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Non-equilibrium Fluctuations in a Ternary Mixture Subjected to a Temperature Gradient

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Abstract
We present the complete theory for the decay rates of non-equilibrium fluctuations in a ternary liquid mixture subjected to a stationary temperature gradient, when the quiescent non-convective state is stable. In the most general case, within Boussinesq approximation, four fluctuating modes exist. Depending on the parameter values, propagative modes may be present, and we discuss numerically some cases where that is so. We complete the work with a discussion of symmetry upon changes in concentration representation, as well as examination of some limiting cases with practical relevance for which analytical progress is possible. We make contact with previous publications, which were based on some kind of approximation.

Keywords Fluctuating Hydrodynamics · Non-equilibrium fluctuations · Ternary systems · Stochastic processes · Onsager regression hypothesis

1 Introduction

The intensity of fluctuations in liquids in non-equilibrium (NE) states, like when subjected to a temperature gradient, can be orders of magnitude larger than around the equivalent equilibrium state at the average temperature [1,2]. This is physically due to a coupling between the temperature fluctuations and the velocity fluctuations parallel to the gradi-

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ent, the latter mixing regions with different local temperature [1,3]. This NE-enhancement of fluctuations was originally predicted on the basis of kinetic theory [4], and later confirmed by fluctuating hydrodynamics [5]. These theoretical predictions were soon verified by dynamic light-scattering experiments in one-component liquids [6], i.e., through the analysis of temperature fluctuations; and, later, also in binary liquid mixtures. In mixtures, a NE-enhancement of concentration fluctuations is due to the presence of a concentration gradient, as it exists in transient free-diffusion processes [7], or as induced by thermodiffusion [8,9]. When external forces like gravity (buoyancy) are present, the existence of gradients (NE conditions) not only affects the intensity of fluctuations, but also their dynamics. Again, this has been first discussed in one-component liquids [10] and later in binary mixtures, both theoretically [11] and experimentally [7,12]. On this regard, the dynamic analysis of the NE fluctuations has been proposed as a novel experimental technique for the simultaneous measurement of diffusion and thermodiffusion coefficients in liquid mixtures [13,14].

The natural continuation of all these studies on NE fluctuations in one-component liquids and binary mixtures is to consider the case of a ternary liquid mixture, which is the topic of the present work. The theoretical study of hydrodynamic fluctuations in ternary liquid mixtures considered first equilibrium states (homogeneous temperature, concentrations and pressure), which has been the topic of various investigations over the years. A first analysis was presented by Lekkerkerker and Laidlaw [15] who considered the most general case of a compressible fluid in which fluctuations in five independent variables, i.e., velocity, temperature, two concentrations and pressure, are coupled. This pioneering study was focused on the dynamics of the fluctuations. Later, van der Elsken and Bot [16] considered not only the decay times, but also the intensity of fluctuations in multicomponent mixtures in equilibrium, deriving an expression for the ratio of the Rayleigh and Brillouin components of the scattering spectrum. More recently, Ivanov and Winkelmann [17] re-derived the expressions of Lekkerkerker and Laidlaw [15] 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, among the equilibrium studies, we mention Bardow [18] 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 [19], to simplify the calculation of the convection threshold in binary fluids. The equilibrium results of Bardow [18] were later reproduced on the basis of Fluctuating hydrodynamics [20] and experimentally confirmed by Heller et al. with dynamic light scattering [21].

The first attempt to evaluate the NE spectrum of thermodynamic fluctuations when a ternary mixture layer is subjected to a stationary temperature gradient, so that a composition gradient is induced by thermodiffusion, considered the case of no external forces (microgravity) [22]. This case is simpler because the dynamics of NE fluctuations in microgravity is the same as the dynamics of the equilibrium ones. Also, microgravity results [22] turn to be more useful than initially appears since, as explicitly shown for binary mixtures [23,24], they also apply to ground conditions in the asymptotic limit of fluctuations of very small lateral size, i.e., with wave number $q \to \infty$. Actually, these [22] first theoretical results at $q \to \infty$ have been used to analyze laboratory experiments with some success [25,26]. In a subsequent investigation [27], buoyancy effects were considered, as required to understand ground experiments at intermediate q. However, to simplify the working equations, this research [27] adopted a large Lewis number, Le, approximation, which is equivalent to assume that temperature fluctuations decay so fast, as compared to concentration fluctuations, that their coupling can be neglected. This large Le approach is normally adequate for liquid mixtures and has been widely used in the literature [18,19,28]. However, as recently demonstrated for binary mixtures [29], neglecting temperature fluctuations one cannot correctly describe the dynamics of sufficiently large fluctuations (small q) where propagative modes (oscillating time correlation functions) do appear. Hence, for a fully understanding of the dynamics of NE fluctuations in a ternary mixture it is required to extend the theory currently available [22,27] to finite Lewis numbers $Le \neq \infty$. This is the main purpose of this work. It should be mentioned that, very recently, a preliminary presentation of the theory to be developed here has appeared [12] but that publication was mostly experimental and centered in the existence of propagative modes also in ternary mixtures. Hence, we shall present here the complete theory that was preliminarily sketched elsewhere [12], giving all the details and completing the discussion.

We shall proceed by first presenting in Sect. 2 the hydrodynamic theory on which is based the evaluation of the decay rates of NE fluctuations in a ternary mixture where a composition gradient is induced by the Soret effect. It is evident that the mathematical expression of the decay rates cannot depend on the representation chosen for the composition, whether mass fraction, mole fraction or other possibilities. This important symmetry property is thoroughly discussed in Sect. 3. The decay rates of fluctuations are presented as the roots of a fourth-order polynomial. Although analytical formulas exist for them, they are so clumsy that it results more practical a numerical evaluation in some representative cases, that is the purpose of Sect. 4. Although in the most general case only a numerical evaluation is feasible, further analytical progress is possible by considering some limits with practical relevance, as presented in Sect. 5. We finalize by summarizing and presenting some concluding remarks in Sect. 6.

2 Hydrodynamic Theory

We consider a layer of a ternary liquid mixture subjected to a stationary temperature gradient in the same direction as gravity. We adopt a system of reference where gravity is in the negative z-axis. The liquid layer is bounded by two horizontal planes, perpendicular to the direction of gravity and parallel to the xy-direction, located at $z = \pm L/2$, where L is the vertical thickness of the layer. A temperature difference ΔT is maintained between these bounding planes, so that the stationary temperature gradient is $\nabla T = \Delta T/L$. Because of Soret effect (thermodiffusion) [30,31] the imposition of an external temperature gradient causes concentration gradients to develop in the ternary fluid mixture. After some transient, if the system is convection-free,[1] steady concentration gradients appear in the system, ∇w_i if mass fractions w_i are used to represent concentrations or ∇x_i if mole fractions x_i are used to represent the composition. Thermodiffusion in ternary liquid mixtures can be quantified either by two frame-dependent [32] thermodiffusion coefficients, $D^{\mathrm{w}}_{T,i}$ if mass fractions w_i are used to represent concentrations or $D^{\mathrm{x}}_{T,i}$ if mole fractions x_i are used to represent the composition; or by a pair of frame-independent [33] thermodiffusion coefficients $D_{T,i}$. Then, the relationship between the stationary temperature and composition gradients is given by:

$$\begin{bmatrix} \nabla w_1 \\ \nabla w_2 \end{bmatrix} = \left[\mathsf{D}^{\mathrm{w}}\right]^{-1} \cdot \begin{bmatrix} D^{\mathrm{w}}_{T,1} \\ D^{\mathrm{w}}_{T,2} \end{bmatrix} \nabla T = \left[\mathsf{D}^{\mathrm{w}}\right]^{-1} \cdot \mathsf{W} \cdot \begin{bmatrix} D_{T,1} \\ D_{T,2} \end{bmatrix} \nabla T \tag{1}$$

