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Long-wavelength nonequilibrium concentration fluctuations induced by the Soret effect

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In this paper we evaluate the enhancement of nonequilibrium concentration fluctuations induced by the Soret effect when a binary fluid layer is subjected to a stationary temperature gradient. Starting from the fluctuating Boussinesq equations for a binary fluid in the large-Lewis-number approximation, we show how one can obtain an exact expression for the nonequilibrium structure factor in the long-wavelength limit for a fluid layer with realistic impermeable and no-slip boundary conditions. A numerical calculation of the wave-number dependence of the nonequilibrium enhancement and of the corresponding decay rate of the concentration fluctuations is also presented. Some physical consequences of our results are briefly discussed.

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I. INTRODUCTION

During the past decades it has become feasible to use quantitative shadowgraphy [1,2] for measuring the intensity of nonequilibrium concentration fluctuations induced by the Soret effect at very small (horizontal) wave numbers q, (i.e., fluctuations with very large length scales). At the small wave numbers probed by shadowgraphy, the intensity of nonequilibrium fluctuations in fluid layers is strongly affected by both gravity and confinement effects. The effects of gravity on nonequilibrium concentration fluctuations have been evaluated theoretically some time ago [3] and the predictions have been confirmed experimentally [4–6], at least qualitatively. The main conclusion of these investigations is that for negative Rayleigh numbers gravity has a damping effect on the nonequilibrium fluctuations, quenching their intensity so that it crosses over from the well-known q^{-4} dependence for large q (which is independent of gravity) to a constant limit at $q \to 0$. However, as previous investigations for a one-component fluid have shown [7,8], effects due to the finite size of the system are also important at these small wave numbers. Furthermore, for positive Rayleigh numbers at which gravity is destabilizing but the system is still stable, confinement becomes the most important effect in the range of wave numbers examined by shadowgraphy.

For these reasons it is interesting to evaluate the combined effects of gravity and confinement on nonequilibrium concentration fluctuations. Previous attempts to address this problem have used mathematically convenient but physically unrealistic boundary conditions [9] or, for realistic boundary conditions, a Galerkin approximation [10]. In the present communication we shall present an *exact* evaluation of the intensity of nonequilibrium concentration fluctuations in the small-q limit with realistic boundary conditions. To simplify the problem we shall adopt a large-Lewis-number ($\mathrm{Le} = a/D$, with a being the thermal diffusivity of the mixture and D the mutual diffusion coefficient) approximation to the Boussinesq equations for a binary mixture, which neglects any contribution from temperature fluctuations. In previous works [11] we have used this approximation to obtain the intensity of "bulk" (i.e., without accounting for boundary conditions) nonequilibrium concentration fluctuations induced by the Soret effect. Other investigators [12,13] have employed the same weak diffusivity (large-Le) approach to study the convective instability in binary liquid mixtures. Consistent with the large-Le approximation, the results of the present paper apply only to mixtures with positive separation ratio.

In this paper we use stochastic fluid mechanics [14] or fluctuating hydrodynamics [15]. Although deterministic (i.e., nonstochastic) fluid mechanics has been successfully employed over the years to describe fluid flows, a correct description of a fluid at a mesoscopic level requires the consideration of stochastic forces (thermal noise). Furthermore, as will be discussed in detail later, our present results add to growing evidence that fluctuating hydrodynamics provides an alternative framework for the theoretical study of fluid stability. Indeed, the presence of a hydrodynamic instability causes the enhancement of nonequilibrium fluctuations to diverge for a certain critical wave number [16].

We shall start by presenting in Sec. II the random Boussinesq equations and shall elucidate how they can be solved in the presence of boundary conditions. The method leads to the presence of so-called mode-coupling coefficients that are discussed more extensively in Sec. III. In Secs. IV and V we show how the hydrodynamic structure factor can be expressed in terms of the mode-coupling coefficients and the decay rates of the hydrodynamic operator. In Sec. VI we derive an explicit expression for the hydrodynamic structure factor in the limit of small wave numbers and in Sec. VII we present the results of a numerical calculation of the structure factor for arbitrary wave numbers. Some conclusions that can be drawn from our analysis are discussed in Sec. VIII.

