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Fluctuating hydrodynamics and concentration fluctuations in ternary mixtures

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ABSTRACT

We use fluctuating hydrodynamics to derive expressions for the spatial and temporal spectra of concentration fluctuations in a ternary liquid mixture in equilibrium. Our results agree with those found by other investigators who have used a procedure in which arbitrary initial values are adopted. Our method of using fluctuating hydrodynamics has the advantage that it can also be extended to deal with fluctuations in systems out of equilibrium.

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1. Introduction

Nowadays, a considerable amount of experimental data is available for diffusion and thermal-diffusion coefficients in binary fluid mixtures. As a consequence, in recent years the focus has been shifting to transport phenomena in ternary systems [1–9]. Studies of transport phenomena in ternary mixtures present some additional challenges. Many of these are related to the difficulty of performing accurate measurements of diffusion matrices, in particular of cross-diffusion coefficients, in low molecular weight liquid mixtures at room temperatures. In this context, it is worth mentioning that the European Space Agency (ESA) is currently performing the *Diffusion and Thermodiffusion Coefficients Measurements in Ternary Mixtures* (DCMIX) experiment onboard the International Space Station (ISS) [10], where microgravity conditions make it possible to perform measurements that otherwise are not possible on earth.

Transport processes are theoretically studied in the framework of nonequilibrium thermodynamics [11–13]. Nonequilibrium thermodynamics is not only a theory of fluxes but also provides a theory of thermal fluctuations [14,15]. Therefore, a complete understanding of thermodynamic transport in ternary systems should include an analysis of the associated thermal fluctuation phenomena. This fact, together with the expected new experimental information from low-gravity experiments [10], motivated us to embark on some further analysis of the nature of thermal concentration fluctuations in ternary mixtures, as they may become accessible in possible subsequent dynamic light-scattering (DLS) experiments.

As reviewed by other authors [14,16], there are two general methods for dealing with thermal fluctuations in equilibrium systems, namely, the arbitrary initial condition (Mountain) method and fluctuating hydrodynamics. The second is based on an extension by Fox and Uhlenbeck [17] of Landau's original ideas [18], and consists in introducing random contributions to the dissipative fluxes and adopting a fluctuation–dissipation theorem (FDT) for their statistical properties. Then, stochastic differential equations have to be solved and the statistical properties of the fluctuating fields are calculated from the known correlation functions of the random dissipative fluxes [15,17].

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Alternatively, one can use an approach, pioneered by Mountain [19,20], and adopted in the well-known books of Boon and Yip [21], Berne and Pecora [22], or Hansen and McDonald [23]. It consists in solving deterministic (with no random contributions) linearized hydrodynamic equations with arbitrary initial conditions. For instance [20], one solves for a concentration fluctuation $\delta c(t)$ as it evolves as a function of the time t starting from an arbitrary initial value $\delta c(0)$. One then multiplies the solution by the arbitrary initial condition, averages over the initial conditions, and obtains the dynamic $\langle \delta c(t) \cdot \delta c(0) \rangle$ correlation function as a function of the static $\langle \delta c(0) \cdot \delta c(0) \rangle$ correlation(s). Equivalently [24], some other authors multiply the hydrodynamic equations by an arbitrary initial condition and average the equations themselves (not their solution), arriving at evolution equations for the dynamic correlations that are then solved. Of course, both paths lead to the same result: an expression relating $\langle \delta c(t) \cdot \delta c(0) \rangle$ with the initial condition $\langle \delta c(0) \cdot \delta c(0) \rangle$. To complete the calculation by the Mountain [19] method one needs expressions for the static correlations, that are obtained from equilibrium statistical physics. In particular, one uses Einstein's hypothesis that the probability of a given fluctuation is proportional to $\exp(\delta S/k_B)$, where δS is the associated entropy fluctuation per molecule and k_B Boltzmann's constant. The two approaches: fluctuating hydrodynamics and arbitrary initial conditions, are fully equivalent for fluctuations in equilibrium systems.