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[1] We always assume in this paper that the system is convection-free.

or

$$\begin{bmatrix}\nabla x_1\\ \nabla x_2\end{bmatrix} = \left[\mathsf{D}^{\mathrm{x}}\right]^{-1}\cdot\begin{bmatrix}D^{\mathrm{x}}_{T,1}\\ D^{\mathrm{x}}_{T,2}\end{bmatrix}\nabla T = \left[\mathsf{D}^{\mathrm{x}}\right]^{-1}\cdot\mathsf{X}\cdot\begin{bmatrix}D_{T,1}\\ D_{T,2}\end{bmatrix}\nabla T \tag{2}$$

where D^{w} is the diffusion matrix in the mass frame of reference (barycentric) and D^{x} the diffusion matrix in the mole frame of reference [34], while the concentration matrices are [33]:

$$\mathsf{X} = \begin{bmatrix}x_1(1-x_1) & -x_1x_2\\ -x_1x_2 & x_2(1-x_2)\end{bmatrix}, \qquad \mathsf{W} = \begin{bmatrix}w_1(1-w_1) & -w_1w_2\\ -w_1w_2 & w_2(1-w_2)\end{bmatrix}. \tag{3}$$

In the context of the present paper, the x_i and w_i in Eq. (3) are to be understood as the average values through the liquid layer. It is important to distinguish between properties that depend on the concentration representation adopted, whether mole or mass fractions, so that superscripts 'x' or 'w' (in upright roman typeface) will be introduced when required. Later on, we will also introduce a third concentration representation, namely, the mass fractions making diagonal the matrix D^{w}, properties pertaining to this third composition representation will be denoted by primes. Quantities that are independent of the concentration representation will be denoted without any superscript.

The stability of the quiescent solution to the hydrodynamics, as given by Eqs. (1)–(2), has been thoughtfully studied in the context of Rayleigh–Bénard convection in ternary mixtures [35–37]. We are not giving here further details, but simply mention that the quiescent solution is indeed stable in an ample parameter range, in particular for negative Rayleigh numbers (heating from above) and positive net separation ratio [37]. The focus of our work is on hydrodynamic NE fluctuations around the quiescent solution. Fluctuations which, eventually, will decay and vanish, as long as the quiescent state is stable. In particular, we are interested in the decay rate of these NE fluctuations as experimentally observable by the dynamic shadowgraph technique [29]. According to the Onsager' regression hypothesis [38], hydrodynamic fluctuations decay by the same hydrodynamic equations as macroscopic perturbations. Although this hypothesis was originally formulated for fluctuations around thermodynamic equilibrium states, progress in recent decades [1] has shown that Onsager regression hypothesis can be extended to fluctuations around non-equilibrium steady states. Hence, for our present purpose, the working equations for the spatiotemporal evolution of NE fluctuations are exactly the same used in the linear stability studies [35–37] (onset of convection) of the quiescent solution. In general, there will be velocity fluctuations $\delta\mathbf{v}(\mathbf{r},t)$, temperature fluctuations $\delta T(\mathbf{r},t)$ and two independent concentrations which, for the time being, we specify in mass fractions $\delta w_1(\mathbf{r},t)$ and $\delta w_2(\mathbf{r},t)$. As discussed in the relevant literature [35–37], in general, the spatio-temporal evolution of all these independent fluctuations will be coupled. However, in the configuration we consider here, by applying a double rotational to the Navier–Stokes equation only the velocity component parallel to the gradient (and to gravity) couples with the other fluctuation fields. As a summary of all previous considerations, the temporal evolution of these NE fluctuation fields is described, in the most general case by:

$$\partial_t(\nabla^2\delta v_z) = \nu\nabla^2(\nabla^2\delta v_z) + g(\partial_x^2+\partial_y^2)[\alpha\,\delta T - \beta_1^{\mathrm{w}}\,\delta w_1 - \beta_2^{\mathrm{w}}\,\delta w_2], \tag{4a}$$

$$\partial_t\,\delta T + \nabla T\,\delta v_z = a\,\nabla^2\delta T, \tag{4b}$$

$$\partial_t\,\delta w_1 + \nabla w_1\,\delta v_z = D^{\mathrm{w}}_{11}\nabla^2\delta w_1 + D^{\mathrm{w}}_{12}\nabla^2\delta w_2 + D^{\mathrm{w}}_{T,1}\,\nabla^2\delta T, \tag{4c}$$

$$\partial_t\,\delta w_2 + \nabla w_2\,\delta v_z = D^{\mathrm{w}}_{21}\nabla^2\delta w_1 + D^{\mathrm{w}}_{22}\nabla^2\delta w_2 + D^{\mathrm{w}}_{T,2}\,\nabla^2\delta T, \tag{4d}$$

where, as explained above, Eq. (4a) is obtained by applying a double rotational to Navier–Stokes equation. Here ν represents the kinematic viscosity of the mixture, α the thermal expansion coefficient and β_i^{w} the solutal expansion coefficients defined for concentrations in mass fraction:

$$\beta_1^{\mathrm{w}} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial w_1}\right)_{T,p,w_2}, \qquad \beta_2^{\mathrm{w}} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial w_2}\right)_{T,p,w_1}, \tag{5}$$

with ρ the mass density of the fluid mixture. Note in Eq. (4) the use of Boussinesq approximation, i.e., all thermodynamic properties are assumed as constants (independent of temperature or concentrations), except for the density in the buoyancy term of the Navier–Stokes equation (4a). As a consequence [39], the dependence of density ρ on pressure is ignored. Flow motions $\delta\mathbf{v}$ are limited to velocities much lower than the speed of sound in the liquid and, hence, incompressibility $\nabla \cdot \delta\mathbf{v}$ implicitly applies in addition to Eq. (4). Equation (4b) is the heat equation with a representing the thermal diffusivity of the mixture, note that Dufour effect has been discharged, since it is only relevant for gas mixtures [40]. Expressions (4c)–(4d) are the two independent equations representing mass balance in a ternary mixture, here D_{ij}^{w} are the four components of the diffusion matrix D^{w} in the barycentric frame of reference [34] and $D_{T,i}^{\mathrm{w}}$ the thermodiffusion coefficients in the same frame of reference which, since the concentration gradients are induced by thermodiffusion, also appeared in Eq. (1). In Eq. (4) composition of the mixture is expressed in mass fractions δw_i. Of course, any measurable quantity, like the decay rates of the fluctuations, cannot depend on whether composition is represented in mass or mole fractions, we shall return to this point later in Sect. 3.

