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Finite-size effects on Soret-induced nonequilibrium concentration fluctuations in binary liquids

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We consider a horizontal binary-liquid layer that is subjected to a stationary temperature gradient while still being maintained in a stable quiescent state without any convection. In such a thermal nonequilibrium state the Soret effect induces concentration fluctuations. In the present paper we show how the finite height of the liquid layer will affect the long-range nature of these nonequilibrium concentration fluctuations at very small wave numbers. Estimates of the wave numbers where light-scattering or shadowgraph experiments will be affected by finite-size effects are presented.

Keywords: Binary Boussinesq Equations; light scattering; nonequilibrium fluctuations; Rayleigh-Bénard convection

Estudiaremos una capa horizontal de un líquido binario sometido a un gradiente estacionario de temperatura mientras el estado de reposo del líquido es estable, lejos de cualquier inestabilidad convectiva. En dicho sistema, el efecto Soret inducirá fluctuaciones de la concentración. En el presente trabajo mostraremos como la altura finita de la capa líquida afectará a la naturaleza de largo alcance de las fluctuaciones de no equilibrio de la concentración, cuando el número de onda de dichas fluctuaciones es muy pequeño. Además presentaremos valores estimados del número de onda para el que los efectos de tamaño finito afectarán a los experimentos de dispersión de la luz o shadowgraph.

Descriptores: Ecuaciones de Boussinesq binarias; dispersión de luz; fluctuaciones fuera del equilibrio; convección de Rayleigh-Bénard

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This paper is dedicated to Professor Leopoldo García-Colín Scherer on the occasion of his 70th birthday.

1. Introduction

In this paper we consider a binary liquid system located between two horizontal plates with different but constant temperatures. A temperature gradient in a liquid mixture induces a concentration gradient through the Soret effect [1–5]. Many studies reported in the literature have been concerned with the effect of Soret-induced concentration gradients on the convective Rayleigh-Bénard instability [6–11]. However, it turns out that there are also interesting fluctuation phenomena present when the liquid mixture is in a hydrodynamically quiescent stable state, far away from any convective instability.

A central feature in the development of nonequilibrium statistical mechanics during the past decades has been the discovery that long-range dynamic correlations are present in fluids that consist of molecules with short-range interactions [12, 13]. Originally it was thought that a fluid in a nonequilibrium state would proceed to thermodynamic equilibrium in two distinct stages: first a microscopic kinetic stage with time scale of the order of the interval between successive molecular collisions, which for liquids is of the same order as the duration of the molecular collisions, after which local equilibrium is established; second a macroscopic stage during which the fluid evolves in accordance with the hydrodynamic equations [14]. In this picture no mechanism exists for the appearance of long-range dynamic correlations away from a macroscopic convective instability. The first indication that long-range dynamic correlations can appear was provided when experiments showed that the thermal conductivity of fluids diverges at the vapor-liquid critical point [15, 16]. This observation contradicted the classical theory of Van Hove who had assumed that the slowing down of the fluctuations near the critical point had only a thermodynamic origin [17, 18]. In evaluating the randomizing nature of molecular collisions one must make a distinction between quantities like mass, momentum and energy that are conserved in a binary collision on the one hand and nonconserved quantities on the other hand. The fast modes associated with nonconserved quantities do indeed decay during a short kinetic stage, but the slow modes associated with conserved quantities persist well beyond the times between successive collisions; a coupling between these modes can result in long-range (mesoscopic) dynamic correlations [19]. The same mode-coupling effects, responsible for the dynamics of the long-range critical fluctuations [20–22] turned out to account also for the presence of long-time tails in the Green-Kubo correlation functions for the transport coefficients [23–25] earlier noticed in computer simulations of molecular dynamics [26, 27].

In the earlier 80's it became apparent that fluids in nonequilibrium states would exhibit dramatic long-range fluctuations due to mode-coupling effects. Specifically, Kirkpatrick, Cohen and Dorfman derived the appropriate expressions for the temperature and the viscous fluctuations in a one-component fluid subjected to a stationary temperature gradient using mode-coupling theory [28], indicating that nonequilibrium fluctuations would enhance and modify the Rayleigh spectrum of scattered light [29]. Subsequently, it became apparent that the same expressions could be obtained on the basis of Landau's fluctuating hydrodynamics, which is also based on the assumption that only the nonconserved quantities decay rapidly over a molecular time scale [30–35]. Physically, the presence of a temperature gradient ∇T leads to nonequilibrium fluctuations because the stationary temperature gradient causes a coupling between the component of the velocity fluctuations parallel to the gradient and the temperature fluctuations with a wave vector perpendicular to the gradient. Velocity fluctuations parallel to the gradient are probing regions with different local equilibrium temperatures, thus causing a nonequilibrium contribution to the temperature fluctuations. Since both the temperature and the viscous (transverse velocity) fluctuations do not propagate, but decay diffusively, the nonequilibrium contributions cannot depend on whether the temperature gradient is in the positive or negative direction and, hence, they depend on the square of the temperature gradient. Moreover, each mode contributes a factor q^{-2}, so that the intensity of the nonequilibrium fluctuations becomes inversely proportional to the fourth power of the wave number q of the fluctuations. The dependence of the intensity of the nonequilibrium fluctuations on $(\nabla T)^2$ and on q^{-4} has been confirmed by light-scattering experiments [36–39]. The presence of such long-range fluctuations in fluids in nonequilibrium states causes a serious difficulty in the further development of irreversible thermodynamics as, *e.g.*, studied by García-Colín and coworkers [40–43].

In the case of a liquid mixture, a temperature gradient ∇T is accompanied by a concentration gradient ∇c through the Soret effect. Just as a temperature gradient causes a coupling between the temperature fluctuations with wave vector **q** perpendicular to the temperature gradient and the transverse-velocity fluctuations in the direction of the temperature gradient, so will a concentration gradient cause a coupling between the concentration fluctuations with wave vector **q** perpendicular to the concentration gradient and the transverse-velocity fluctuations in the direction of the concentration gradient. Hence, in a liquid mixture subjected to a temperature gradient not only nonequilibrium temperature and viscous fluctuations will be present, but also nonequilibrium concentration fluctuations as first pointed out by Law and Nieuwoudt [44, 45], and as also analyzed by Velasco and García-Colín [46] and by Segrè and Sengers [47]. The intensity of the nonequilibrium concentration fluctuations should be proportional to the square of the concentration gradient ∇c and again inversely proportional to the fourth power of the wave number q. The case of nonequilibrium concentration fluctuations in a colloidal suspension in the presence of a concentration gradient has been considered by Schmitz [48]. Vailati and Giglio [49] have extended the theory to treating the effect of time-dependent concentration profiles on the structure factor of a binary liquid.

The divergence of the intensity of nonequilibrium fluctuations for small wave numbers, *i.e.*, for large wavelengths cannot go on indefinitely. For very small wave numbers the dependence of the nonequilibrium fluctuations on q will be affected by the presence of gravity even when the liquid is in a stable nonconvective state. The effects of gravity on the nonequilibrium fluctuations, both in one-component liquids and in liquid mixtures have been analyzed by Segrè *et al.* [47, 50] for the case of negative Rayleigh numbers. For nonequilibrium concentration fluctuations in a binary liquid mixture, the effects of gravity have been further evaluated by Sengers and Ortiz de Zárate [51]. It turns out that for negative Rayleigh numbers gravity has a damping effect on the nonequilibrium fluctuations, causing the q^{-4} divergence in the intensity of these fluctuations to become saturated at small q and to approach a finite plateau in the limit $q \to 0$. This gravitationally induced crossover behavior for very small q has been observed experimentally by Vailati and Giglio [52, 53].

