominator, as it is obvious from dimensional considerations

1 and similar to the other components. One observes that 2 the effect of the random diffusive fluxes, when gravity 3 is present, is to add a contribution to the amplitude of 4 cNEFs that is linear in the gradients, while the contribu- 5 tion of the random stress is quadratic in the gradients. As 6 already anticipated, for real experimental conditions [32] 7 the effect of random diffusion fluxes is unobservable.

8 Throughout this Section the correlation matrix be- 9 tween composition fluctuations has been expressed in terms 10 of ‘diagonal’ concentrations δc_i . For the benefit of the 11 reader, we finalize now by explicitly quoting the transfor- 12 mation to fluctuations in real concentrations, that is quite 13 direct since the transformation matrix $\underline{\underline{U}}_m$ of 14 Eq. (18) does not involve either frequency ω or wave vector 15 \mathbf{q} . Hence, for fluctuations δc_i , as a consequence of Eq. (32), 16 one can define a correlation matrix without primes

$$\langle \delta c_n^*(\omega, \mathbf{q}) \delta c_m(\omega', \mathbf{q}') \rangle = C_{nm}(\omega, q) \times (2\pi)^4 \delta(\omega - \omega') \delta(\mathbf{q} - \mathbf{q}'). \quad (45)$$

17 such that

$$\underline{\underline{C}}'(\omega, q) = \underline{\underline{U}}_m \cdot \underline{\underline{C}}(\omega, q) \cdot (\underline{\underline{U}}_m)^\top. \quad (46)$$

18 It is worth noting that the decay rates and amplitudes for 19 the fluctuations in the ‘diagonal’ concentrations used in 20 this paper depend only on the eigenvalues \hat{D}_i and, hence, 21 not in all the components of the diffusion matrix. However, 22 Eq. (46) shows that when converting to real concentra- 23 tions one has to use the matrix $\underline{\underline{U}}_m$, and hence, one needs 24 to know the complete diffusion matrix $\underline{\underline{D}}$, as it is clear from 25 the definition (18) of the transformation matrix. In opti- 26 cal experiments one actually measures fluctuations of the 27 refractive index, which are related to fluctuations in con- 28 centrations through the corresponding matrix of contrast 29 factors [32]. Contrast factors can only be measured for real 30 concentrations, but can be converted to ‘diagonal’ concen- 31 trations by an algebra similar to Eq. (46). Again, for this 32 conversion it is required the knowledge of the whole diffu- 33 sion matrix $\underline{\underline{D}}$.

Authors researching on convection in ternary mixtures [41–43], instead of the two solutal Rayleigh numbers Ra_n of Eq. (27), use a single Rayleigh number Ra and two ‘diagonal’ separation ratios ψ'_n , defined by:

$$Ra = -\frac{gL^4\alpha \nabla T}{\nu a_T}, \quad (47)$$

$$\psi'_n = -\frac{\beta'_n \nabla c'_n}{\alpha \nabla T} \quad (48)$$

34 where a_T and α are the thermal diffusivity and the ther- 35 mal expansion coefficient of the mixture, respectively. Sep- 36 aration ratios in real concentrations ψ_n , defined like in 37 Eq. (48) but without the primes, are also sometimes used. 38 Also, the so-called net separation ratio $\Psi = \psi'_1 + \psi'_2 =$ 39 $\psi_1 + \psi_2$, is utilized. From Eq. (29) follows that Ψ is invari- 40 ant under the transformation to diagonal concentrations. 41 Note that, from Eq. (3), the separation ratios ψ_i can be

42 expressed as a combination of the diffusion matrix $\underline{\underline{D}}$ and 43 the thermal diffusion coefficients D_{Ti} .

In this work we neglect temperature fluctuations, while 45 researchers in convection typically do not [41–43]. This is 46 the reason why these other investigators [41–43] need three 47 dimensionless parameter to define the problem, while here 48 two is enough. It is easy to obtain the relation between the 49 solutal Rayleigh numbers used here and the parameters 50 used elsewhere, namely

$$Ra_n = Le_n Ra \psi'_n, \quad (49)$$

51 where $Le_n = a_T/\hat{D}_n$ are the two Lewis numbers of the 52 ternary mixture. Since the theory presented in this work 53 is developed under the approximation of very large Lewis 54 numbers, the present results will be valid only for large 55 (absolute) values of Ra_n inside the stability zone of Fig. 2.