One difference between studies on fluctuations and on linear stability (convection) lies on the boundary conditions. Generically, convection thresholds depend critically on the boundary conditions adopted for the disturbance fields. It is also true that boundary conditions (confinement effects) not only affect the intensity, but also the decay rate of the fluctuations, as experimentally and theoretically analyzed elsewhere for binary mixtures [41,42]. However, these confinement effects only manifest for fluctuations of a very large size, $qL \simeq 5.11$ for binary mixtures [41,42], where q is the (lateral) spatial wave number of the fluctuation. In typical dynamic shadowgraph experiments, there is a minimum detectable wave number, $q_{\min}$, which is determined by the size of the detector [29]. That means confinement effects will only be observable for thin layers, of the order $L \simeq 5.11/q_{\min}$, which for experiments without magnification translates into a few mm. Hence, from a practical point of view, and for layers of a thickness above 5 mm, one can completely disregard confinement effects (boundary conditions) on the decay rate of the fluctuations [29]. In that case, to solve Eq. (4), one can apply a 3D spatial Fourier transform to the evolution of the fluctuations, obtaining in matrix form:

$$\partial_t \begin{bmatrix} \delta v_z \\ \delta T \\ \delta w_1 \\ \delta w_2 \end{bmatrix} = - \begin{bmatrix} \nu q^2 & -g\alpha\, q_\parallel^2/q^2 & g\beta_1^{\mathrm{w}} q_\parallel^2/q^2 & g\beta_2^{\mathrm{w}} q_\parallel^2/q^2 \\ \nabla T & a q^2 & 0 & 0 \\ \nabla w_1 & D_{T,1}^{\mathrm{w}} q^2 & D_{11}^{\mathrm{w}} q^2 & D_{12}^{\mathrm{w}} q^2 \\ \nabla w_2 & D_{T,2}^{\mathrm{w}} q^2 & D_{21}^{\mathrm{w}} q^2 & D_{22}^{\mathrm{w}} q^2 \end{bmatrix} \begin{bmatrix} \delta v_z \\ \delta T \\ \delta w_1 \\ \delta w_2 \end{bmatrix} \tag{6}$$

where $q_\parallel^2 = q_x^2 + q_y^2$ is the component of the fluctuations wave vector in the horizontal plane. Physical optics theory of shadowgraphy [43] shows that experimental signals are obtained upon integration of the fluctuating fields over the height of the layer. Since in the shadowgrah experiments considered here, the height of the layer is several times $1/q_{\min}$, integration in real space over z from $-L/2$ to $L/2$ is approximatively equal to take $q_\perp \simeq 0$ in Fourier space [1,44]. Hence, following previous works and for the rest of this paper the approximation $q_\parallel \cong q$ applies. Next, as shown elsewhere [18,27,36,37] the working equations simplify by performing a (linear) change of variables in the concentration representation, so as to diagonalize the diffusion matrix. After such change to diagonal (primed) concentrations, we obtain:

$$\partial_t \begin{bmatrix} \delta v_z \\ \delta T \\ \delta w'_1 \\ \delta w'_2 \end{bmatrix} = - \begin{bmatrix} \nu q^2 & -\alpha g & \beta_1^{\mathrm{w}\prime} g & \beta_2^{\mathrm{w}\prime} g \\ \nabla T & a q^2 & 0 & 0 \\ \nabla w'_1 & D_{T,1}^{\mathrm{w}\prime} q^2 & \hat{D}_1 q^2 & 0 \\ \nabla w'_2 & D_{T,2}^{\mathrm{w}\prime} q^2 & 0 & \hat{D}_2 q^2 \end{bmatrix} \begin{bmatrix} \delta v_z \\ \delta T \\ \delta w'_1 \\ \delta w'_2 \end{bmatrix}, \tag{7}$$

where $\hat{D}_i$ are the eigenvalues of the diffusion matrix, which are invariant in the mass and in the mole frames of reference [34]. The relation between variables with and without prime is expressed by the transformation matrix [18,27]:

$$\mathsf{U} = \begin{bmatrix} 1 & \dfrac{D_{22}^{\mathrm{w}} - \hat{D}_2}{D_{21}^{\mathrm{w}}} \\ \dfrac{D_{11}^{\mathrm{w}} - \hat{D}_1}{D_{12}^{\mathrm{w}}} & 1 \end{bmatrix}. \tag{8}$$

Then, we have:

$$\mathsf{U}^{\mathsf{T}} \cdot \begin{bmatrix} \beta_1^{\mathrm{w}\prime} \\ \beta_2^{\mathrm{w}\prime} \end{bmatrix} = \begin{bmatrix} \beta_1^{\mathrm{w}} \\ \beta_2^{\mathrm{w}} \end{bmatrix}, \qquad \begin{bmatrix} \nabla w'_1 \\ \nabla w'_2 \end{bmatrix} = \mathsf{U} \cdot \begin{bmatrix} \nabla w_1 \\ \nabla w_2 \end{bmatrix}, \tag{9a}$$

$$\begin{bmatrix} D_{T,1}^{\mathrm{w}\prime} \\ D_{T,2}^{\mathrm{w}\prime} \end{bmatrix} = \mathsf{U} \cdot \begin{bmatrix} D_{T,1}^{\mathrm{w}} \\ D_{T,2}^{\mathrm{w}} \end{bmatrix}, \qquad \mathsf{U}^{-1} \cdot \begin{bmatrix} D_{11}^{\mathrm{w}} & D_{12}^{\mathrm{w}} \\ D_{21}^{\mathrm{w}} & D_{22}^{\mathrm{w}} \end{bmatrix} \cdot \mathsf{U} = \begin{bmatrix} \hat{D}_1 & 0 \\ 0 & \hat{D}_2 \end{bmatrix}. \tag{9b}$$

Next, we switch to dimensionless variables, we adopt L as unit of length and $L^2/\hat{D}_1$ as unit of time, where $\hat{D}_1$ is the smaller (slower) eigenvalue; while α and $\beta_i^{\mathrm{w}\prime}$ are used to make dimensionless temperature and (diagonal) concentration fluctuations. Hence, dimesionless variables are:

$$\tilde{q} = qL, \quad \delta\tilde{v}_z = \frac{L}{\hat{D}_1}\delta v_z, \quad \delta\tilde{T} = \alpha \frac{gL^3}{\hat{D}_1^2}\,\delta T,$$
$$\delta\tilde{w}'_1 = \beta'_1 \frac{gL^3}{\hat{D}_1^2}\,\delta w'_1, \quad \delta\tilde{w}'_2 = \beta'_2 \frac{gL^3}{\hat{D}_1^2}\,\delta w'_2, \tag{10}$$

where the dimensionless number $gL^3/\hat{D}_1^2$ is used to further simplify the resulting equations. Notice that here we adopt as unit of time $\hat{D}_1$, while other authors [37] prefer to use the kinematic viscosity, ν. In the new dimensionless (tilde) variables above, Eq. (7) reads

$$\partial_{\tilde{t}} \begin{bmatrix} \delta\tilde{v}_z \\ \delta\tilde{T} \\ \delta\tilde{w}'_1 \\ \delta\tilde{w}'_2 \end{bmatrix} = - \begin{bmatrix} \dfrac{\nu\tilde{q}^2}{\hat{D}_1} & -1 & 1 & 1 \\ \alpha g L^4 \dfrac{\nabla T}{\hat{D}_1^2} & \dfrac{a}{\hat{D}_1}\tilde{q}^2 & 0 & 0 \\ \beta'_1 g L^4 \dfrac{\nabla w'_1}{\hat{D}_1^2} & \dfrac{\beta'_1}{\alpha\hat{D}_1} D_{T,1}^{\mathrm{w}\prime}\,\tilde{q}^2 & \tilde{q}^2 & 0 \\ \beta'_2 g L^4 \dfrac{\nabla w'_2}{\hat{D}_1^2} & \dfrac{\beta'_2}{\alpha\hat{D}_1} D_{T,2}^{\mathrm{w}\prime}\,\tilde{q}^2 & 0 & \dfrac{\hat{D}_2}{\hat{D}_1}\tilde{q}^2 \end{bmatrix} \begin{bmatrix} \delta\tilde{v}_z \\ \delta\tilde{T} \\ \delta\tilde{w}'_1 \\ \delta\tilde{w}'_2 \end{bmatrix}. \tag{11}$$