Unlike the Mountain approach, fluctuating hydrodynamics can be extended to also deal with fluctuations in systems in nonequilibrium states, as theoretically shown and experimentally confirmed for one-component and binary fluid mixtures [15,25,26]. It turns out that the decay rates of nonequilibrium fluctuations are generally the same as equilibrium fluctuations at wave numbers where boundary effects can be neglected (see, e.g. Ref. [27]). The most significant difference between equilibrium and nonequilibrium fluctuations is in the intensity of these fluctuations: the presence of gradients induces a huge enhancement of the intensity of the fluctuations. This enhancement is caused by mode-coupling phenomena at the linear level that are not present in equilibrium and which lead to highly anisotropic fluctuations that are spatially long ranged in nonequilibrium. The problem with the arbitrary initial-condition (Mountain) approach is that there is not, in general, an accepted expression for the "entropy" in a nonequilibrium system, from which to get the static correlation(s); e.g. $\langle \delta c(0) \cdot \delta c(0) \rangle$, for concentration fluctuations.

Thermal fluctuations in ternary liquid mixtures have been investigated theoretically so far only by the arbitrary initial-condition approach. Therefore, a first necessary step in developing the theory of nonequilibrium fluctuations in ternary systems is to re-derive the equilibrium results on the basis of fluctuating hydrodynamics, which is the main purpose of the present paper. In Section 2 we present the equations of fluctuating hydrodynamics for a ternary system in an approximation that is adequate for liquid mixtures. In Section 3 we then derive the time-dependent correlation function of the concentration fluctuations, as they can be observed in, e.g., DLS experiments. In Section 4 we show the equivalence of the expression for the thermal fluctuations derived from fluctuating hydrodynamics for equilibrium fluids with those obtained by previous authors [28–31] on the basis of the Mountain method [19,20].

2. Fluctuating hydrodynamics of a ternary mixture in a large Lewis number approximation

A first modern analysis of thermal fluctuations in ternary fluid mixtures was presented by Lekkerkerker and Laidlaw [28]. They considered the generic case of a compressible fluid in which up to five hydrodynamic modes are coupled, and obtained the full spectrum of the fluctuations at any wave number in the hydrodynamic regime. This original study was performed closely following the Mountain approach, but was focused on the dynamics of the fluctuations so that an explicit discussion of the equal-time (static) correlation functions was not included. Later, van der Elsken and Bot [29] considered the intensity of fluctuations in multicomponent mixtures in equilibrium, and derived an expression for the Landau–Placzek ratio, *i.e.*, the ratio of the intensities of Rayleigh and Brillouin scattering. They used statistical mechanics [19,20,24], and their results are relevant for the statics of the fluctuations only. More recently, Ivanov and Winkelmann [30] re-derived the expressions of Lekkerkerker and Laidlaw [28] 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, Bardow [31] combined previous works, studying in a single paper both the statics and the dynamics of fluctuations in equilibrium ternary systems. In addition, Bardow [31] adopted some approximations that are adequate for mixtures in the liquid state, taking advantage of the property that concentration fluctuations in liquids relax much more slowly than temperature fluctuations. This is equivalent to the large Lewis number approximation,¹ introduced by Velarde and Schechter [32], to simplify the calculation of the stability diagram of convection in binary fluids.