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II. FLUCTUATING BINARY BOUSSINESQ EQUATIONS AT LARGE Le

To describe fluctuations in a fluid layer confined between two horizontal bounding plates, which are maintained at different temperatures, we start from the linearized fluctuating Boussinesq equations for a binary mixture. The Boussinesq approximation is based on the assumption that the separation between the bounding plates is small enough so that the spatial variation of the thermophysical properties in the fluid layer can be neglected, except for the dependence of the density in the buoyancy terms as a function of temperature and concentration. More details on the justification of Boussinesq approximation can be found in the relevant literature [17,18]. Moreover, to further simplify the working equations we adopt a large-Lewis-number approximation [12]. This approximation has been employed successfully previously [11] for calculating the structure factor of the nonequilibrium fluid in the absence of boundary conditions. In the large-Le limit, the linearized random Boussinesq equations read

$$0=\nu\nabla^4\delta v_z-\beta g(\partial_x^2+\partial_y^2)\delta c+\frac{1}{\rho}\{\boldsymbol{\nabla}\times[\boldsymbol{\nabla}\times(\boldsymbol{\nabla}\cdot\delta\Pi)]\}_z, \tag{1a}$$

$$\partial_t\delta c=D\nabla^2\delta c-\delta v_z\nabla c_0-\frac{1}{\rho}\boldsymbol{\nabla}\cdot\delta\mathbf{J}, \tag{1b}$$

where $\delta v_z(\mathbf{r},t)$ and $\delta c(\mathbf{r},t)$ represent the fluctuations in the vertical component of the velocity and in the solute mass fraction, respectively. Here, ν represents the kinematic viscosity, ρ the density, and g the gravitational acceleration constant. For convenience, we assume that the heavier component is chosen to represent the (mass fraction) concentration c of the mixture, so that without loss of generality we can assume the solutal expansion coefficient $\beta>0$. In Eqs. (1) it is assumed that the stationary concentration gradient ∇c_0 is induced, through the Soret effect, by an externally applied stationary temperature gradient. Hence, the concentration gradient will be parallel (or antiparallel) to the temperature gradient (directed in the vertical z direction) and the magnitude ∇c_0 of the concentration gradient will be related to the magnitude ∇T_0 of the imposed temperature gradient by

$$\nabla c_0=-c(1-c)S_T\nabla T_0, \tag{2}$$

where S_T represents the Soret coefficient of the binary mixture. Sometimes, to describe thermal diffusion a separation ratio, ψ, is introduced by [19],

$$\psi=\frac{\beta}{\alpha_T}c(1-c)S_T, \tag{3}$$

where α_T is the thermal expansion coefficient of the mixture. The separation ratio has the advantage that its sign is independent of the component selected to define the concentration c of the mixture [11].

In accordance with the basic principles of fluctuating hydrodynamics [15,16], we have added to the right-hand-side (RHS) of Eqs. (1) the random components of the dissipative fluxes, namely $\delta\Pi(\mathbf{r},t)$ representing a random deviatoric stress tensor and $\delta\mathbf{J}(\mathbf{r},t)$ representing a random diffusion flow. As discussed elsewhere [11,12], the large-Le limit implies that temperature fluctuations, and also the associated random heat flux, are neglected. For later use, we need the correlation functions among the components of the dissipative fluxes, which are given by the fluctuation-dissipation theorem for a (incompressible) binary fluid mixture, namely [16,20],

$$\begin{aligned}\langle\delta\Pi_{ij}(\mathbf{r},t)\cdot\delta\Pi_{kl}(\mathbf{r}',t')\rangle&=2k_B\bar{T}_0\eta(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})\\&\quad\times\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'),\\ \langle\delta J_i(\mathbf{r},t)\cdot\delta J_j(\mathbf{r}',t')\rangle&=2k_B\bar{T}_0\rho D\left(\frac{\partial c}{\partial\mu}\right)_{p,T}\delta_{ij}\\&\quad\times\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'),\end{aligned} \tag{4}$$

while, by virtue of the Curie principle, the random stress and random diffusion are uncorrelated. In Eqs. (4) k_B is the Boltzmann's constant, $\eta=\nu\rho$ represents the shear viscosity and $\mu=\mu_1-\mu_2$ represents the difference of chemical potentials (per unit mass) between the heavier (1) and the lighter (2) components of the mixture. Its derivative with respect to the concentration (always positive) is often expressed in terms of the osmotic compressibility [21]. For later application of the fluctuation-dissipation theorem (4), we have identified the temperature $T_0(\mathbf{r})$ with its average value $\bar{T}_0$ in the fluid layer; the same approximation is used for the other fluid properties. This approximation is consistent with the Boussinesq approximation and it has been shown to be adequate for the evaluation of the dominant nonequilibrium effects on the fluctuations [22]. Indeed, the nonequilibrium effects on fluctuations arising from inhomogeneously correlated thermal noise are negligible compared to those arising from the coupling between fluctuating fields, as e.g, appearing in Eq. (1b) [22].