In addition, when the product qL becomes of order unity, one must expect that the nonequilibrium fluctuations will be affected by the finite height L of the liquid layer subjected to the temperature gradient. Finite-size effects on the nonequilibrium temperature and viscous fluctuations in a one-component liquid have recently been studied by Ortiz de Zárate *et al.* [54, 55]. It is the purpose of the present paper to analyze finite-size effects on the nonequilibrium concentration fluctuations in a liquid mixture, a problem which so far has not been treated in the literature.

A complete derivation of the contributions from nonequilibrium fluctuations should be based on the linearized hydrodynamic equations supplemented with random-noise terms as was done by Law and Nieuwoudt [44] and by Segrè and Sengers [47]. However, since in liquid mixtures temperature fluctuations decay much faster than concentration fluctuations, one can obtain a very good approximation for the contribution of the nonequilibrium fluctuations to the structure factor by starting from a simplified set of linearized Boussinesq equations as we have demonstrated in a recent review on the subject [51]. Physically it means that we can neglect any coupling of the concentration fluctuations with the temperature fluctuations through the imposed temperature gradient and only consider the coupling between the concentration fluctuations and the transverse-velocity (viscous) fluctuations through the concentration gradient induced by the Soret effect.

We shall proceed as follows. In Sec. 2 we formulate the linearized Boussinesq equations for a binary liquid and establish our notation for the fluctuating quantities. In Sec. 3 we introduce some approximations into the linearized Boussinesq equations as earlier proposed by Schechter and Velarde [7, 56] for simplifying the analysis of the convective instability in a two-component liquid. In Sec. 4 we show

how the well known expression for the contribution of the nonequilibrium concentration fluctuations in a binary liquid subjected to a stationary temperature gradient can be recovered from the simplified set of linearized Boussinesq equations when supplemented with random-noise terms. In Sec. 5 we then evaluate the modifications needed to account for the boundary conditions due to the presence of two horizontal planes confining the liquid layer to a finite height L. In Sec. 6 we consider the consequences of any finite-size effects on the nonequilibrium concentration fluctuations for the interpretation of light-scattering or shadowgraph experiments. Some concluding remarks are presented in Sec. 7.

2. The linearized Boussinesq equations for a binary liquid

The system we are considering in this paper is a binary liquid bounded by two horizontal planes separated by a distance L. Across this liquid layer a stationary temperature gradient is established by maintaining the two horizontal planes at different temperatures; ∇T_0 represents the magnitude of the temperature gradient which is assumed to act in the Z-direction perpendicular to the bounding planes. As a consequence of the Soret effect, a stationary concentration gradient also develops in the system with magnitude ∇c_0. The relationship between the concentration gradient ∇c_0 and the temperature gradient ∇T_0 is given by:

$$\nabla c_0 = -c(1-c)S_T \nabla T_0, \tag{1}$$

where S_T is the Soret coefficient and c is the (average) concentration expressed as weight fraction (w/w) of component 1 of the mixture. Equation (1) defines the Soret coefficient S_T of component 1 in component 2. For isotropic mixtures S_T is a scalar quantity and the induced concentration gradient is parallel to the imposed temperature gradient but, depending on the sign of S_T, can have the same or the opposite direction. When S_T is positive, concentration and temperature gradients have opposite directions, with component 1 migrating to the colder region. When S_T is negative, concentration and temperature gradients have the same direction, with component 1 migrating to the warmer region. Note that, because of conservation of mass, when S_T of component 1 in component 2 is positive, then S_T of component 2 in component 1 is negative and *viceversa*. In this paper, c designates the concentration of component 1.

We want to study small fluctuations around the conducting state, *i.e.*, fluctuations around the quiescent and stable state of the fluid. We do not consider any fluctuations in the pressure p related to propagating modes that leads to Brillouin scattering. The appropriate set of equations for our problem are the linearized Boussinesq equations for a binary system [7, 8, 10, 57], which read

$$\frac{\partial}{\partial t}(\nabla^2 w) = \nu \nabla^2(\nabla^2 w) + g\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)[\alpha\theta - \beta\Gamma], \tag{2}$$

$$\frac{\partial \theta}{\partial t} = D_{\text{th}} \nabla^2 \theta - w \nabla T_0, \tag{3}$$

and

$$\frac{\partial \Gamma}{\partial t} = D\left[\nabla^2 \Gamma + \frac{\alpha}{\beta}\psi \nabla^2 \theta\right] - w \nabla c_0, \tag{4}$$

where $\theta(\mathbf{r}, t)$ represents the local fluctuation of the temperature (δT), $w(\mathbf{r}, t)$ denotes the local fluctuations of the z-component of the velocity (δu_z), and $\Gamma(\mathbf{r}, t)$ denotes the local fluctuation of the concentration of component 1 of the mixture (δc). The fluctuations $\theta(\mathbf{r}, t)$, $w(\mathbf{r}, t)$ and $\Gamma(\mathbf{r}, t)$ depend on the position $\mathbf{r}(x, y, z)$ and on the time t. The coefficient ν is the kinematic viscosity, D_{th} the thermal diffusivity, ρ the density, and λ_{T} the thermal conductivity of the mixture, while D represents the binary diffusion coefficient and g the gravitational acceleration constant. The symbol $\alpha = -\rho^{-1}(\partial\rho/\partial T)_{p,c}$ represents the thermal expansion coefficient and, similarly, $\beta = \rho^{-1}(\partial\rho/\partial c)_{p,T}$ represents the concentration expansion coefficient. Note that β is positive when component 1 is the heavier component and β is negative when component 1 is the lighter component. Finally, ψ is the dimensionless separation ratio, which is defined by

$$\psi = c(1-c)S_T \frac{\beta}{\alpha}. \tag{5}$$

The parameter ψ is the ratio of the density gradient $\beta\nabla c_0$ produced by the concentration gradient to the density gradient $-\alpha\nabla T_0$ produced by the temperature gradient; $\psi = -(\beta\nabla c_0)/(\alpha\nabla T_0)$.

By adopting Eqs. (2)–(4) we assume that all thermophysical properties of the binary liquid depend only weakly on temperature or concentration so that the variation of these properties as a function of z is negligibly small; in practice this is a very good approximation [37]. For the same reason, in Eq. (5) the concentration c of component 1 represents an average value in the liquid layer; replacing the local concentration by an average concentration is only questionable for extremely dilute solutions [7].

The Boussinesq approximation assumes the liquid to be incompressible [58], so that the coefficient D_{th} in Eq. (3) can indeed be identified with the thermal diffusivity $\lambda_{\text{T}}/\rho c_{\text{P}}$, where c_{P} is the specific isobaric heat capacity. As usual, the Dufour effect has been neglected in Eqs. (2)–(4), since it is relevant only in binary gas mixtures and in liquids near the vapor-liquid critical point [57]. In addition, and following the usual literature [58], to eliminate the hydrostatic-pressure gradient from the equations we find it convenient to consider Eq. (2) for $\nabla^2 w$ by taking a double curl in the equation for the fluctuating fluid velocity $\delta\mathbf{u}$.

In Eqs. (2)–(4) we presented the linearized version of the Boussinesq equations for a binary liquid. Neglecting the nonlinear terms is only justified when the liquid layer is in a quiescent conductive stable state. The linear stability of the binary Boussinesq equations has been studied by many investigators [7, 9, 59]. As is well known, the stability of the quiescent state depends on the values of the dimensionless Rayleigh number Ra, and of the dimensionless separation ratio, ψ [7]. In this paper, we shall focus our attention on the finite-size effects on the structure factor of the liquid mixture and not consider gravity effects, which have been evaluated in other publications [47, 50]. The approximation $g = 0$ implies neglecting the bouyancy term in Eq. (2), making the Rayleigh number of our problem to be zero. As is discussed in the relevant literature [7], for $\mathrm{Ra} = 0$, the quiescent state is stable independent of the value of the separation ratio. Consequently, by adopting the $g \to 0$ limit of the Boussinesq equations, the conducting state will always be stable. In this situation the set of differential equations [Eqs. (2)–(4)] describes correctly the spatial and temporal evolution of the fluctuations around the quiescent state of the liquid.