In a ternary mixture, there are two independent concentrations c_1 and c_2 that we take as mass fractions. We define the two corresponding diffusion fluxes, \mathbf{J}_1 and \mathbf{J}_2 , in the barycentric frame of Ref. [12], having units of mass per second and surface area. Hence, Fick's law in isotropic systems is expressed by a 2×2 diffusion matrix \mathbf{D} (with SI units of $\text{m}^2 \text{s}^{-1}$) linearly relating the two fluxes with the two concentration gradients. As it is the case in binary mixtures, for ternary systems the diffusion matrix \mathbf{D} will, in general, depend on concentrations and/or temperature [3–6]. However, in this paper we shall adopt the approximation of constant \mathbf{D} , since we are dealing with small fluctuations around a uniform concentration state (equilibrium). Furthermore, as was also done by Barlow [31], we adopt a large Lewis number approximation meaning that

¹ Here we adopt the IUPAC/IUPAP definition $Le = a/D$, where a is the thermal diffusivity and D the diffusion coefficient. However, many authors use a definition of the Lewis number that is the inverse of the one adopted here. Thus, what for us is a large Lewis number approximation is for some other authors a small Lewis number approximation.

the thermal diffusivity a is much larger than the two eigenvalues of the diffusion matrix. Similarly to the case of binary mixtures [32–34], in the limit $Le \rightarrow \infty$ any coupling between the concentration fluctuations (δc_1 and δc_2 for a ternary mixture) and the temperature fluctuations vanishes and one only needs to consider coupling between the concentration fluctuations and the transverse-velocity fluctuations [33]. Furthermore, for fluctuations in an equilibrium state, the coupling between velocity and concentrations also vanishes [31], so that the fluctuating hydrodynamics equations simplify to:

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

where ρ is the mass density of the fluid. Eqs. (1) are equivalent to Eqs. (7) and (8) used by Bardow [31] with the following differences: first, we use here concentrations in terms of mass fractions instead of mole fractions. Second, Eqs. (7) and (8) of Bardow [31] are for c_1 and c_2 themselves, while Eqs. (1) here are for fluctuations around an equilibrium state: $\delta c_1 = c_1 - c_{1,E}$ and $\delta c_2 = c_2 - c_{2,E}$. This makes no difference because the equilibrium concentrations, $c_{1,E}$ and $c_{2,E}$, are spatially uniform. The third and most important difference is the presence in Eqs. (1) of random dissipative fluxes $\delta \mathbf{J}_1$ and $\delta \mathbf{J}_2$. According to fluctuating hydrodynamics [15,18], the linear phenomenological laws for the dissipative fluxes (the fluxes appearing in the expression of the entropy production) have to be supplemented with random contributions reflecting the stochastic nature of molecular motion. In a ternary mixture, the two independent diffusion fluxes imply the presence of two random contributions. The stochastic properties of these two random fluxes are: zero average, $\langle \delta \mathbf{J}_1 \rangle = \langle \delta \mathbf{J}_2 \rangle = 0$; and correlation functions given by the fluctuation–dissipation theorem [15,18], which in this case reads,

$$\langle \delta J_{i,k}^*(\mathbf{r}, t) \delta J_{j,m}(\mathbf{r}', t') \rangle = 2k_B L_{ij} \delta_{km} \delta(t - t') \delta(\mathbf{r} - \mathbf{r}') \tag{2}$$

where L_{ij} represents the Onsager matrix of phenomenological coefficients (with $L_{12} = L_{21}$) and where the indices k and m span the three spatial coordinates $k, m \in \{x, y, z\}$ (we are implicitly assuming that the system is isotropic). The matrix L relates the dissipative fluxes (\mathbf{J}_1 and \mathbf{J}_2) linearly with the thermodynamic “forces” that appear in the expression of the entropy production associated with these fluxes, which are the gradients of the chemical potential differences divided by the temperature, $\nabla(\hat{\mu}_1/T)$ and $\nabla(\hat{\mu}_2/T)$. Here $\hat{\mu}_1 = \mu_1 - \mu_3$ is the chemical potential difference between component 1 of the mixture and component 3 (solvent), 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 here are per unit mass, while in the work of Bardow [31] chemical potentials per mole have been used.