Finally, to complete the formulation of our problem, we need the boundary conditions for the fluctuating fields. In this paper we shall consider realistic rigid and impermeable walls, so that the relevant boundary conditions are

$$\delta v_z=\partial_z\delta v_z=\partial_z\delta c=0,\quad \text{at } z=\pm\tfrac{1}{2}L. \tag{5}$$

Since in the large-Le approximation temperature fluctuations are neglected, there is no contribution from the Soret effect to the solute flux at the walls.

To solve the system of stochastic differential equations (1) subjected to the boundary conditions (5), as usual [23,24], we apply a Fourier transformation in time and in the horizontal plane, so as to obtain

$$\begin{pmatrix}\nu(q_\parallel^2-\partial_z^2)^2 & \beta g q^2\\ \nabla c_0 & i\omega+D(q_\parallel^2-\partial_z^2)\end{pmatrix}\begin{pmatrix}\delta v_z\\ \delta c\end{pmatrix}=\mathbf{F}(\omega,\mathbf{q}_\parallel,z), \tag{6}$$

where $\mathbf{q}_\parallel=\{q_x,q_y\}$ is a Fourier wave vector in the horizontal plane and $q_\parallel$ its magnitude. Next, to solve Eq. (6), we apply a method previously developed to solve the fluctuating Boussinesq equations for a one-component fluid [24]. Thus, we shall consider the following eigenvalue problem:

$$\mathcal{H}\cdot\mathbf{U}_N^{(\mathrm{R})}(q_\parallel,z)=\Gamma_N(q_\parallel)[\mathcal{D}\cdot\mathbf{U}_N^{(\mathrm{R})}(q_\parallel,z)], \tag{7}$$

where the (right) eigenfunctions

$$\mathbf{U}_N^{(\mathrm{R})}(q_\parallel,z)=\begin{bmatrix} V_N(q_\parallel,z)\\ \Xi_N(q_\parallel,z)\end{bmatrix}, \tag{8}$$

must satisfy for $z=\pm\frac{1}{2}L$ the boundary conditions

$$V_N(q_\parallel,z)=0,$$

$$\partial_z V_N(q_\parallel,z)=0,$$

$$\partial_z \Xi_N(q_\parallel,z)=0. \tag{9}$$

In Eq. (7) we have introduced (linear) differential operators $\mathcal{H}$ and $\mathcal{D}$ defined by

$$\mathcal{H}=\begin{pmatrix} \nu(q_\parallel^2-\partial_z^2)^2 & \beta g q^2\\ \nabla c_0 & D(q_\parallel^2-\partial_z^2)\end{pmatrix},$$

$$\mathcal{D}=\begin{pmatrix} 0 & 0\\ 0 & 1\end{pmatrix}. \tag{10}$$

We have anticipated that the solution to Eq. (7) subjected to boundary conditions (9) is an infinite numerable set of eigenvalues Γ_N and corresponding right eigenfunctions $\mathbf{U}_N^{\mathrm{R}}(q_\parallel,z)$ (see Sec. V below), and we have used the index N to distinguish among the infinite number of solutions.

To understand how the eigenvalue problem (7) is used to solve Eq. (6), we must consider the adjoint of the hydrodynamic operator, $\mathcal{H}^\dagger$. Here, we shall adopt the usual definition of adjoint [25], so that for any pair of two-dimensional functions $\mathbf{U}_1(z)=\{V_1(z),\Xi_1(z)\}$ and $\mathbf{U}_2(z)=\{V_2(z),\Xi_2(z)\}$, defined in the interval $z\in\left[-\frac{1}{2}L,\frac{1}{2}L\right]$ and satisfying the boundary conditions (9), the adjoint $\mathcal{H}^\dagger$ of the hydrodynamic operator satisfies

$$\int_{-(1/2)L}^{(1/2)L}\mathbf{U}_1^*\cdot(\mathcal{H}\mathbf{U}_2)dz=\int_{-(1/2)L}^{(1/2)L}(\mathcal{H}^\dagger\mathbf{U}_1)^*\cdot\mathbf{U}_2 dz. \tag{11}$$