Next, we introduce the Lewis (Le), Prandtl (Pr), diffusion eigenvalue ratio (Dr) and Rayleigh (Ra) dimensionless numbers, namely [45]:

$$Le = \frac{a}{\hat{D}_1}, \quad Pr = \frac{\nu}{a}, \quad Dr = \frac{\hat{D}_2}{\hat{D}_1}, \quad Ra = -\alpha g L^4 \frac{\nabla T}{\nu a}. \tag{12}$$

Notice that here we define a single Lewis number for a ternary mixture, using the smaller eigenvalue of the diffusion matrix (in consistency with the adopted dimensionless time). Other authors [37] have used various Lewis numbers for ternary mixtures, defined according to the different components of the diffusion matrix. In addition to the dimensionless quantities of Eq. (12), for the diagonal concentrations, one can define separation ratios in the barycentric frame of reference as:

$$\psi_i^{\mathrm{w}'} = \frac{\beta_i^{\mathrm{w}'}}{\alpha \hat{D}_i} D_{T,i}^{\mathrm{w}'}. \tag{13}$$

The steady concentration gradients are induced by thermodiffusion, hence, in diagonal concentrations one has:

$$\nabla w_i' = -\frac{D_{T,i}^{\mathrm{w}'}}{\hat{D}_i} \nabla T, \tag{14}$$

which can be also obtained by switching Eq. (1) to diagonal concentrations with the transformation matrix U of Eq. (8). Substitution of Eqs. (12)–(14) into Eq. (11) finally gives:

$$\partial_{\tilde{t}} \begin{bmatrix} \delta\tilde{v}_z \\ \delta\tilde{T} \\ \delta\tilde{w}_1' \\ \delta\tilde{w}_2' \end{bmatrix} = - \begin{bmatrix} Le Pr\, \tilde{q}^2 & -1 & 1 & 1 \\ -Pr Le^2 Ra & Le\, \tilde{q}^2 & 0 & 0 \\ Pr Le^2 Ra\, \psi_1^{\mathrm{w}'} & \psi_1^{\mathrm{w}'} \tilde{q}^2 & \tilde{q}^2 & 0 \\ Pr Le^2 Ra\, \psi_2^{\mathrm{w}'} & Dr \psi_2^{\mathrm{w}'} \tilde{q}^2 & 0 & Dr\, \tilde{q}^2 \end{bmatrix} \begin{bmatrix} \delta\tilde{v}_z \\ \delta\tilde{T} \\ \delta\tilde{w}_1' \\ \delta\tilde{w}_2' \end{bmatrix}. \tag{15}$$

Starting here, all following development are in the dimensionless variables defined by Eq. (10), so that since there is no possible confusion and for lighten notation, we shall drop from here on the tildes from the corresponding variables. Equation (15) shows that, in general, the temporal evolution of fluctuations with wave number q will be given as the sum of four exponentials, or four modes. The corresponding four (dimensionless) decay rates, $\Gamma_i(q)$ will be the eigenvalues of the matrix:

$$\mathsf{M}(q) = \begin{bmatrix} Le Pr\, q^2 & -1 & 1 & 1 \\ -Pr Le^2 Ra & Le\, q^2 & 0 & 0 \\ Pr Le^2 Ra\, \psi_1^{\mathrm{w}'} & \psi_1^{\mathrm{w}'} q^2 & q^2 & 0 \\ Pr Le^2 Ra\, \psi_2^{\mathrm{w}'} & Dr \psi_2^{\mathrm{w}'} q^2 & 0 & Dr\, q^2 \end{bmatrix}. \tag{16}$$

Hence, the four $\Gamma_i(q)$ are the roots of the algebraic equation:

$$\det\left[\mathsf{M}(q) - \Gamma(q)\, \mathsf{1}\right] = 0, \tag{17}$$

which turns out to be a polynomial of the 4th degree in Γ with real coefficients. Note from Eq. (15) that, as long as the real part of the four roots of Eq. (17) is positive, any fluctuations around the quiescent state of Eq. (1) will eventually decay to zero. Of course, this is exactly the same condition as for (linear) stability of the quiescent state against convection [35–37]. However, a direct comparison is not possible because we are not considering here boundary conditions. All developments in this paper are valid only when the real part of the four roots Γ_i of Eq. (17) is positive.

Equation (17), with $\mathsf{M}(q)$ given by Eq. (16), represents the main result of this paper. In what follows, we shall discuss its solutions Γ_i, as a function of q. First, in Sect. 4, by numerically solving Eq. (17) for different values of the five mixture parameters: Dr, Le, Pr, $\psi_1^{\mathrm{w}'}$, $\psi_2^{\mathrm{w}'}$ and Ra. Later, in Sect. 5 in some particular cases where further analytical progress is possible. But before that, we first discuss the issue of the invariance of $\Gamma_i(q)$ upon concentration representation, an important theme of the present work.

3 Symmetry in the Concentration Representation

Although, initially, decay rates $\Gamma_i(q)$ can be obtained by solving Eqs. (16) and (17), it turns out that further simplification is still possible by an additional change of variables in the concentration representation. Indeed, if instead of using variables $\delta w_1'$ and $\delta w_2'$, one uses $\delta w_1' + \delta w_2'$ and $Dr\ \delta w_1' + \delta w_2'$, to obtain the decay rates of the fluctuations one needs to compute the eigenvalues of the matrix:

$$\mathsf{M}'(q) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & Dr & 1 \end{bmatrix} \cdot \mathsf{M}(q) \cdot \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & Dr & 1 \end{bmatrix}^{-1} \tag{18}$$

or

$$\mathsf{M}'(q) = \begin{bmatrix} LePr\, q^2 & -1 & 1 & 0 \\ -PrLe^2Ra & Le\, q^2 & 0 & 0 \\ PrLe^2Ra\psi & [(Dr+1)\psi - \hat{\psi}]q^2 & (Dr+1)q^2 & -q^2 \\ PrLe^2Ra\hat{\psi} & Dr\psi\, q^2 & Dr\, q^2 & 0 \end{bmatrix}, \tag{19}$$

which has the same number of zeros as the original matrix $\mathsf{M}(q)$. The advantage of Eq. (19) is to show that decay rates $\Gamma_i(q)$ do actually depend only on two concentration-dependent parameters, namely the net separation ratio $\psi = \psi_1^{\mathrm{w}'} + \psi_2^{\mathrm{w}'}$ [37] and the combination $\hat{\psi} = Dr\psi_1^{\mathrm{w}'} + \psi_2^{\mathrm{w}'}$, which are invariant when changing from real to diagonal concentrations. Indeed, using Eq. (9) and after some algebra it may be shown that [27]:

$$\begin{aligned} \psi \equiv \psi_1^{\mathrm{w}'} + \psi_2^{\mathrm{w}'} &= \frac{1}{\alpha}\left[\beta_1^{\mathrm{w}'}\ \beta_2^{\mathrm{w}'}\right] \begin{bmatrix} \hat{D}_1 & 0 \\ 0 & \hat{D}_2 \end{bmatrix}^{-1} \begin{bmatrix} D_{T,1}^{\mathrm{w}'} \\ D_{T,2}^{\mathrm{w}'} \end{bmatrix} \\ &= \frac{1}{\alpha}\left[\beta_1^{\mathrm{w}}\ \beta_2^{\mathrm{w}}\right] \begin{bmatrix} D_{11}^{\mathrm{w}} & D_{12}^{\mathrm{w}} \\ D_{21}^{\mathrm{w}} & D_{22}^{\mathrm{w}} \end{bmatrix}^{-1} \begin{bmatrix} D_{T,1}^{\mathrm{w}} \\ D_{T,2}^{\mathrm{w}} \end{bmatrix} = \frac{1}{\alpha}\left[(\boldsymbol{\beta}^{\mathrm{w}})^{\mathsf{T}} \cdot [\mathsf{D}^{\mathrm{w}}]^{-1} \cdot \mathbf{D}_T^{\mathrm{w}}\right] = \psi, \end{aligned} \tag{20}$$