As is well known [12,28,31], the experimentally accessible diffusion matrix D is proportional to the product of the Onsager matrix L by the equation of state (EOS) matrix G of derivatives of chemical potential differences:

$$G_{ij} = \left(\frac{\partial \hat{\mu}_i}{\partial c_j} \right)_T \tag{3}$$

In particular, we have

$$\begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} = \frac{1}{\rho T} \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{bmatrix} \left(\frac{\partial \hat{\mu}_1}{\partial c_1} \right)_T & \left(\frac{\partial \hat{\mu}_1}{\partial c_2} \right)_T \\ \left(\frac{\partial \hat{\mu}_2}{\partial c_1} \right)_T & \left(\frac{\partial \hat{\mu}_2}{\partial c_2} \right)_T \end{bmatrix} \tag{4}$$

where T is the temperature. Note that we follow the nomenclature of de Groot and Mazur [11] instead of the nomenclature of Taylor and Krishna [12], and that the Onsager matrix L as defined here is ρT times the inverse of the Onsager matrix H as used by Bardow [31]: $H = \rho T L^{-1}$.

Because of a Maxwell thermodynamic relation, the EOS matrix G is symmetric [12,31]. From the symmetry of G the following relation between Onsager and diffusion coefficients can be derived:

$$L_{12}(D_{11} - D_{22}) - D_{21}L_{11} + D_{12}L_{22} = 0 \tag{5}$$

In addition, the symmetry of the Onsager matrix implies the following relation between diffusion coefficients and chemical-potential derivatives [12,28,31]:

$$-D_{12}G_{11} + G_{12}D_{11} = -D_{21}G_{22} + G_{12}D_{22} \tag{6}$$

that is independent of whether one uses the convention of de Groot and Mazur [11] or of Taylor and Krishna [12] for the Onsager matrix. As discussed by many other authors [12,28,31,35–38], Eq. (6) is a direct consequence of the Onsager reciprocal relations, meaning that the four components of the diffusion matrix of a ternary system are not independent, but are related by the equilibrium properties of the system. Eq. (6) has been experimentally verified in several systems for which precise concentration measurements are possible, like molten metal alloys [35], molten silicates [36] or electrolyte solutions [37]. Kett and Anderson [38] verified Eq. (6) for low molecular weight nonassociating liquid mixtures. However, as reviewed by Bardow [31], recent diffusion measurements in some nonideal ternary liquid mixtures could not confirm Eq. (6),

a fact that indicates large experimental inaccuracies. The DCMIX experiment [10] is expected to yield accurate diffusion matrices for selected ternary systems, in particular cross-diffusion coefficients. These measurements, when combined with good EOS model(s) for the ternary mixture, are expected to pass the quality-control test of Eq. (6).

3. Correlation functions of concentration fluctuations

We can readily calculate the correlation functions among the various concentration fluctuations by applying, as in previous investigations [28,31], spatiotemporal Fourier transforms to Eqs. (1). In addition we need to apply also a Fourier transformation to the fluctuation–dissipation expression (2). Details of this procedure are not given here, since they are similar to many examples that can be found in the literature, such as in Ref. [15]. The final result is conveniently expressed in terms of a correlation matrix $C_{ij}(\omega, q)$, defined by

$$\langle \delta c_i^*(\omega, \mathbf{q}) \delta c_j(\omega', \mathbf{q}') \rangle = C_{ij}(\omega, q) (2\pi)^4 \delta(\omega - \omega') \delta(\mathbf{q} - \mathbf{q}') \quad (7)$$

where ω is the frequency and \mathbf{q} the wave vector of the fluctuations. The correlation matrix is expressed as the sum of two diffusion modes:

$$C(\omega, q) = \frac{k_B T}{\rho} \mathbf{G}^{-1} \left[A_1 \frac{2\hat{D}_1 q^2}{\omega^2 + \hat{D}_1^2 q^4} + A_2 \frac{2\hat{D}_2 q^2}{\omega^2 + \hat{D}_2^2 q^4} \right] \quad (8)$$

where \hat{D}_1 and \hat{D}_2 are the eigenvalues of the diffusion matrix:

$$\hat{D}_{1,2} = \frac{1}{2} [D_{11} + D_{22} \pm \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}}] \quad (9)$$

The larger \hat{D}_1 eigenvalue is customarily referred to as the cooperative diffusion coefficient, while the smaller \hat{D}_2 eigenvalue is referred to as the interdiffusion coefficient. The result (8), containing two diffusion modes and coming from fluctuating hydrodynamics, fully agrees with the expression obtained by other investigators [28,30,31] on the basis of the Mountain method.