3. Linearized Boussinesq equations for small Lewis number

In order to determine the contribution from concentration fluctuations to the structure factor of a binary liquid mixture, it is convenient to make a number of additional approximations to the standard Boussinesq equations [51]. First of all, to a good approximation the decay rates of the viscous fluctuations, the temperature fluctuations and the concentration fluctuations can be directly identified with νq^2, $D_{\mathrm{th}} q^2$ and $D q^2$, respectively [38]. Furthermore, the diffusion coefficient D is in practice much smaller than the kinematic viscosity ν and the thermal diffusivity D_{th}. Thus, the viscous and thermal fluctuations decay much faster than the concentration fluctuations. Moreover, because of the dependence of the refractive index on the concentration, the intensity of light scattered by the concentration fluctuations is usually appreciably larger than that from the viscous or the temperature fluctuations. Hence, in many cases one can readily determine the concentration fluctuations with Rayleigh scattering independently from the much faster decaying viscous and temperature fluctuations [38, 39, 60, 61]. As elucidated in a recent review of the subject [51], to deal with the concentration fluctuations we shall retain only the more relevant physical terms in the Boussinesq equations [Eqs. (2)–(4)] by adopting an approximate set of linearized equations earlier considered by Velarde and Schechter [56] for a convective-instability analysis.

The Velarde-Schechter approximation consists of scaling the distances by the finite height of the layer, L, and the time by the diffusional time $\tau_{\mathrm{D}} = L^2/D$, and then perform a series expansion of the full Boussinesq equations in terms of the Lewis number $\mathrm{Le} = D/D_{\mathrm{th}}$. It is worth noting that for regular liquid mixtures Le is a small quantity ($\simeq 10^{-3}$). In this series expansion only terms of order zero in Le are retained. To clarify this approximation scheme, we first switch to dimensionless variables, using L as the length scale and τ_{D} as the time scale [56]

$$\tilde{w} = \frac{wL}{D}, \qquad \tilde{t} = \frac{tD}{L^2},$$
$$\tilde{\mathbf{r}} = \frac{\mathbf{r}}{L}, \qquad \tilde{\theta} = \frac{\theta}{L\,\nabla T_0}, \tag{6}$$

Multiplying Eq. (2) by $L^5/(DD_{\mathrm{th}})$, Eq. (3) by $L/(\nabla T_0 D_{\mathrm{th}})$, and Eq. (4) by L^2/D, we obtain in terms of dimensionless variables

$$\mathrm{Le}\frac{\partial}{\partial \tilde{t}}(\tilde{\nabla}^2 \tilde{w}) = \mathrm{Pr}\tilde{\nabla}^2(\tilde{\nabla}^2 \tilde{w}) - \mathrm{Ra}Sc\left(\frac{\partial^2}{\partial \tilde{x}^2} + \frac{\partial^2}{\partial \tilde{y}^2}\right)\left(\tilde{\theta} + \frac{\psi}{\Delta c_0}\Gamma\right), \tag{7}$$

$$\mathrm{Le}\frac{\partial \tilde{\theta}}{\partial \tilde{t}} = \tilde{\nabla}^2\tilde{\theta} - \mathrm{Le}\tilde{w}, \tag{8}$$

$$\frac{\partial \Gamma}{\partial \tilde{t}} = \left(\tilde{\nabla}^2\Gamma - \Delta c_0 \tilde{\nabla}^2\tilde{\theta}\right) - \tilde{w}\Delta c_0, \tag{9}$$

where $\mathrm{Pr} = \nu/D_{\mathrm{th}}$ is the Prandtl number and where $\Delta c_0 = L\nabla c_0$ is a dimensionless concentration difference. If we now take the limit $\mathrm{Le} \to 0$ of the equations, we obtain $\tilde{\theta}(\mathbf{r}, t) = 0$; thus to zeroth order in Le, the temperature fluctuations can be neglected. Reverting the equations for $w(\mathbf{r}, t)$ and $\Gamma(\mathbf{r}, t)$ to dimensional form, taking at this point the $g \to 0$ limit (neglecting the buoyancy term), and supplementing the equations with the corresponding random-noise terms, we finally obtain [51]:

$$0 = \nu\nabla^2(\nabla^2 w) + \frac{1}{\rho}\{\nabla \times [\nabla \times (\nabla \cdot \delta\mathsf{T})]\}_z, \tag{10}$$

$$\frac{\partial \Gamma}{\partial t} = D\nabla^2\Gamma - w\nabla c_0 + \nabla \delta\mathbf{J}. \tag{11}$$

The primary physical meaning of Eqs. (10) and (11) is that for small values of the Lewis number we can neglect any coupling between the concentration fluctuations and the temperature fluctuations and retain only the coupling between concentration fluctuations and viscous (transverse-velocity) fluctuations through the Soret-induced stationary concentration gradient ∇c_0 in Eq. (11). As a consequence, the imposed temperature gradient ∇T_0 will appear in the final expression for the nonequilibrium structure factor, in this small-Lewis-number approximation, only through the induced concentation gradient, Eq. (1). Hence, our derivation will be equally valid when the concentration gradient ∇c_0 does not result from an imposed temperature gradient, but arises from any other cause, as in the case of an isothermal free-diffusion process [49].

Equations (10) and (11) are the starting point for the analysis of the concentration fluctuations to be performed in this paper. For this purpose, the Velarde-Schechter approximation to the full linearized Boussinesq equations have been supplemented with random-noise terms representing the contributions from rapidly varying short-range fluctuations, in accordance with the standard fluctuating-hydrodynamics approach [44, 62–64]. As discussed in the Introduction, these random-noise terms represent the rapidly decaying nonconserved degrees of freedom, to be distinguished from the conserved degrees of freedom described by the hydrodynamic evolution equations. Thus in Eq. (10) we have introduced $\delta\mathsf{T}(\mathbf{r}, t)$ as a random stress tensor following [62, 63] and in Eq. (11) we have introduced $\delta\mathbf{J}(\mathbf{r},t)$ as a random solute flux following [44, 64]. Since in the approximation we are using for the hydrodynamics of the system, the temperature fluctuations do not couple to concentration or viscous fluctuations, we do not need to consider a random heat flux. The subscript z in Eq. (10) indicates that this random-noise term is to be identified with the Z-component of the vector between curly brackets. This procedure of supplementing the random Boussinesq equations for a binary system with random-noise terms has previously been used by Schöpf and Zimmermann to study the influence of noise close to the convective instability [65].

Finally, we mention that the small-Lewis-number approximation adopted by us, has also been widely employed in the literature to simplify the stability analysis of a binary mixture [7, 56, 66, 67]. As discussed in the relevant publications [7, 56], the Le → 0 approximation has several shortcomings; in particular, it does not describe correctly the situation with $\mathrm{Ra} > 0$ and $\psi < 0$, missing the interesting Hopf bifurcation and codimension-two instability point. But as commented earlier, we restrict ourselves here to the limit $g \to 0$, in which case the Le → 0 approximation is adequate to describe the concentration fluctuations, as will be shown below.