An explicit expression for the adjoint of $\mathcal{H}$ can be obtained by simple inspection,

$$\mathcal{H}^\dagger=\begin{pmatrix} \nu(q_\parallel^2-\partial_z^2)^2 & \nabla c_0\\ \beta g q_\parallel^2 & D(q_\parallel^2-\partial_z^2)\end{pmatrix}. \tag{12}$$

Indeed, upon substitution of $\mathcal{H}^\dagger$ given by Eq. (12), it can be shown that Eq. (11) holds in the usual way [25], i.e., by integrating by parts and by using the boundary conditions (9). Next, in addition to the eigenvalue problem (7), let us consider the "adjoint" problem, namely

$$\mathcal{H}^\dagger\cdot\mathbf{U}_N^{(\mathrm{L})}(q_\parallel,z)=\Gamma_N^*(q_\parallel)\mathcal{D}\cdot\mathbf{U}_N^{(\mathrm{L})}(q_\parallel,z), \tag{13}$$

where we have anticipated that the left eigenvalues are the complex conjugates of the right eigenvalues. Indeed, corresponding to the solution (8) of Eq. (7) with decay rate Γ_N, another two-dimensional function can be constructed,

$$\mathbf{U}_N^{(\mathrm{L})}(q_\parallel,z)=\begin{bmatrix} \nabla c_0 V_N(q_\parallel,z)\\ \beta g q_\parallel^2 \Xi_N(q_\parallel,z)\end{bmatrix}, \tag{14}$$

which is a solution of the adjoint problem, Eq. (13), with eigenvalue Γ_N^*, as can be easily demonstrated by simple substitution and by taking into account the expressions (10) and (12) of the hydrodynamic operator and its adjoint.

Next, on comparing the right and left problem, Eqs. (7) and (13), respectively, and by using that the differential operator $\mathcal{D}$ is self-adjoint: $\mathcal{D}^\dagger=\mathcal{D}$, it can be readily demonstrated that [25]

$$[\Gamma_M(q_\parallel)-\Gamma_N(q_\parallel)]\int_{-(1/2)L}^{(1/2)L}\mathbf{U}_N^{(\mathrm{L})*}(q_\parallel,z)\{\mathcal{D}\mathbf{U}_M^{(\mathrm{R})}(q_\parallel,z)\}dz=0. \tag{15}$$

Equation (15) implies that the integral must be zero for $N\neq M$. Hence, the set of right eigenfunctions has the important property of being "orthogonal" to the set of left eigenfunctions [25], in the sense that

$$\int_{-(1/2)L}^{(1/2)L}\mathbf{U}_N^{(\mathrm{L})*}(q_\parallel,z)\{\mathcal{D}\mathbf{U}_M^{(\mathrm{R})}(q_\parallel,z)\}dz=B_N(q_\parallel)\,\delta_{NM}, \tag{16}$$

where B_N is to be interpreted as the "norm" of the (right) eigenfunction $\{V_N,\Xi_N\}$, or

$$B_N(q_\parallel)=\beta g q_\parallel^2\int_{-(1/2)L}^{(1/2)L}\Xi_N^2(q_\parallel,z)dz. \tag{17}$$

At this point it should be mentioned that, upon following an argument similar to that of Schmitz and Cohen [24] for a one-component fluid, it can be demonstrated that $\Gamma_N^*=\Gamma_N$, implying that the eigenvalues are real. As a consequence, the eigenfunctions can also be normalized to be real-valued functions (see Sec. V below). Notice that, since the eigenfunctions are real, their norms $B_N(q_\parallel)$ will be real and positive.