so that the net separation ratio is a quantity invariant upon change between concentrations with and without primes. Similarly, the quantity $(Dr\psi_1^{\mathrm{w}'} + \psi_2^{\mathrm{w}'})$ is also invariant upon change to diagonal concentrations, since:

$$\begin{aligned} Dr\psi_1^{\mathrm{w}'} + \psi_2^{\mathrm{w}'} &= \frac{\hat{D}_2}{\alpha}\left[\frac{\beta_1^{\mathrm{w}'} D_{T,1}^{\mathrm{w}'}}{\hat{D}_1^2} + \frac{\beta_2^{\mathrm{w}'} D_{T,2}^{\mathrm{w}'}}{\hat{D}_2^2}\right] = \frac{\hat{D}_2}{\alpha}\left[\beta_1^{\mathrm{w}'}\ \beta_2^{\mathrm{w}'}\right] \begin{bmatrix} \hat{D}_1 & 0 \\ 0 & \hat{D}_2 \end{bmatrix}^{-2} \begin{bmatrix} D_{T,1}^{\mathrm{w}'} \\ D_{T,2}^{\mathrm{w}'} \end{bmatrix} \\ &= \frac{\hat{D}_2}{\alpha}\left[\beta_1^{\mathrm{w}}\ \beta_2^{\mathrm{w}}\right] \begin{bmatrix} D_{11}^{\mathrm{w}} & D_{12}^{\mathrm{w}} \\ D_{21}^{\mathrm{w}} & D_{22}^{\mathrm{w}} \end{bmatrix}^{-2} \begin{bmatrix} D_{T,1}^{\mathrm{w}} \\ D_{T,2}^{\mathrm{w}} \end{bmatrix} \\ &= \frac{\hat{D}_2}{\alpha}\left[(\boldsymbol{\beta}^{\mathrm{w}})^{\mathsf{T}} \cdot [\mathsf{D}^{\mathrm{w}}]^{-2} \cdot \mathbf{D}_T^{\mathrm{w}}\right] \equiv \hat{\psi}. \end{aligned} \tag{21}$$

As already anticipated, this property is expected, i.e., the expression of physically measurable quantities (the decay times) cannot depend on whether normal or diagonal concentrations are used in the theory. The $\Gamma_i(q)$ should only depend on quantities that are invariant upon change in the concentration representation. Hence, evaluation of the eigenvalues of the matrix in Eq. (19) stresses that decay times do only depend on parameters invariant upon switching between real or diagonal concentrations.

In this paper we are using thermodiffusion coefficients and corresponding separation ratios in the barycentric frame of reference. It is interesting to represent the two parameters, net separation ratio ψ and $\hat{\psi}$, in terms of the frame-invariant thermodiffusion coefficients introduced in Ref. [33] and reviewed at the beginning of Sect. 2, around Eq. (1). For that purpose, we first note that the concentration matrices defined by Eq. (3) can be used to change derivatives with respect to mass fraction to derivatives with respect to mole fraction [33], then the relation between solutal expansion coefficients in the two frames of reference is:

$$\boldsymbol{\beta}^{\mathrm{x}} = \mathsf{X}^{-1} \cdot \mathsf{W} \cdot \boldsymbol{\beta}^{\mathrm{w}}. \tag{22}$$

In addition, from Eq. (1) we have that the frame-invariant thermodiffusion coefficients are given by:

$$\mathbf{D}_T = \mathsf{X}^{-1} \cdot \mathbf{D}_T^{\mathrm{x}} = \mathsf{W}^{-1} \cdot \mathbf{D}_T^{\mathrm{w}}. \tag{23}$$

Hence, the net separation ratio ψ of Eq. (20) can be expressed as:

$$\begin{aligned}
\alpha\psi &= \left\{(\boldsymbol{\beta}^{\mathrm{w}})^{\mathsf{T}} \cdot [\mathsf{D}^{\mathrm{w}}]^{-1} \cdot \mathbf{D}_T^{\mathrm{w}}\right\} = \left\{(\boldsymbol{\beta}^{\mathrm{w}})^{\mathsf{T}} \cdot [\mathsf{D}^{\mathrm{w}}]^{-1} \cdot \mathsf{W} \cdot \mathbf{D}_T\right\} \\
&= \left\{(\boldsymbol{\beta}^{\mathrm{x}})^{\mathsf{T}} \cdot \mathsf{X} \cdot \mathsf{W}^{-1} \cdot [\mathsf{D}^{\mathrm{w}}]^{-1} \cdot \mathsf{W} \cdot \mathsf{X}^{-1} \cdot \mathsf{X} \cdot \mathbf{D}_T\right\} = \left\{(\boldsymbol{\beta}^{\mathrm{x}})^{\mathsf{T}} \cdot [\mathsf{D}^{\mathrm{x}}]^{-1} \cdot \mathsf{X} \cdot \mathbf{D}_T\right\} \\
&= \left\{(\boldsymbol{\beta}^{\mathrm{x}})^{\mathsf{T}} \cdot [\mathsf{D}^{\mathrm{x}}]^{-1} \cdot \mathbf{D}_T^{\mathrm{x}}\right\}
\end{aligned} \tag{24}$$

where use has been made of Eq. (20) in Ref. [33] for the relationship between Fick diffusion matrices in the mass and mole frame of reference and the fact that both X and W are symmetric matrices. Hence, according to Eq. (24), we conclude that the net separation ratio ψ is invariant not only when switching between real and diagonal concentrations, but also when switching from concentrations in mass fraction to concentrations in mole fraction. Although we are not giving here the details, a calculation similar to that displayed in Eq. (24) shows that the same happens for $\hat{\psi}$. Of course, these are expected results: The final theoretical expression for physically measurable quantities, like the decay rates of fluctuations, must be independent of whether, in the development of the theory, the composition of the mixtures is expressed in mass or mole fraction.

4 Numerical Evaluation of the Decay Rates of Non-equilibrium Fluctuations

As demonstrated in Sect. 2 the (dimensionless) decay rates are obtained by evaluating the roots, $\Gamma_i(q)$, of Eq. (17). Although an analytical solution is in principle possible, the formulas for the roots of a quartic polynomial are so unwieldy that in practice is preferable to discuss $\Gamma_i(q)$ numerically in some representative cases. That is the purpose of this section.

We start by noting that in the limit of large wave number, $q \to \infty$, simple inspection of the matrix $\mathsf{M}(q)$ of Eq. (16) shows that the four decay rates of the fluctuations will be:

$$\Gamma_1 = q^2, \quad \Gamma_2 = Dr\, q^2, \quad \Gamma_3 = Le\, q^2, \quad \Gamma_4 = LePr\, q^2, \tag{25}$$

in increasing order, since the parameters Dr, Le and Pr are generically larger than 1 for a ternary liquid mixture. Note that, in this limit, the four decay rates are real and positive. Hence, the quiescent solution is stable against fluctuations of very small size (with $q \to \infty$). The modes with large-q decay rates equal to q^2 and $Dr\ q^2$ are the two concentration modes (slow and fast) of a ternary mixture (the particular case $Dr = 1$ will be discussed in Sect. 5.3). The third mode of Eq. (25), with decay rate $Le\ q^2$ corresponds to temperature fluctuations and the fourth one, with decay rate $LePr\ q^2$ to viscous (wall-normal velocity) fluctuations. Since refractive index depends on temperature and concentrations, but not on fluid velocity, this fourth mode is not directly observable optically.