56 5 Conclusions

57 In this paper we have analyzed, on the basis of fluctuat- 58 ing hydrodynamics, the spatiotemporal spectrum of com- 59 position fluctuations in a ternary mixture that is driven 60 out of equilibrium by the imposition of an external steady 61 temperature gradient. As is well-know, in these condi- 62 tions steady concentrations gradients appear in the system 63 due to the Soret effect. To simplify the problem we have 64 adopted a series of approximations, adequate for liquid 65 mixtures and for the experimental conditions under which 66 these NE fluctuations are observed. Following Bardow [4] 67 we found advantageous to use as independent variables 68 the linear combination of concentrations diagonalizing the 69 diffusion matrix, as further explained in Sect. 3.1.

70 Our final result is Eq. (36) showing that the composi- 71 tion autocorrelation matrix can be expressed as the sum 72 of two diffusion modes with decay rates $\Gamma_i(q) = \gamma_i(q) q^2$ 73 given by Eq. (26), the first main result of this work. For 74 fluctuations of large wave number q , these modes are purely 75 diffusive and the associated diffusivities can be identified 76 with the two eigenvalues $\gamma_i = \hat{D}_i$ of the diffusion matrix, 77 independent of the fluctuation wave number, as earlier 78 discussed in a previous publication [31]. However, as a 79 consequence of buoyancy, there is a mixing between these 80 two modes for fluctuations of larger size, as described by 81 Eq. (26). This mixing of modes may even lead to the ap- 82 pearance of *propagating* modes, as further discussed in 83 Sect. 4.2. It is interesting to note the different behavior at 84 $q \rightarrow 0$ of the two modes, discussed in detail in Sect. 4.1.

85 The amplitudes of the two modes in Eq. (36) is given 86 by Eq. (38), while the total amplitude of equal-time fluc- 87 tuations is given Eq. (40). The calculation of these ampli- 88 tudes, which represents a second main result of the present 89 paper, has been done from the random stress only. In- 90 deed, in Sect. 4.5 it is discussed that this contribution is 91 dominant over the contribution from the random diffusion 92 flows.

93 Our present calculations are of high relevance for shad- 94 owgraph experiments in ternary mixtures currently un- 95 der development, whose preliminary results are already

available [32], including a contribution in this same Topical Issue [40]. It will also undoubtedly contribute to the current DCMIX [50] and SCCO [35] and the upcoming NEUF-DIX [51] space experiments, whose goals are a better understanding of diffusion and thermal diffusion in multi-component liquid mixtures, starting from ternaries. In addition, the results presented here also contribute to the effort of better understanding the appearance of convection in ternary mixtures that is presently under development [43].

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Appendix A. The particular case $\hat{D}_1 = \hat{D}_2$

In the main text of this article it was assumed everywhere that the two eigenvalues of the diffusion matrix are different. Next, we consider the particular case $\hat{D}_1 = \hat{D}_2 = \hat{D}$, so that the diffusion matrix cannot be diagonalized so that this case is not covered by the theoretical developments in the paper. This situation might be of relevance when two decay rates cannot be distinguished experimentally [32]. If the two eigenvalues of the diffusion matrix are equal, then $\underline{\underline{D}}$ is most conveniently expressed as:

$$\underline{\underline{D}} = \begin{bmatrix} \hat{D} - \sqrt{-D_{12}D_{21}} & D_{21} \\ D_{12} & \hat{D} + \sqrt{-D_{12}D_{21}} \end{bmatrix}, \quad (\text{A.1})$$

where we ordered the components in such a way that $D_{11} < D_{22}$ and, since $\underline{\underline{D}}$ still is a diffusion matrix, one must have in this case that $D_{12}D_{21} < 0$. Since now one cannot perform the transformation to diagonal concentrations of Sect. 3.1, to solve for the fluctuating concentrations one has to invert directly the linear response matrix $\underline{\underline{M}}(\omega, \mathbf{q})$ of Eq. (11), before transformation to $\underline{\underline{M}}'(\omega, \mathbf{q})$. However, the calculation is not more complicated than the one with diagonal concentrations, because Eq. (A.1) can now be used to simplify the expressions. For instance, due to the mixing of modes caused by gravity, there are still two different decay times $\Gamma_i(\mathbf{q}) = \gamma_i(\mathbf{q}) q^2$ that depend on the fluctuations wave vector. Some algebra leads to:

$$\gamma_{1,2}(\mathbf{q}) = \hat{D} \left(1 + \frac{q_{\text{RO}}^4 q_{\parallel}^2}{q^6} \right) \left[1 \mp \sqrt{1 + \frac{\tilde{U}}{q_{\text{RO}}^4 q_{\parallel}^2}} \right], \quad (\text{A.2})$$

where q_{RO} here is still given by Eq. (37) that, for the case of equal eigenvalues, simplifies to:

$$q_{\text{RO}}^4 = \frac{-g(\beta_1 \nabla c_1 + \beta_2 \nabla c_2)}{2\nu \hat{D}}. \quad (\text{A.3})$$

Dimensionless parameter \tilde{U} in Eq. (A.2) is given by:

$$\tilde{U} = \frac{-g \left[(\beta_2 D_{21} - \beta_1 \sqrt{-D_{12}D_{21}}) \nabla c_1 + (\beta_1 D_{12} - \beta_2 \sqrt{-D_{12}D_{21}}) \nabla c_2 \right]}{\nu \hat{D}^2 q_{\text{RO}}^4} \quad (\text{A.4})$$

Similar to the case of two distinct eigenvalues, examined in the main text, one can observe from Eq. (A.2) that in the limit of large wave number ($q^6 \gg q_{\text{RO}}^4 q_{\parallel}^2$) the two mass diffusivities $\gamma_i(q)$ converge to \hat{D} , independent of q . However, in the limit of small q , one of the decay times is diffusive $\propto q^{-2}$ while the other presents an acceleration due to buoyancy. Also, a study of the stability of the quiescent solution can be performed. In this case of equal eigenvalues, stability means q_{RO} to be real (as was for distinct eigenvalues) and $2 - \tilde{U} > 0$.

Following equivalent steps to those in the main text, the correlation matrix of concentration fluctuations can also be computed for this particular case of equal eigenvalues. Here, we shall only present the results for the statics, equivalent to those of Sect. 4.4, and under the approximation of Eq. (33) that amounts to evaluate only the nonequilibrium part. Since in the case of equal eigenvalues the concentrations cannot be diagonalized, the only correlation matrix discussed here is that defined by Eq. (45) in terms of real concentrations. Some algebra allows to express it as:

$$\underline{\underline{C}}_{\text{NE}}(q) = \frac{k_B T}{2\rho\nu \hat{D}} \frac{\underline{\underline{A}}(q)}{q^4 + q_{\text{RO}}^4}, \quad (\text{A.5})$$

where, again, we adopt the approximation $q_{\parallel} \simeq q$. The amplitude matrix $\underline{\underline{A}}(q)$ in the case of a ternary mixture with equal eigenvalues continues to depend on the wave number. Its elements can be expressed in this case as:

$$A_{nm}(q) = \nabla c_n \nabla c_m + \frac{q^4 \nabla c'_n \nabla c'_m}{q^4 - (2 - \tilde{U}) q_{\text{RO}}^4}, \quad (\text{A.6})$$

where here primes are used to simplify notation, as:

$$\begin{aligned} \nabla c'_1 &= \frac{D_{22}}{\hat{D}} \nabla c_1 - \frac{D_{12}}{\hat{D}} \nabla c_2 \\ \nabla c'_2 &= -\frac{D_{21}}{\hat{D}} \nabla c_1 + \frac{D_{11}}{\hat{D}} \nabla c_2 \end{aligned} \quad (\text{A.7})$$

The structure of the correlation matrix, Eqs. (A.5)-(A.7), is similar to the case of distinct eigenvalues analyzed in Sect. 4.4. The main difference being that, since the two density gradients $\beta_1 \nabla c_1$ and $\beta_2 \nabla c_2$ are expected to be of the same order of magnitude, the local maximum mentioned after Eq. (43) seldom appears.

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