We now have all the ingredients needed to solve the linear stochastic differential equation (7) with the boundary conditions (5) by expanding the solution in a series of right eigenfunctions,

$$\begin{pmatrix}\delta v_z(\omega,\mathbf{q}_\parallel,z)\\ \delta c(\omega,\mathbf{q}_\parallel,z)\end{pmatrix}=\sum_{N=1}^{\infty}G_N(\omega,\mathbf{q}_\parallel)\begin{pmatrix}V_N(q_\parallel,z)\\ \Xi_N(q_\parallel,z)\end{pmatrix}. \tag{18}$$

Since the eigenfunctions satisfy the boundary conditions (9), the fluctuating fields, represented as a series of eigenfunctions, will satisfy the boundary conditions (5). To obtain the coefficients $G_N(\omega,\mathbf{q}_\parallel)$, we substitute Eq. (18) into Eq. (6) and then project (with the usual scalar product) the result onto the set of left eigenfunctions $\mathbf{U}_M^{(\mathrm{L})}$. Using the orthogonality relationship, Eq. (16), we readily solve for the amplitudes of the linear response operator,

$$G_N(\omega,\mathbf{q}_\parallel)=\frac{F_N(\omega,\mathbf{q}_\parallel)}{B_N(q_\parallel)[i\omega+\Gamma_N(q_\parallel)]}, \tag{19}$$

where the parameter $F_N(\omega,\mathbf{q}_\parallel)$ represent the projection (with the usual scalar product) of the random noise vector $\mathbf{F}$ onto the Nth left eigenfunction, namely

$$\begin{aligned}F_N(\omega,\mathbf{q}_\parallel)&=\int_{-(1/2)L}^{(1/2)L}\mathbf{U}_N^{(\mathrm{L})*}(q_\parallel,z)\cdot\mathbf{F}(\omega,\mathbf{q}_\parallel,z)dz\\&=\int_{-(1/2)L}^{(1/2)L}[\nabla c_0 V_N(q_\parallel,z)F_0(\omega,\mathbf{q}_\parallel,z)\\&\quad+\beta g q_\parallel^2\Xi_N(q_\parallel,z)F_1(\omega,\mathbf{q}_\parallel,z)]dz.\end{aligned}\tag{20}$$

Here, $F_0(\omega,\mathbf{q}_\parallel,z)$ and $F_1(\omega,\mathbf{q}_\parallel,z)$ are the components of the vector of random forces appearing on the RHS of Eq. (6); for instance,

$$\begin{aligned}F_1(\omega,\mathbf{q}_\parallel,z)=\frac{-1}{\rho}\{&iq_x\delta J_x(\omega,\mathbf{q}_\parallel,z)\\&+iq_y\delta J_y(\omega,\mathbf{q}_\parallel,z)+\partial_z\delta J_z(\omega,\mathbf{q}_\parallel,z)\},\end{aligned}\tag{21}$$

while $F_0(\omega,\mathbf{q}_\parallel,z)$ has a more complicated expression that can be found in Ref. [16].

As usual, the eigenvalues Γ_N are referred to as *decay rates*, and the eigenfunctions as *hydrodynamic modes*, or simply *modes*.

III. MODE-COUPLING COEFFICIENTS

Our goal in this paper is to calculate the dynamic structure factor, $S(\omega,\mathbf{q})$, as measured in low-angle light scattering or in shadowgraph experiments. For this purpose, we need the correlation functions among the various random noise terms $F_N(\omega,\mathbf{q}_\parallel)$. From the definition (20) and the (partially Fourier transformed) fluctuation-dissipation theorem for a binary fluid mixture (4), we see that these correlation functions can be conveniently expressed in terms of a noise correlation matrix, namely

$$\begin{aligned}&\left(\frac{\partial n}{\partial c}\right)^2\langle F_N^*(\omega,\mathbf{q}_\parallel)\cdot F_M(\omega',\mathbf{q}'_\parallel)\rangle\\&\quad=C_{NM}(q_\parallel)(2\pi)^3\delta(\omega-\omega')\delta(\mathbf{q}_\parallel-\mathbf{q}'_\parallel),\end{aligned}\tag{22}$$

where n represents the refractive index of the mixture. In Eq. (22) $C_{NM}(q_\parallel)$ are the elements of a noise correlation matrix, and the introduction of the derivative of the index of refraction will simplify expressions for the amplitude of the nonequilibrium fluctuations, see Eq. (29) below. The quantities $C_{NM}(q_\parallel)$ are also referred to as *mode-coupling* coefficients [24], similarly to those in the theory for a one-component fluid [16,23,26], and can be expressed as