For decreasing values of q, a numerical investigation of Eq. (17) shows that the decay rates $\Gamma_i(q)$ progressively deviate from the asymptotic values of Eq. (25). In particular for positive ψ and negative Ra and small enough q, see Sect. 5.1, two of the roots of Eq. (17) form a pair of complex conjugate numbers with positive real part. This means that fluctuations, before decaying eventually to zero, exhibit oscillatory behavior. It is customary to refer to this situation as propagating, or propagative, hydrodynamic modes [10,46–48]. For typical values of the parameters of a ternary mixture the two modes that mix to become propagative are the ones corresponding to temperature fluctuations and viscous fluctuations. One example of this situation is shown in the left panel of Fig. 1, where the inverse real part of the four $\Gamma_i(q)$ (the so-called decay times, $\tau_i(q)$) and the imaginary part are plotted as a function of

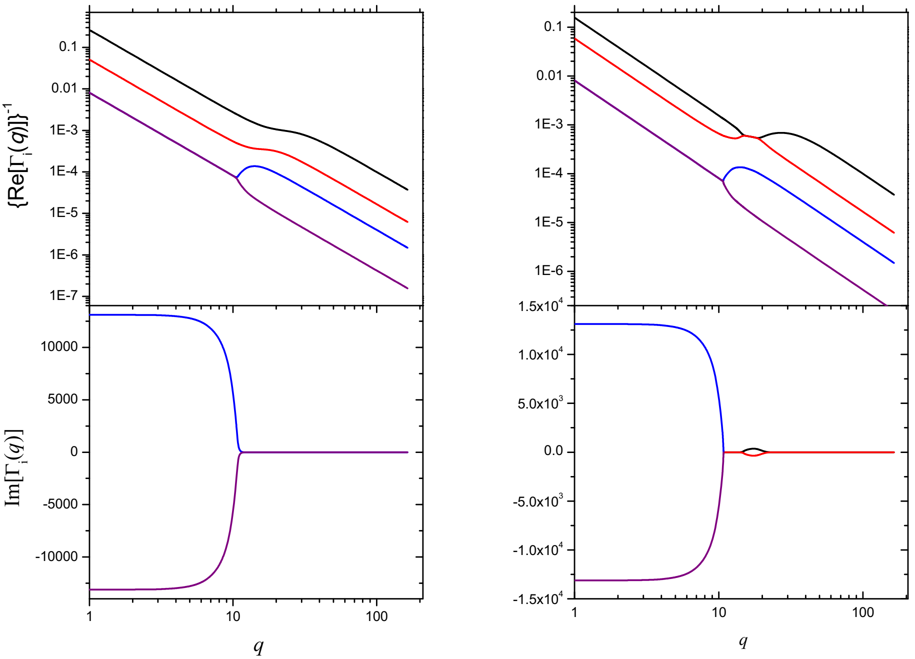

Fig. 1 (Color online) Left panel: Inverse real part of the dimensionless decay rates (i.e., dimensionless decay times, at top) and imaginary part of the dimensionless decay rates (i.e., oscillatory frequency, at bottom) of the four decay modes of fluctuations in a ternary mixture subjected to a stationary temperature gradient, as a function of the dimensionless q. Mixture parameters are: $Le = 25$, $Pr = 9.5$, $Dr = 6.0$, $\psi_1^{w\prime} = 1.2$ and $\psi_2^{w\prime} = 0.7$ and the Rayleigh number $Ra = -10^4$. Right panel: Same as in left panel, but for parameters $\psi_1^{w\prime} = 2.0$ and $\psi_2^{w\prime} = -0.1$, note in this case the appearance of two zones of propagative modes, one due to the mixing of the two concentration modes

q. The plot in left panel of Fig. 1 is for a mixture with $Le = 25$, $Pr = 9.5$, $Dr = 6.0$, $\psi_1^{\mathrm{w}\prime} = 1.2$ and $\psi_2^{\mathrm{w}\prime} = 0.7$ and a Rayleigh number $Ra = -10^4$, which roughly correspond to a low molecular weight polymer dissolved in a mix solvent [12]. We found numerically that, when the two separation ratios $\psi_i^{\mathrm{w}\prime}$ are positive, the behavior of $\Gamma_i(q)$ is qualitatively similar to that shown in the left panel of Fig. 1. This situation has been recently observed experimentally [12].

However, in some cases the $\Gamma_i(q)$ scenario is a bit different and somewhat more complicated. We have found numerically that when the separation ratio $\psi_2^{\mathrm{w}\prime}$ corresponding to the fastest concentration mode is negative, the two concentration modes may mix to become a propagative pair for a 'window' of intermediate wave numbers. An example of this situation is shown in the right panel of Fig. 1, which contains the same information as the left panel of Fig. 1, but for a mixture with $\psi_1^{\mathrm{w}\prime} = 2.0$ and $\psi_2^{\mathrm{w}\prime} = -0.1$. Note that the net separation ratio ψ is the same for the two mixtures represented in right and left panels of Fig. 1. Notice in the right panel of Fig. 1 the mixing, at intermediate values of q, of the two concentration modes to become a propagative pair. This mixing only occurs in a finite range of wave numbers, while at smaller q the regular situation (see Sect. 5.1) of mixing between the temperature and the viscous modes is recovered. To our knowledge, this situation of intermediate mixing of the two concentration modes has not been observed experimentally yet.

We finalize this section by the following consideration: Fitting experimental decay rates for a ternary mixture to the numerical solution of Eq. (17), in addition to Le, Pr and Ra, provides two diffusion eigenvalues, $\hat{D}_1$ and $\hat{D}_2$, and two separation ratios, let's say the two invariants ψ and $\hat{\psi}$. Actually, a preliminary study in this direction has been recently published [12]. However, with only these four parameters one cannot reconstruct the whole diffusion matrix and the two thermodiffusion coefficients in an arbitrary reference frame, which amounts to six independent coefficients. Namely, one cannot invert Eqs. (20)–(21) for ψ and $\hat{\psi}$, plus the two equations for the eigenvalues $\hat{D}_i$, to obtain the four D_{ij}^{w} and the two $D_{T,i}^{\mathrm{w}}$. There are four equations for six unknowns. We conclude that dynamic shadowgraph alone cannot give a complete characterization of diffusion and thermodiffusion in a ternary mixture, opposite to the case of a binary mixture where a complete characterization by shadowgraphy is possible [12,13]. However, the two frame-independent separation ratios, ψ and $\hat{\psi}$, can indeed be obtained from monochromatic dynamic shadowgraph in a ternary mixture. Since, as elucidated in Sect. 3, these two parameters are the most relevant for the description of thermodiffusion in ternary mixtures, the utility of the dynamic shadowgraph technique is clear.

5 Analytical Evaluation of the Decay Rates in Different Limits

As discussed in the previous section, in the most general case, only a numerical evaluation of the decay rates is feasible. However, further analytical progress in the solution of Eq. (17) for the decay rates $\Gamma_i(q)$ is still possible by considering specific limits with practical relevance. This is the purpose of the present section. In Sect. 5.1 we consider the case of fluctuations with large lateral size (small q). Next, in Sect. 5.2 the case of large Lewis number, where we also make contact with previous works [27]. Finally, in Sect. 5.3 we deal with the particular cases $Dr = 1$ and $Dr = 0$, which turn out to be relevant in some practical circumstances.