The dimensionless matrices A_1 and A_2 in Eq. (8) control the relative amplitude of the two diffusion modes. They depend only on the dynamics (diffusion matrix). Some long but otherwise straightforward algebra, with the help of Eq. (5), yields:

$$A_{1,2} = \pm \frac{\hat{D}_{1,2}^2 \mathbf{D}^T - (\det \mathbf{D})^2 (\mathbf{D}^T)^{-1}}{\hat{D}_{1,2} (\hat{D}_1^2 - \hat{D}_2^2)} \quad (10)$$

where \mathbf{D}^T is the transpose of the diffusion matrix and $\det \mathbf{D}$ its determinant (units of diffusion squared). Application of Fourier anti-transforms in the two frequencies to Eq. (7) yields:

$$\langle \delta c_i^*(\mathbf{q}, t) \delta c_j(\mathbf{q}', t') \rangle = C_{ij}(q, |t - t'|) (2\pi)^3 \delta(\mathbf{q} - \mathbf{q}') \quad (11)$$

where, due to the time invariance of the equilibrium state, the time-correlation matrix depends only on the difference $|t - t'|$. From Eq. (8) one arrives at:

$$C(q, \tau) = \frac{k_B T}{\rho} \mathbf{G}^{-1} [A_1 \exp(-\hat{D}_1 q^2 \tau) + A_2 \exp(-\hat{D}_2 q^2 \tau)] \quad (12)$$

demonstrating that the time-correlation functions, as measured in DLS experiments probing times of the order of the diffusive decay times, will be composed of two exponentials, with decay rates $\hat{D}_1 q^2$ and $\hat{D}_2 q^2$ determined by the eigenvalues of the diffusion matrix. Two diffusive modes are routinely measured by DLS in ternary systems consisting of two different polymers in a solvent (see, for instance, Ref. [39]), or the same polymer at two different molecular weights in a solvent. However, as discussed by Bardow [31], available ternary DLS experiments in low molecular weight fluids report only a single mass diffusion mode. This may be due to very different numerical magnitudes of the two amplitude matrices of Eq. (10), as Bardow [31] has pointed out. But we should also mention the intrinsically more difficulty of DLS experiments in low molecular weight mixtures as compared to polymer solutions. Diffusion in polymers is orders of magnitude slower and the intensity of concentration fluctuations² is usually larger, two facts that cooperate to make DLS simpler and more reliable in polymers as compared with regular mixtures. In addition, for low-molecular weight mixtures it may happen that only one of the eigenvalues of the diffusion matrix is negligible compared to the thermal diffusivity of the mixture.

It is important to note from Eq. (10) that:

$$A_1 + A_2 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = 1 \quad (13)$$

² As determined by the matrix \mathbf{G}^{-1} in Eqs. (12) and (14), and also by the concentration derivatives of the refraction index that we do not discuss here.

As a consequence, the equal-time correlation matrix,

$$C(q, 0) = \frac{k_B T}{\rho} G^{-1} \tag{14}$$

does not depend on the dynamics of the system (i.e., it does not depend on the matrix D), as it is to be expected physically. Eq. (14) agrees with the one obtained by van der Elsken and Bot [29] for the equal-time correlation functions on the basis of the Mountain method, i.e., from the expression of the entropy fluctuation.