4. Calculation of the "Bulk" Structure Factor

Before evaluating any finite-size effects on the nonequilibrium concentration fluctuations, we first review the derivation of their contribution to the "bulk" structure factor, *i.e.*, the structure factor in the absence of any boundary conditions [51]. For this purpose we apply a temporal and spatial Fourier transform to Eqs. (10) and (11), so as to obtain

$$\begin{pmatrix} -\nu q^4 & 0 \\ \nabla c_0 & i\omega + Dq^2 \end{pmatrix} \begin{bmatrix} w(\omega,\mathbf{q}) \\ \Gamma(\omega,\mathbf{q}) \end{bmatrix} = \begin{bmatrix} F_1(\omega,\mathbf{q}) \\ F_2(\omega,\mathbf{q}) \end{bmatrix}. \tag{12}$$

In Eqs. (12), F_1 and F_2 represent Langevin random-noise terms, which are related to the Fourier transforms of the random stress tensor $\delta\mathsf{T}(\omega,\mathbf{q})$ and of the random solute flux $\delta\mathbf{J}(\omega,\mathbf{q})$ by

$$\begin{bmatrix} F_1(\omega,\mathbf{q}) \\ F_2(\omega,\mathbf{q}) \end{bmatrix} = \begin{bmatrix} i\rho^{-1}\left\{q^2\left[\mathbf{q}\cdot\delta\mathsf{T}(\omega,\mathbf{q})\right]_z - q_z\mathbf{q}\cdot\left[\mathbf{q}\cdot\delta\mathsf{T}(\omega,\mathbf{q})\right]\right\} \\ i\mathbf{q}\cdot\delta\mathbf{J}(\omega,\mathbf{q}) \end{bmatrix}. \tag{13}$$

In this paper we identify the structure factor $S(\omega,q)$ as the function that determines the intensity of the scattered Rayleigh light as a function of the frequency ω and the scattering vector q arising from concentration fluctuations only. Consequently, this structure factor $S(\omega,q)$ is related to the autocorrelation function $\langle\Gamma^*(\omega,\mathbf{q})\cdot\Gamma(\omega',\mathbf{q}')\rangle$ of the concentration fluctuations by

$$\langle\Gamma^*(\omega,\mathbf{q})\cdot\Gamma(\omega',\mathbf{q}')\rangle = \left(\frac{\partial c}{\partial n}\right)^2_{p,T} S(\omega,\mathbf{q}) \times(2\pi)^4\delta(\omega-\omega')\delta(\mathbf{q}-\mathbf{q}'), \tag{14}$$

where $(\partial n/\partial c)_{p,T}$ represents the effect of the concentration dependence of the refractive index n on the light-scattering intensity.

The correlation functions between the Langevin noise terms F_1 and F_2, needed to calculate $S(\omega,q)$ from Eq. (14), can be obtained from the known correlation functions between the different components of the random stress tensor and the random solute flux. In nonequilibrium fluctuating hydrodynamics it is assumed that the correlation functions of these random-noise terms retain their local equilibrium values, which are short-ranged in space and in time [44, 68, 69]. As mentioned earlier, the conserved degrees of freedom actually develop long-ranged correlations in nonequilibrium states, but the random stress tensor and the random solute flux represent the nonconserved degrees of freedom, thus they are expected to remain short-ranged, even out of equilibrium. Upon substituting into Eq. (13) the expressions for the correlation functions of $\delta\mathsf{T}$ as, for instance, given by Eqs. (3.12) in Ref. 62, and from the correlation functions of $\delta\mathbf{J}$, as given by [44, 64], we obtain [51, 54]

$$\begin{aligned} \langle F_1^*(\omega,\mathbf{q})\cdot F_1(\omega',\mathbf{q}')\rangle &= 2k_{\mathrm{B}}T\frac{\nu}{\rho}q_{\parallel}^2 q^4 \\ &\quad\times(2\pi)^4\delta(\omega-\omega')\delta(\mathbf{q}-\mathbf{q}'), \\ \langle F_2^*(\omega,\mathbf{q})\cdot F_2(\omega',\mathbf{q}')\rangle &= 2k_{\mathrm{B}}T\frac{D}{\rho}\left(\frac{\partial c}{\partial\mu}\right)_{p,T} q^2 \\ &\quad\times(2\pi)^4\delta(\omega-\omega')\delta(\mathbf{q}-\mathbf{q}'), \\ \langle F_1^*(\omega,\mathbf{q})\cdot F_2(\omega',\mathbf{q}')\rangle &= \langle F_2^*(\omega,\mathbf{q})\cdot F_1(\omega',\mathbf{q}')\rangle = 0, \end{aligned} \tag{15}$$

where $\mu = \mu_1 - \mu_2$ is the difference between the chemical potentials per unit mass of the two components of the mixture, k_{B} is Boltzmann's constant, and $q_{\parallel}$ represents the magnitude of the wave vector $\mathbf{q}$ in the xy-plane, *i.e.*, $q_{\parallel}^2 = q_x^2 + q_y^2$. Note that the correlation functions between the random-noise terms F_1 and F_2 are short ranged both in space and in time, as they are represented by delta functions. Now, inverting Eqs. (12) and using Eqs. (14) and (15), we obtain for the nonequilibrium structure factor of the binary liquid, in the Le → 0 approximation

$$S(\omega,\mathbf{q}) = S_{\mathrm{E}}\left[1 + \frac{(\nabla c_0)^2}{\nu D}\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\frac{q_{\parallel}^2}{q^6}\right]\frac{2\,Dq^2}{\omega^2 + D^2q^4}, \tag{16}$$

where S_{E} is the equilibrium static structure factor, given by [70]

$$S_{\mathrm{E}} = \frac{k_{\mathrm{B}}T}{\rho}\left(\frac{\partial n}{\partial c}\right)^2_{p,T}\left(\frac{\partial c}{\partial \mu}\right)_{p,T}. \tag{17}$$

Integration of Eq. (16) for $S_{\mathrm{NE}}(\omega, \mathbf{q})$ over all frequencies ω, yields the static structure factor $S(\mathbf{q}) = 1/(2\pi)\int S(\omega, \mathbf{q})\, d\omega$

$$S(\mathbf{q}) = S_{\mathrm{E}}\left\{1 + \tilde{S}^0_{\mathrm{NE}}\frac{\tilde{q}_{\parallel}^2}{\tilde{q}^6}\right\}, \tag{18}$$

with $\tilde{q} = qL$ and

$$\tilde{S}^0_{\mathrm{NE}} = \left(\frac{\partial \mu}{\partial c}\right)_{p,T}\frac{(\nabla c_0)^2 L^4}{\nu D}. \tag{19}$$

In Eqs. (18) and (19) we have introduced the finite height of the liquid layer L to write the result as a function of dimensionless wave numbers so as to facilitate the comparison with the finite-size calculation to be performed in next section. We note that both the dynamic structure factor, given by Eq. (16), and the static structure factor, given by Eq. (18), have an equilibrium and a nonequilibrium contribution. For the equilibrium contribution, as expected, we recover the well known expression for the concentration fluctuations of a binary liquid in thermal equilibrium [70]. The dimensionless product $\tilde{S}^0_{\mathrm{NE}}\tilde{q}_{\parallel}^2/\tilde{q}^6$ inside the brackets in Eqs. (16) and (18) represents the modification (enhancement) to the Rayleigh scattering due to the nonequilibrium concentration fluctuations resulting from the presence of a concentration gradient. The intensity of the nonequilibrium fluctuations is proportional to the square of the concentration gradient $(\nabla c_0)^2$ and inversely proportional to the fourth power of the wave number q^{-4}. This algebraic type of dependence on the wave number q is now considered to be a general feature of fluctuations in system in stationary nonequilibrium states [13, 71, 72].