5.1 Decay Rates for Small *q*

We consider first the case of small values of q, where it is possible to obtain analytically the first terms of the power expansions of $\Gamma_i(q)$. For that, one substitutes into Eq. (17):

$$\Gamma(q) = \Gamma_0 + \Gamma_1 q^2 + \Gamma_2 q^4 + \cdots , \tag{26}$$

expands in powers of q^2 the resulting expression, and cancels term by term. By this procedure, we have calculated up to order q^2 the four roots of Eq. (17). For the stable conditions of $\psi > 0$ and $Ra < 0$ [35–37] we obtain:

$$\begin{aligned} \Gamma_1(q) = 0 + \frac{1}{2}\left[Dr + 1 + \frac{\psi\, Le}{1+\psi}\right] \\ \times \left\{1 - \sqrt{1 - \frac{4(1+\psi)[Dr(1+\psi) + \hat{\psi} Le]}{[(Dr+1)(1+\psi) + \psi\, Le]^2}}\right\} q^2 + \mathcal{O}(q^4) \end{aligned} \tag{27}$$

$$\begin{aligned} \Gamma_2(q) = 0 + \frac{1}{2}\left[Dr + 1 + \frac{\psi\, Le}{1+\psi}\right] \\ \times \left\{1 + \sqrt{1 - \frac{4(1+\psi)[Dr(1+\psi) + \hat{\psi} Le]}{[(Dr+1)(1+\psi) + \psi\, Le]^2}}\right\} q^2 + \mathcal{O}(q^4) \end{aligned} \tag{28}$$

$$\Gamma_3(q) = +\mathrm{i}Le\sqrt{-(1+\psi)Pr\,Ra} + \frac{1 + Pr(1+\psi)}{2(1+\psi)} Le\, q^2 + \mathcal{O}(q^4) \tag{29}$$

$$\Gamma_4(q) = -\mathrm{i}Le\sqrt{-(1+\psi)Pr\,Ra} + \frac{1 + Pr(1+\psi)}{2(1+\psi)} Le\, q^2 + \mathcal{O}(q^4) \tag{30}$$

We observe that the real part of the four decay rates at small q displays a diffusive behavior, i.e., they are proportional to q^2 physically meaning that the larger (spatially) a fluctuation is, the more slowly it decays. This can be also observed in the top panels of Fig. 1 where the decay times (inverse of the real part of the decay rates) were plotted in a double logarithmic scale. Equations (29)–(30) give a simple analytical expression for the oscillation frequency of large fluctuations (small q) which reaches a limiting value independent of their size, as also clearly observed in the bottom panels of Fig. 1. Equations (29)–(30) also show that, for small q, the temperature and the viscous mode always mix to form a propagative pair.

Note that Eqs. (27)–(30) represent the mathematical limit at $q \to 0$ of the solutions to Eq. (17), hence, they are physically valid as long as Eq. (17) is valid itself. In particular, small q in this context means large (spatial) fluctuations, but not too large for confinement effects to become relevant, see discussion before Eq. (6) in Sect. 2. To describe the dynamics of extremely large fluctuations, boundary conditions need to be implemented in the theory, and deviations with respect to Eqs. (27)–(30) are expected.

5.2 Large Lewis Number Limit

Liquid mixtures typically display large values of the Lewis, Le, and the Prandtl, Pr, numbers. This fact has been used in the past [27] to develop a simplified theory that only pertains to the decay rates of the two concentration modes. Of course, the results of Ref. [27] can also be obtained as a limiting case of the more complete theory presented here. In particular, one can look perturbatively for large-Le solutions $\Gamma_i(q)$ to Eq. (17) by expressing the roots $\Gamma_i(q)$

as a series in powers of Le^{-1}, namely

$$\Gamma(q) = Le\ \left\{\Gamma_0(q) + \Gamma_1(q)Le^{-1} + \Gamma_2(q)\ Le^{-2} + \cdots\right\}. \tag{31}$$

In addition, it should be noted that the results of Ref. [27] were expressed in terms of the net solutal Rayleigh number, $Ra_\mathrm{s} = RaLe\psi$ (see Sect. 5.3), instead of the thermal Rayleigh number Ra adopted here. That means previous approximations [27] are equivalent to take the $Le \to \infty$ of the complete theory as presented in this paper, everywhere except in the $RaLe$ combination. Then, substituting into Eq. (17), $\Gamma(q)$ by Eq. (31) and the product $RaLe$ by Ra_s/ψ, with Ra_s the net *solutal* Rayleigh number[2] and expanding the resulting expression in powers of Le^{-1}, to cancel the leading $\mathcal{O}(Le^{-4})$ term one obtains four solutions

$$\Gamma_0(q) = \begin{bmatrix} q^2 \\ Pr\ q^2 \\ 0 \\ 0 \end{bmatrix}. \tag{32}$$

The solution at $Le \to \infty$ of the temperature and viscous mode are the same as the asymptotic expressions of Eq. (25). The two solutions with $\Gamma_0(q) = 0$ in Eq. (32) correspond to the two concentration modes. To obtain the first non-vanishing term in the large-Le expansion of these two modes one needs to cancel the $\mathcal{O}(Le^{-3})$ in the power series expansion of Eq. (17), arriving readily at:

$$\Gamma_1(q) = \frac{q^2}{2}\left(Dr + 1 - \frac{Ra_\mathrm{s}}{q^4}\right)\left[1 \mp \sqrt{1 - \frac{4Dr\left(1 - \dfrac{\hat{\psi}Ra_\mathrm{s}}{Dr\,\psi q^4}\right)}{\left(Dr + 1 - \dfrac{Ra_\mathrm{s}}{q^4}\right)^2}}\right], \tag{33}$$

which is exactly the same as Eq. (26) of Ref. [27]. To compare both expressions it should be reminded that here we are using dimensionless decay rates with $L^2/\hat{D}_1$ as unit of time, and that in Ref. [27], actually two solutal Rayleigh numbers, Ra_1 and Ra_2, were used, whose equivalence with the parameters preferred here is:

$$\begin{aligned} \hat{D}_i Ra_i &= \hat{D}_1 Ra_1 + \hat{D}_2 Ra_2 = \hat{D}_1 Le\psi\ Ra = \hat{D}_1 Ra_\mathrm{s}, \\ Ra_1 + Ra_2 &= \frac{Le\hat{\psi}}{Dr}\ Ra = \frac{\hat{\psi}Ra_\mathrm{s}}{Dr\,\psi}. \end{aligned} \tag{34}$$

In conclusion, we find consistency between the full theory of hydrodynamic fluctuations in a ternary liquid subjected to a steady temperature gradient, as presented here, and previous approximations based in the large Lewis number approach [27]. It is preferable to apply approximations first, in order to simplify the set of hydrodynamic equations, instead of working out the solution to the complete set hydrodynamic equations and apply the approximation at the final result. The simpler route (approximations first) was the one adopted in Ref. [27], while here we have demonstrated the equivalence of the two approaches and made contact with the previous results.

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[2] The solutal Rayleigh number is, initially, defined for a binary mixture. Here we extend the concept to a ternary mixture by substituting the single separation ratio of a binary with the net separation ratio.