4. Comparison with work of previous authors

Eqs. (8)–(10) give the relative amplitude of the two diffusion modes that can be observed in a ternary mixture by DLS experiments. Our results have been obtained on the basis of fluctuating hydrodynamics, and are suitable as a starting point for an analysis of thermal fluctuations in a ternary mixture subjected to a temperature gradient. Here we compare our results from fluctuating hydrodynamics with previous results obtained for fluctuations of ternary mixtures in equilibrium on the basis of the arbitrary-initial-condition method [28,31].

Lekkerkerker and Laidlaw [28] studied the spectra of light scattered by a ternary mixture, that is expressed in terms of the time correlation functions of the various thermodynamic fields. Lekkerkerker and Laidlaw [28] did not adopt the large Lewis number approximation, so that their results contain five coupled hydrodynamic modes, instead of only the two present in our current Eq. (8). However, if one takes the large Lewis number limit to the Lekkerkerker and Laidlaw [28] expressions, one does reproduce our results. The large Lewis number approximation is adequate for liquid mixtures, and it is simpler and more transparent to take this limit in the original equations rather than in the final results. Moreover, for liquids the decay times of thermal or viscous modes are well separated from the decay times of diffusive modes. Hence, in DLS experiments probing the correlation-time range corresponding to the relaxation of the concentration fluctuations, thermal and viscous modes have already fully decayed and cannot be observed.

Bardow [31] did adopt the same large Lewis number approximation that we used here. In addition, he discussed the relative amplitude of the two diffusive modes and not just the dynamics as Lekkerkerker and Laidlaw [28] did. As mentioned earlier, the analysis of Bardow [31] was based on the Mountain method which cannot be extended to nonequilibrium. A comparison with his results for the relative equilibrium intensities of the two diffusive modes is less obvious, since Bardow has presented the amplitudes in terms of certain uncoupled concentration variables, $\delta\hat{c}_i$, whose definition depends on the diffusion matrix.

Hence, we need to check whether it is possible to express our result, given by Eq. (8), in terms of the uncorrelated single-mode concentration fluctuations, $\delta\hat{c}_i$ introduced by Bardow [31]. First, to look for uncorrelated modes one has to diagonalize the amplitude matrices: $G^{-1}A_1$ and $G^{-1}A_2$, noting that, because of Eq. (13), the same hat-concentrations that diagonalize the first matrix will automatically diagonalize the second matrix also (the matrix G^{-1} is itself symmetric). Second, it turns out that the determinants of both amplitude matrices are zero, meaning that each of the two matrices has an eigenvalue zero. We conclude from these observations that the decomposition in single-mode uncorrelated hat-concentrations exists, and the $\delta\hat{c}_i$ are linearly related to the actual concentrations as $\delta c_i = P_{ij}\delta\hat{c}_j$, where the transformation matrix P is indeed correctly given by Eq. (13) in Bardow [31]. To evaluate the amplitude of the fluctuations of these uncorrelated concentrations from our current Eq. (8), one needs to compute

$$\begin{aligned} P^{-1}G^{-1}A_1(P^{-1})^T &= \frac{1}{\hat{G}_1} \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \\ P^{-1}G^{-1}A_2(P^{-1})^T &= \frac{1}{\hat{G}_2} \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \end{aligned} \tag{15}$$

so that $1/\hat{G}_1$ is the nonzero eigenvalue of the first amplitude matrix, and $1/\hat{G}_2$ the nonzero eigenvalue of the second amplitude matrix. The expressions, that we obtain for \hat{G}_1 and \hat{G}_2 after substituting Eq. (10) for A_1 and A_2 , reproduce exactly the equations obtained by Bardow (Eqs. (18) and (19) in Ref. [31]). We thus conclude that the expressions obtained by Bardow [31] on the basis of the Mountain method agree completely with the expressions obtained by us from fluctuating hydrodynamics, as it is to be expected for fluctuations in a fluid in equilibrium.

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