For a further discussion of the theory of the "bulk" nonequilibrium concentration fluctuations presented here, we refer to a recent review [51]. The important point to be noted for the purpose of the present paper is that the validity of Eqs. (16) and (18) has been verified by light-scattering experiments in a polymer solution in the dilute and semi-dilute solution regime where the theory should be applicable [60, 61]. In addition, the theory has also further been confirmed by shadowgraph experiments performed in free-diffusion processes [73, 74]. As mentioned in Sec. 3, because of the Le → 0 approximation, Eqs. (16) and (18) are also applicable to isothermal diffusion.

5. Modifications of the structure factor due to finite-size effects

Equations (16) and (18) imply that the intensity of the non-equilibrium fluctuations would diverge as $q \to 0$. However, there are two other effects that have to be considered for very small q. First, for fluctuations with very long wavelengths one can no longer neglect the bouyancy term in Eq. (2). As commented earlier, for negative Rayleigh numbers gravity causes a long-wavelength damping of the non-equilibrium fluctuations, causing the non-equilibrium enhancement to saturate and reach a finite limit at $q \to 0$ [47, 50–53]. Second, when the wavelength of the fluctuations is no longer small compared to the height L of the liquid layer, limitations due to the boundary conditions imposed by the horizontal plates confining the liquid layer need to be taken into account. In a previous publication we have demonstrated how the effect of gravity can readily be incorporated in the derivation of the contribution of non-equilibrium concentration fluctuations to the "bulk" structure factor described in Sec. 4 [51]. In the present paper we focus our attention on the modification of Eq. (18) for the intensity of the non-equilibrium concentration fluctuations due to the presence of boundaries at $z = 0$ and at $z = L$. In doing so, we follow a procedure previously used for evaluating finite-size effects on the non-equilibrium temperature and viscous fluctuations in a one-component liquid [54, 55].

As in Sec. 4, we again Fourier transform in time and space but, to accomodate the effect of boundary conditions in the z-direction we restrict the spatial Fourier transformation to the x and y directions, parallel to the plates. We then deduce from Eqs. (10) and (11) the following set of linear differential equations

$$\begin{bmatrix} -\nu\left(\dfrac{d^2}{dz^2} - q_{\parallel}^2\right)^2 & 0 \\ \nabla c_0 & i\omega - D\left(\dfrac{d^2}{dz^2} - q_{\parallel}^2\right) \end{bmatrix} \begin{bmatrix} w(\omega, \mathbf{q}_{\parallel}, z) \\ \Gamma(\omega, \mathbf{q}_{\parallel}, z) \end{bmatrix} = \begin{bmatrix} F_1(\omega, \mathbf{q}_{\parallel}, z) \\ F_2(\omega, \mathbf{q}_{\parallel}, z) \end{bmatrix}, \tag{20}$$

where $F_1(\omega, \mathbf{q}_{\parallel}, z)$ and $F_2(\omega, \mathbf{q}_{\parallel}, z)$ represent now partial transforms of the random-noise terms F_1 and F_2 in Eqs. (10) and (11). They have complicated expressions as a function of the partial Fourier transform $\delta\mathrm{T}(\omega, \mathbf{q}_{\parallel}, z)$ and $\delta\mathbf{J}(\omega, \mathbf{q}_{\parallel}, z)$, but the actual expressions are similar to those obtained for the problem of nonequilibrium fluctuations in a one-component liquid presented in a previous publication [55]. As is often done in the literature [7, 9, 59], for the sake of simplicity, we assume here stress-free boundary conditions for the vertical velocity and permeable walls for the concentration, so that

$$\begin{aligned} \Gamma(\omega, \mathbf{q}_\parallel, z) &= 0 \qquad \text{at} \qquad z = 0, L, \\ w(\omega, \mathbf{q}_\parallel, z) &= 0 \qquad \text{at} \qquad z = 0, L, \\ \frac{d^2}{dz^2} w(\omega, \mathbf{q}_\parallel, z) &= 0 \qquad \text{at} \qquad z = 0, L. \end{aligned} \tag{21}$$

Note that these boundary conditions imply the absence of any possible fluctuations in the concentration and velocity of the fluid adjacent to the walls. The set of boundary conditions [Eqs. (21)] corresponds to a liquid bounded by two free and permeable surfaces, which is rather unrealistic [59, 75]. For the case of a liquid confined between two rigid and impermeable surfaces, no-slip boundary conditions in the velocity and zero value of the z derivative of the concentration are more appropriate [9, 59]. Nevertheless, for the sake of mathematical simplicity, we adopt here the boundary conditions given by Eqs. (21). We expect that the conclusions of this work will be modified only quantitatively, not qualitatively, for the more realistic no-slip impermeable boundary conditions, as is the case for the nonequilibrium fluctuations in a one-component liquid [55].

To search for a solution of Eqs. (20) we represent $w(\omega, \mathbf{q}_\parallel, z)$ and $\Gamma(\omega, \mathbf{q}_\parallel, z)$ as a series expansion in a complete set of eigenfunctions satisfying the boundary conditions [Eqs. (21)]. Because of the simplicity of these boundary conditions, an appropriate set of eigenfunctions is just given by the Fourier sine basis in the $[0, L]$ interval [58]. We thus assume:

$$\begin{bmatrix} w(\omega, q_\parallel, z) \\ \Gamma(\omega, q_\parallel, z) \end{bmatrix} = \sum_{N=1}^{\infty} \begin{bmatrix} A_N(\omega, \mathbf{q}_\parallel) \\ B_N(\omega, \mathbf{q}_\parallel) \end{bmatrix} \sin\left(\frac{N\pi z}{L}\right). \tag{22}$$

To deduce the coefficients $A_N(\omega, q_\parallel)$ and $B_N(\omega, q_\parallel)$ from Eqs. (20), we need to represent the random-noise terms $F_1(\omega, \mathbf{q}_\parallel, z)$ and $F_2(\omega, \mathbf{q}_\parallel, z)$ also as a Fourier sine series

$$\begin{bmatrix} F_1(\omega, \mathbf{q}_\parallel, z) \\ F_2(\omega, \mathbf{q}_\parallel, z) \end{bmatrix} = \sum_{N=1}^{\infty} \begin{bmatrix} F_{1,N}(\omega, q_\parallel) \\ F_{2,N}(\omega, q_\parallel) \end{bmatrix} \sin\left(\frac{N\pi z}{L}\right), \tag{23}$$

where we have introduced the set of random functions $F_{1,N}(\omega, \mathbf{q}_\parallel)$ and $F_{2,N}(\omega, \mathbf{q}_\parallel)$, which are the projections of the random-noise terms onto the eigenfunction basis. They are given by

$$\begin{bmatrix} F_{1,N}(\omega, q_\parallel) \\ F_{2,N}(\omega, q_\parallel) \end{bmatrix} = \frac{2}{L} \int_0^L \begin{bmatrix} F_1(\omega, \mathbf{q}_\parallel, z) \\ F_2(\omega, \mathbf{q}_\parallel, z) \end{bmatrix} \sin\left(\frac{N\pi z}{L}\right) dz. \tag{24}$$

Representing the random-noise terms by Eqs. (23), one readily deduces from Eqs. (20) expressions for the coefficients of the Fourier series $A_N(\omega, q_\parallel)$ and $B_N(\omega, q_\parallel)$

$$A_N(\omega, q_\parallel) = \frac{F_{1,N}(\omega, q_\parallel)}{\nu\left(\dfrac{N^2\pi^2}{L^2} + q_\parallel^2\right)^2}, \tag{25}$$

and

$$B_N(\omega, q_\parallel) = \frac{F_{2,N}(\omega, q_\parallel) - A_N(\omega, q_\parallel)\nabla c_0}{\left[i\omega + D\left(\dfrac{N^2\pi^2}{L^2} + q_\parallel^2\right)\right]}. \tag{26}$$