5.3 The Particular Cases of $Dr = 1$ and $Dr = 0$

In shadowgraph experiments with some ternary mixtures it is difficult to separate experimentally the two independent concentration modes [25,26]. Hence, it is convenient from a practical point of view to provide expressions for the decay rates in the limit $Dr \to 1$, or $\hat{D}_1 = \hat{D}_2$. Note that $Dr = 1$ also means that $\psi = \hat{\psi}$ and, as a consequence, $\Gamma_1 = q^2$ is an exact solution of Eq. (17) for the eigenvalues of the matrix $\mathsf{M}(q)$, namely:

$$\det\left[\mathsf{M}(q) - \Gamma\ \mathbb{1}\right] = (\Gamma - q^2)\{\Gamma^3 - [Le(Pr+1)+1]q^2\Gamma^2 + A_1(q)\, q^4\Gamma + A_0(q)\} \tag{35}$$

with

$$\begin{aligned} A_1(q) &= PrLe^2 + (Pr+1)Le - (\psi+1)RaPr\frac{Le^2}{q^4}, \\ A_0(q) &= PrLe^2 - (\psi Le + \psi + 1)RaPr\frac{Le^2}{q^4}. \end{aligned} \tag{36}$$

Comparing with the complete theory for binary mixtures [29], one finds that the third-degree polynomial in the right-hand side of Eq. (35) here is exactly the same as Eq. (7) of Ref. [29]. Hence, in addition to $\Gamma_1 = q^2$, the other three decay rates of a ternary mixture with $Dr = 1$ will be identical to those of a binary mixture with the same parameter values (Le, Pr, ψ, Ra). In other words, the other three decay rates correspond to an hypothetical binary mixture with diffusion coefficient $D = \hat{D}_1 = \hat{D}_2$. Hence, we refer to the relevant literature [29] for a deeper discussion of the other three decay rates. For illustration purpose we show here, in Fig. 2, a representative case, for parameter values $Le = 25$, $Pr = 9.5$, $\psi = \hat{\psi} = 1.50$ and the Rayleigh number $Ra = -10^4$. We observe in Fig. 2 that, except for $\Gamma_1 = q^2$, the decay rate scenario corresponds to that of the left panel of Fig. 1, that is, for large fluctuation size (small q) a mixing of the temperature and viscous mode appears, giving a pair of complex

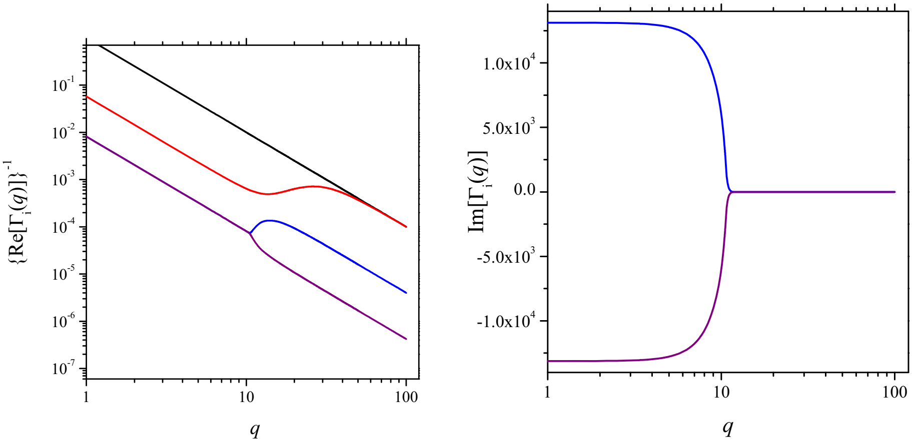

Fig. 2 (Color online) Left: Inverse real part of the dimensionless decay rates (i.e., dimensionless decay times) of the four decay modes of fluctuations in a ternary mixture with $Dr = 1$ and subjected to a stationary temperature gradient, as a function of the dimensionless q. Note that $\Gamma_1 = q^2$ (black line) is an exact solution. Right: Imaginary part of the dimensionless decay rates (i.e., oscillatory frequency) as a function of the dimensionless q. Other Mixture parameters are: $Le = 25$, $Pr = 9.5$, $\psi = \hat{\psi} = 1.90$ and the Rayleigh number $Ra = -10^4$

conjugate Γ-roots to Eq. (35) and, thus, the presence of propagative modes. For the case of actual binary mixtures, this scenario has been experimentally verified [29]. Of course, for this particular case of $Dr = 1$, the small-q behavior of the decay rates can also be obtained by simply taking $Dr = 1$ in Eqs. (27)–(30), with the result:

$$\Gamma_1(q) = 0 + q^2 \tag{37}$$

$$\Gamma_2(q) = 0 + \left[1 + \frac{\psi\, Le}{1+\psi}\right] q^2 + \mathcal{O}(q^4) \tag{38}$$

$$\Gamma_3(q) = +\mathrm{i}Le\sqrt{-(1+\psi)Pr\,Ra} + \frac{1+Pr(1+\psi)}{2(1+\psi)}Le\, q^2 + \mathcal{O}(q^4), \tag{39}$$

$$\Gamma_4(q) = -\mathrm{i}Le\sqrt{-(1+\psi)Pr\,Ra} + \frac{1+Pr(1+\psi)}{2(1+\psi)}Le\, q^2 + \mathcal{O}(q^4), \tag{40}$$

where, as explained above, all higher order terms in $\Gamma_1(q)$ vanish, while Eqs. (38)–(40) here exactly reproduce Eqs. (8) in Ref. [29]. For such a comparison, please note that Eqs. (8) in Ref. [29] are written in terms of the *solutal* Rayleigh number, $Ra_\mathrm{s} = Le\psi Ra$.

We finalize by considering the case of $Dr = 0$ and $\psi_2' = 0$, which represents the binary mixture limit. One can readily see that, in that particular case, it vanishes one of the four eigenvalues of the hydrodynamic matrix $\mathsf{M}(q)$ of Eq. (16), while the other three coincide with the decay rates of a binary mixture with $D = \hat{D}_1$ and $\psi = \psi_1'$. Decay rates of non-equilibrium fluctuations in a binary mixture have been investigated in a previous publication [29] to which we refer the interested reader.

6 Concluding Remarks

The present paper presents a complete theory for the dynamics of spontaneous thermodynamic fluctuations in a ternary liquid mixture subjected to a stationary temperature gradient, and under the action of gravity for a liquid layer with thickness large enough to be insensitive to confinement effects. We consider, at linear order, all the four hydrodynamic modes contributing to the Rayleigh spectrum, with all their respective couplings. The only approximations adopted in the hydrodynamic equations are Boussinesq and neglecting of Dufour effect, which are supposed to be well justified for liquids.

The decay rates are theoretically obtained as the roots of a quartic equation. Hence, it is more practical to investigate them numerically, what we did in Sect. 4. For realistic parameter values of a ternary mixture, positive ψ and negative Ra, we have identified two different scenarios for the dependence of decay rates on the fluctuations wave number, summarized in Fig. 1. In both cases, and depending on q, propagative modes are observed. One of the scenarios, where temperature and viscous fluctuations mix and become propagative, has been recently observed experimentally [12]. The second scenario, where the two concentration modes mix and become propagative, is described here for the first time and is yet to be observed.

Throughout this paper it has been assumed that the concentration gradients existing in the NE ternary mixture are induced by the Soret effect. However, the results presented in this paper for the decay times can easily be adapted, as is the case in binary mixtures [7], to situations where concentration gradients are present due to other causes, like during free-diffusion. We note that propagative modes in isothermal free diffusion in binary mixtures were predicted [49] some time ago and recently computationally observed [48]. In this case propagative modes arise because of a coupling between concentration and viscous modes.

We expect the developments presented in this paper to be useful for scientist dealing with NE fluctuations in complex systems as, for instance, the ones involved in the recently approved space mission *Giant Fluctuations*, to be conducted by ESA at the ISS [50,51].

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