In this paper we are interested in the autocorrelation function of the concentration fluctuations. It follows from Eqs. (22) that this function can be expressed as

$$\langle \Gamma^*(\omega, \mathbf{q}_\parallel, z) \cdot \Gamma(\omega', \mathbf{q}'_\parallel, z') \rangle = \sum_{N=1}^{\infty} \sum_{M=1}^{\infty} \langle B_N^*(\omega, q_\parallel) \cdot B_M(\omega', q'_\parallel) \rangle \sin\left(\frac{N\pi}{L} z\right) \sin\left(\frac{M\pi}{L} z'\right). \tag{27}$$

To evaluate the autocorrelation function $\langle B_N^*(\omega, q_\parallel) \cdot B_M(\omega', q'_\parallel) \rangle$, it is necesary to evaluate the correlation functions between the different projections of the random-noise terms, $F_{1,N}(\omega, \mathbf{q}_\parallel)$ and $F_{2,N}(\omega, \mathbf{q}_\parallel)$. The autocorrelation function $\langle F_{1,N}^*(\omega, \mathbf{q}_\parallel) \cdot F_{1,M}(\omega', \mathbf{q}'_\parallel) \rangle$ has been evaluated previously [54]. For the purpose of the present paper we have evaluated for the first time the autocorrelation $\langle F_{2,N}^*(\omega, \mathbf{q}_\parallel) \cdot F_{2,M}(\omega', \mathbf{q}'_\parallel) \rangle$ as well as the cross correlations. However, the method of evaluation is similar to the one implemented previously for the random heat flow instead of the random solute flow. For further details of the procedure we refer to previous publications [54, 55]. Our final results are

$$\begin{aligned} \langle F_{1,N}^*(\omega, \mathbf{q}_\parallel) \cdot F_{1,M}(\omega', \mathbf{q}'_\parallel) \rangle &= 2k_\mathrm{B}T \frac{\nu}{\rho} \frac{2}{L} q_\parallel^2 \left(q_\parallel^2 + \frac{N^2\pi^2}{L^2}\right)^2 \delta_{NM} (2\pi)^3 \delta(\omega - \omega') \delta(\mathbf{q}_\parallel - \mathbf{q}'_\parallel), \\ \langle F_{1,N}^*(\omega, \mathbf{q}_\parallel) \cdot F_{2,M}(\omega', \mathbf{q}'_\parallel) \rangle &= \langle F_{2,N}^*(\omega, \mathbf{q}_\parallel) \cdot F_{1,M}(\omega', \mathbf{q}'_\parallel) \rangle = 0, \\ \langle F_{2,N}^*(\omega, \mathbf{q}_\parallel) \cdot F_{2,M}(\omega', \mathbf{q}'_\parallel) \rangle &= 2k_\mathrm{B}T \frac{D}{\rho} \left(\frac{\partial c}{\partial \mu}\right)_{p,T} \frac{2}{L} \left(q_\parallel^2 + \frac{N^2\pi^2}{L^2}\right) \delta_{NM} (2\pi)^3 \delta(\omega - \omega') \delta(\mathbf{q}_\parallel - \mathbf{q}'_\parallel). \end{aligned} \tag{28}$$

In this evaluation we continue to assume, as in Sec. 4, that the correlation functions between the different components of the random stress tensor and the random solute flux retain their equilibrium values. This assumption remains valid as long as L is a macroscopic distance, much larger than the molecular distances in the liquid [54].

Equation (14), relating the autocorrelation function of the concentration fluctuations to their contribution to the structure factor now becomes [54, 62]:

$$\langle \Gamma^*(\omega, \mathbf{q}_\parallel, z) \cdot \Gamma(\omega', \mathbf{q}'_\parallel, z')\rangle = \left(\frac{\partial c}{\partial n}\right)^2_{p,T} S(\omega, \mathbf{q}_\parallel, z, z')(2\pi)^3 \delta(\omega - \omega')\delta(\mathbf{q}_\parallel - \mathbf{q}'_\parallel). \tag{29}$$

Substituting Eqs. (26) and (27) into Eq. (29) and making use of Eq. (28), we obtain for the structure factor

$$S(\omega, \mathbf{q}_\parallel, z, z') = S_\mathrm{E} \frac{2}{L} \sum_{N=1}^{\infty} \left[1 + \frac{(\nabla c_0)^2}{\nu D}\left(\frac{\partial \mu}{\partial c}\right)_{p,T} \frac{q_\parallel^2}{\left(q_\parallel^2 + \frac{N^2\pi^2}{L^2}\right)^3}\right] \frac{2D\left(q_\parallel^2 + \frac{N^2\pi^2}{L^2}\right)}{\omega^2 + D^2\left(\frac{N^2\pi^2}{L^2} + q_\parallel^2\right)^2} \times \sin\left(\frac{N\pi}{L} z\right) \sin\left(\frac{N\pi}{L} z'\right), \tag{30}$$

with S_E again defined by Eq. (17).

We note that due to the cylindrical symmetry of the problem, the result depends only on the magnitude $q_\parallel$ of the vector $\mathbf{q}_\parallel$. As in Sec. 4, we are interested here in the static structure factor representing the total intensity of the contribution from the concentration fluctuations, which is obtained by integration over the frequency ω: $S(q_\parallel, z, z') = 1/(2\pi) \int S(\omega, q_\parallel, z, z')\, d\omega$, so that

$$S(\mathbf{q}_\parallel, z, z') = S_\mathrm{E}\left[\delta(z - z') + \tilde{S}^0_\mathrm{NE} \frac{2}{L} \sum_{N=1}^{\infty} \frac{\tilde{q}_\parallel^2 \sin\left(N\pi\tilde{z}\right) \sin\left(N\pi\tilde{z}'\right)}{\left(\tilde{q}_\parallel^2 + N^2\pi^2\right)^3}\right] \tag{31}$$

with $\tilde{S}^0_\mathrm{NE}$ again defined by Eq. (19). As in Eq. (18) we have again introduced a dimensionless wave number $\tilde{q}$ such that $\tilde{q} = qL$. As was the case in the absence of any boundary conditions, the structure factor contains a contribution $S_\mathrm{E}\delta(z - z')$ from short-range equilibrium concentration fluctuations and a contribution from long-range nonequilibrium concentration fluctuations, as further discussed below.

6. Consequences for light-scattering or shadowgraph experiments

In this section we address the question whether the effects due to the finite height of the liquid layer can be observed experimentally. For this purpose we consider the two experimental techniques which, thus far, have been sucessfully employed to observe nonequilibrium fluctuations, namely, small-angle light scattering and shadowgraphy. Small-angle light-scattering has been employed by Sengers and coworkers [38, 39, 60, 61] and by Giglio and coworkers [52, 53, 76]. A schematic representation of such a light-scattering experiment is shown in Fig. 1. The scattering medium is a thin horizontal liquid layer bounded by two parallel plates whose temperatures can be controlled independently so as to establish an uniform temperature gradient across the liquid layer. The temperature gradient can be parallel or antiparallel to the gravity. The horizontal plates are furnished with windows allowing laser light to propagate through the liquid in the direction parallel to the gravity and to the temperature gradient. Light scattered over an angle ϕ arises from fluctuations with a wave number q such that [70]

$$q = 2q_0 \sin\left(\frac{\phi}{2}\right), \tag{32}$$

where q_0 is the wave number of the incident light inside the scattering medium. To observe any nonequilibrium effects one needs to observe the scattered-light intensity at small wave numbers and, hence, at very small scattering angles.

From the electromagnetic theory [70] it follows that the scattering intensity $S(\mathbf{q})$ is obtained from an integration of the structure factor over the scattering volume, so that [54, 62]

$$S(q_\parallel, q_\perp) = \frac{1}{L} \int_0^L \int_0^L \mathrm{e}^{-i q_\perp (z - z')} S(q_\parallel, z, z')\, dz dz'. \tag{33}$$

In Eq. (33) it is assumed that the scattering volume extends over the full height of the fluid layer as is the case in small-angle light scattering from a thin liquid layer. In this situation scattered light received in the collecting pinhole of the detector indeed arises from all the points illuminated by the laser beam over the height of the liquid layer. From the Bragg condition [Eq. (32) and the geometrical arrangement shown in Fig. 1, we note that $q_\parallel$ and $q_\perp$ in an actual light-scattering experiment are not independent variables, because they are related to the scattering angle, ϕ, by

$$q_\parallel = q \cos\left(\frac{\phi}{2}\right) = 2q_0 \sin\left(\frac{\phi}{2}\right) \cos\left(\frac{\phi}{2}\right),$$
$$q_\perp = q \sin\left(\frac{\phi}{2}\right) = 2q_0 \sin^2\left(\frac{\phi}{2}\right). \tag{34}$$

Equation (34) shows that for small-angle experiments $q_\parallel \simeq q$ and $q_\perp \simeq 0$ is a very good approximation. For actual small-angle nonequilibrium light-scattering experiments, this approximation is always adopted.

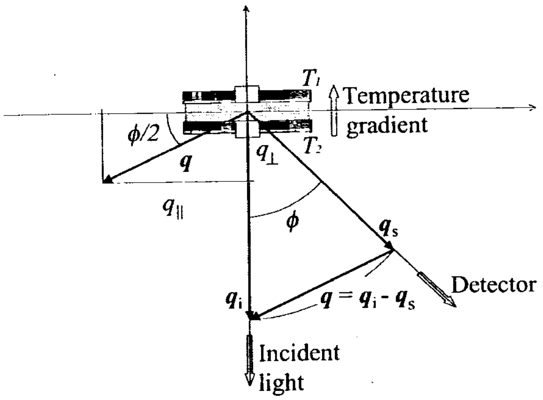

FIGURE 1. Schematic representation of a low-angle nonequilibrium light-scattering experiment. $\mathbf{q}_i$ is the wave vector of the incident light, $\mathbf{q}_s$ is the wave vector of the scattered light. The magnitude $q = |\mathbf{q}_i - \mathbf{q}_s|$ of the scattering wave vector is related to the scattering angle ϕ by $q = 2q_0 \sin(\phi/2)$, where q_0 is the magnitude of the wave vector $\mathbf{q}_i$ of the incident light inside the liquid. For clarity, the magnitude of the scattering angle ϕ has been exaggerated.

Recently, nonequilibrium concentration fluctuations have also been investigated by quantitative shadowgraph techniques [73, 74, 77]. The experimental arrangement is similar to the one depicted in Fig. 1, but instead of using a laser beam, an extended uniform monochromatic light source is employed to illuminate the sample. Then many shadowgraph images of a plane perpendicular to the temperature gradient are obtained with a CCD (Charged Coupled Device) detector, which measures a spatial distribution of intensity $I(\mathbf{x})$, where $\mathbf{x}$ is a two-dimensional position vector in the imaging plane. For each image a shadowgraph signal is defined by

$$i(\mathbf{x}) = \frac{I(\mathbf{x}) - I_0(\mathbf{x})}{I_0(\mathbf{x})}, \tag{35}$$

where $I_0(\mathbf{x})$ is the blank intensity distribution, when there are no fluctuations in the index of refraction of the sample. In practice, $I_0(\mathbf{x})$ is calculated by averaging over many shadowgraph images, so that fluctuations cancel out and the resulting $I_0(\mathbf{x})$ contains only contributions coming from nonuniform illumination of the sample. From physical and geometrical optics, it can be demonstrated that the modulus squared of the two-dimensional Fourier transform of the shadowgraph signal, $|i(\mathbf{q})|^2$, after azimuthal averaging can be expressed as [73, 74, 78]

$$\overline{|i(\mathbf{q})|^2}(q) = \hat{T}(q) S(q_\parallel = q, q_\perp = 0), \tag{36}$$

where the overline indicates an azimuthal average, in which case the result depends only on the magnitude of the two-dimensional Fourier vector $\mathbf{q}$. The symbol $\hat{T}(q)$ represents an optical transfer function, which can be derived from the optical arrangement used to produce the shadowgraph pictures; it includes contributions from the response of the CCD detector and the dependence of refractive index on concentration [73, 74, 78]. Therefore, an analysis of the spectrum of the shadowgraph pictures can be employed to experimentally determine the structure factor of the fluid in the plane $q_\perp = 0$.

It is interesting to note the equivalence between small-angle light-scattering and shadowgraph techniques, in the sense that both methods give us $S(q_\parallel = q, q_\perp = 0)$, where for light scattering q is the scattering wave vector as given by Eq. (32), while for shadowgraph techniques q is the modulus of the two-dimensional Fourier vector in the imaging plane; in both cases the observed $S_{\mathrm{NE}}(q)$ depends only on the magnitude of the wave vector q. As noted by Bodenschatz *et al.*, what it is actually measured in these experiments is a kind of vertical average of the fluctuations [79].

If we substitute Eq. (31) into Eq. (33), using the small-angle approximation $q_\parallel \simeq q$, $q_\perp \simeq 0$, perform the summation of the series in Eq. (31) and the double integration in Eq. (33), we obtain [54]

$$S(\tilde{q}) = S_{\mathrm{E}}\{1 + \tilde{S}^0_{\mathrm{NE}} \tilde{S}_{\mathrm{NE}}(\tilde{q})\}, \tag{37}$$

where $\tilde{S}^0_{\mathrm{NE}}$ was defined previously by Eq. (19), and where $\tilde{S}_{\mathrm{NE}}(\tilde{q})$ is a dimensionless normalized nonequilibrium enhancement, which includes the finite-size effects, given by

$$\tilde{S}_{\mathrm{NE}}(q) = \frac{1}{\tilde{q}^4}\left\{1 + \frac{\tilde{q}^2[\cosh(\tilde{q}) - 1] + \sinh(\tilde{q})[7\tilde{q} - 15\sinh(\tilde{q})]}{4\tilde{q}\sinh(\tilde{q})[\cosh(\tilde{q}) + 1]}\right\}. \tag{38}$$

Equation (38) constitutes our final result for the contribution from the nonequilibrium concentration fluctuations to the structure factor in the small-angle approximation, $q_\parallel \simeq q$. The term inside the square bracket in Eq. (38) accounts for the finite-size effects as can be seen by comparing it with $\tilde{S}_{\mathrm{NE}}(q) = 1/\tilde{q}^4$ deduced by applying the small-angle approximation toEq. (18) for the "bulk" structure factor.

The normalized nonequilibrium concentration-fluctuations enhancement $\tilde{S}_{\mathrm{NE}}(q)$, given by Eq. (38), is plotted in Fig. 2 as a solid curve on a double-logarithmic scale for the case $L = 0.1$ cm, which is typical height of fluid layers in experiments [38, 61, 73, 74]. A simple inspection of the solid curve in Fig. 2 shows that for large values of the wave number q, the term inside the brackets in Eq. (38) approaches unity and we recover the q^{-4} dependence of the nonequilibrium enhancement in the absence of finite-size effects. However, such dependence on q^{-4} cannot go on indefinitely with decreasing wave numbers and, as shown in Fig. 2, the finite size of the system causes a crossover to a q^2 dependence of the nonequilibrium enhancement at very small wave numbers. For $q \to 0$, the nonequilibrium enhancement becomes

$$\tilde{S}_{\mathrm{NE}}(\tilde{q}) \xrightarrow{\tilde{q} \to 0} \frac{17}{20160}\tilde{q}^2, \tag{39}$$

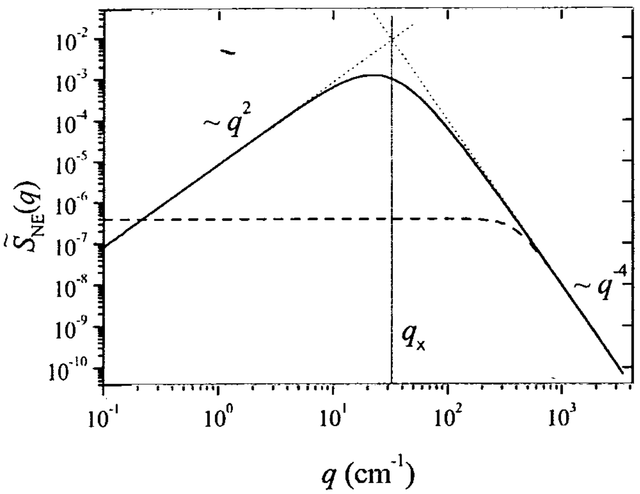

FIGURE 2. Double-logarithmic plot of the wave-number dependence of the normalized nonequilibrium concentration-fluctuation contribution $\tilde{S}_{NE}$. The solid line is $\tilde{S}_{NE}$ taking into account finite-size effects, but neglecting gravity, as given by Eq. (38), for a liquid layer with a height $L = 1$ mm. The dashed line is $\tilde{S}_{NE}$ taking into account gravity effects, but neglecting gravity, as given by Eq. (41), for a "roll-off" scattering wave number $q_{RO} = 400$ cm^{-1}. $q_\times$ is the crossover scattering wave number as defined by Eq. (40).

indeed compensating the divergent q^{-4} dependence when finite-size effects are neglected and causing an asymptotic dependence on q^2, as shown in Fig. 2. From Eq. (39) we may define a characteristic wave number

$$q_\times = \left(\frac{20160}{17}\right)^{1/6}\frac{1}{L} \simeq \frac{3.25}{L}, \tag{40}$$

which, for $L = 0.1$ cm, corresponds to $q_\times \simeq 33$ cm^{-1}. From Fig. 2 we see that $\tilde{S}_{NE}(q)$ exhibits a maximum at $q \simeq q_\times$, so that $q_\times$ may be interpreted as a "crossover" wave number separating the q^{-4} dependence and the q^2 dependence of the nonequilibrium enhancement.

It is worth observing that the existence of a maximum at $\simeq q_\times$ (numerically we find the position of the maximum at about $\simeq 2.222/L = 0.68q_\times$), indicates that, even in the absence of gravity, the simple presence of a temperature gradient selects a particular length scale in the system for which nonequilibrium fluctuations are maximally enhanced. This length scale becomes macroscopically evident above the convective instability, where spatiotemporal patterns with a particular length scale appear.

As mentioned earlier, not only the finite size of the system, but also gravity will cause deviations from the q^{-4} dependence of the nonequilibrium enhancement. These effects were first analyzed by Segrè and Sengers [47], who predicted that the q^{-4} divergence will saturate to a constant value independent of q for small wave numbers. This prediction has been confirmed experimentally [52, 53]. The most recent presentation of gravity effects can be found in Ref. [51], where the problem is studied starting from the linearized fluctuating Boussinesq equations in the small Lewis number approximation. From Eqs. (14) and (15) in Ref. [51], we find that the structure factor of a fluid subjected to a temperature gradient, accounting for the effects of gravity but neglecting finite-size effects, can be rearranged in a form like Eq. (37) such that:

$$S(\tilde{q}) = S_E[1 + \tilde{S}^0_{NE}\tilde{S}_{NE}(\tilde{q})] = S_E\left\{1 + \frac{\tilde{S}^0_{NE}}{\tilde{q}^4 + \tilde{q}^4_{RO}}\right\}. \tag{41}$$

Due to the presence of gravity, there is a slight difference between the dimensionless nonequilibrium enhancement $\tilde{S}^0_{NE}$ in Eq. (41) and $\tilde{S}^0_{NE}$ as defined by Eq. (19). But in practice, this small difference can be neglected. From Eq. (41), we observe that the gravitationally induced saturation of the q^{-4} divergence occurs at a "roll-off" wave number q_{RO} which is given by [51, 52]

$$q_{RO} = \left(\frac{g\beta\nabla T_0}{\nu D}\right)^{1/4}, \tag{42}$$

while $\tilde{q}_{RO} = q_{RO}L$. To facilitate the comparison between gravity and finite-size effects, we have added in Fig. 2, as a dashed curve, the function $S_{NE}(q)$ as given by Eq. (41). For this plot in Fig. 2 we have employed $q_{RO} = 400$ cm^{-1}, which is the value calculated by Vailati and Giglio [52] for a critical mixture of aniline and cyclohexane subjected to a temperature gradient $\nabla T_0 = 163$ Kcm^{-1}. From Fig. 2 we conclude that, depending on the size of the system and the applied temperature gradient, finite-height effects may be equally important as deviations from the q^{-4} behavior due to gravity. Therefore, for the interpretation of actual small-angle light-scattering experiments both effects should be taken into account simultaneously.

From the plots in Fig. 2 it can be also concluded that quenching of the q^{-4} divergence as a result of finite-size effects is even stronger than that caused by gravity, making the nonequilibrium contribution to the scattering function to vanish as $q \to 0$. The conclusion that this crossover from the q^{-4} to the q^2 dependence as a result of the finite size of the system occurs at wave numbers around $q_\times \simeq \pi/L$ seems intuitively plausible. The observation that the nonequilibrium concentration fluctuations vanish as $q \to 0$ is a consequence of the imposed condition of the absence of concentration and velocity fluctuations at the boundaries.

Small-angle nonequilibrium scattering experiments so far performed in liquid mixtures have probed wave numbers down to $q = 100$ cm^{-1} [52]. At such wave numbers deviations from the q^{-4} divergence are likely caused by a mixture of gravity and finite-size effects. Shadowgraph experiments performed with binary liquids [73, 74] have probed wave numbers of a similar magnitude. But for one-component liquids close to the convective instability, shadowgraph experiments probing even smaller wave numbers have been reported [80] (down to $\tilde{q} \simeq 2$). In fluctuations near the convective instability inclusion of both boundary conditions and gravity is essential [81]. Although this topic is beyond the scope of the present paper, we note that such experiments [80] do show a maximum enhancement of non-equilibrium structure factor at a nonzero value of the wave number q.

7. Concluding remarks

In this paper we have evaluated the structure factor in a horizontal layer of a binary liquid with finite height L, subjected to a vertical stationary concentration gradient induced by a temperature gradient through the Soret effect. Rayleigh scattering or shadowgraph experiments probe index-of-refraction fluctuations that, in the small-Lewis-number approximation, arise from concentration fluctuations. We have elucidated how the well known q^{-4} dependence of the nonequilibrium enhancement of the structure factor in a nonequilibrium situation is quenched by the finite height of the system yielding a crossover to a q^2 dependence at very small values of the wave number q of the fluctuations. This means that the simple presence of a temperature gradient selects a particular length scale in the system, for which fluctuations are maximally enhanced. We find that for liquid mixtures the deviations from the q^{-4} behavior due to the finite size of the system could be just as important as deviations caused by the presence of gravity. Therefore, for a quantitative interpretation of low-angle light scattering or shadowgraph experiments, it is important to account for both gravity and finite-size effects simultaneously.

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