$$\begin{aligned}C_{NM}(q_\parallel)=&\left(\frac{\partial n}{\partial c}\right)^2 2k_B\bar{T}_0q_\parallel^2\Bigg\{\frac{(\nabla c_0)^2\nu}{\rho}\int_{-L/2}^{L/2}\int dzdz'V_N^*(q_\parallel,z)\\&\times V_M(q_\parallel,z')\left[q_\parallel^4+q_\parallel^2\left(\frac{d^2}{dz^2}+\frac{d^2}{dz'^2}+4\frac{d}{dz}\frac{d}{dz'}\right)\right.\\&\left.+\frac{d^2}{dz^2}\frac{d^2}{dz'^2}\right]\delta(z-z')\\&+\frac{\beta^2g^2D}{\rho}\left(\frac{\partial c}{\partial\mu}\right)q_\parallel^2\int_{-L/2}^{L/2}\int\Xi_N^*(q_\parallel,z)\Xi_M(q_\parallel,z')\\&\times\left(q_\parallel^2+\frac{d}{dz}\frac{d}{dz'}\right)\delta(z-z')dzdz'\Bigg\}.\end{aligned}\tag{23}$$

In the double integrals of Eq. (23), both variables z and z' vary over the interval $[-L/2,L/2]$. In the derivation of Eq. (23), we have used that the fluctuation-dissipation theorem for a binary liquid mixture (4) includes the property that the cross correlations between the components of the random current and the random diffusion flux vanish.

To simplify Eq. (23) we integrate by parts the different terms, so as to move the differential operators inside the double integrals from the delta functions to the components of the eigenfunctions preceding it. Note that, since in all cases an even number of integrations are required, there will not be any change of sign as a result of this process. After this procedure the differential operators inside the integrals apply to the V_N and Ξ_N functions, and the delta functions are isolated. Thus, the integration in the variable z' can readily be performed. We then continue to integrate by parts, but now using the boundary conditions (9), so as to finally obtain

$$\begin{aligned}C_{NM}(q_\parallel)=S_\mathrm{E}2q_\parallel^2\Bigg\{&(\nabla c_0)^2\nu\left(\frac{\partial\mu}{\partial c}\right)\int_{-L/2}^{L/2}V_N^*(q_\parallel,z)\\&\times[(q_\parallel^2-\partial_z^2)^2V_M(q_\parallel,z)]dz+\beta^2g^2Dq_\parallel^2\\&\times\int_{-L/2}^{L/2}\Xi_N^*(q_\parallel,z)\\&\times[(q_\parallel^2-\partial_z^2)\Xi_M(q_\parallel,z)]dz\Bigg\}.\end{aligned}\tag{24}$$

To simplify the notation in Eq. (24), we have introduced the intensity S_E of the equilibrium concentration fluctuations, which is given by [21]

$$S_\mathrm{E}=\left(\frac{\partial n}{\partial c}\right)_T^2\frac{k_B\bar{T}_0}{\rho}\left(\frac{\partial c}{\partial\mu}\right)_T.\tag{25}$$

Notice that from Eq. (23), and recalling that the hydrodynamic modes are real, it follows that $C_{NM}(q_\parallel)=C_{MN}(q_\parallel)$, which means that the matrix of mode-coupling coefficients is symmetric. Combining the fact that the decay rates and the hydrodynamic modes are real numbers with the right eigenvalue problem, Eq. (7), and the orthogonality condition (16), we can further simplify Eq. (24) for the mode-coupling coefficients and conveniently split them as the sum of two contributions, namely

$$C_{NM}(q_\parallel)=S_\mathrm{E}[2\beta gq_\parallel^2\Gamma_N(q_\parallel)B_N(q_\parallel)\delta_{NM}+A_D\hat{C}_{NM}^{\mathrm{NE}}(q_\parallel)],\tag{26}$$

where $\hat{C}_{NM}^{\mathrm{NE}}(q_\parallel)$ represents nonequilibrium enhancement coefficients. In terms of the hydrodynamic modes, they are given by

$$\hat{C}_{NM}^{\mathrm{NE}}(q_\parallel)=2\nu^2Dq_\parallel^2\int_{-L/2}^{L/2}V_N^*(q_\parallel,z)[(\partial_z^2-q_\parallel^2)^2V_M(q_\parallel,z)]dz.\tag{27}$$

Furthermore, in Eq. (26) we have introduced the quantity A_D (units of length^{-4}) to represent the strength of the nonequilibrium enhancement. This parameter was previously used in

Ref. [11] for the description of the "bulk" fluctuations (notice that there is a sign error inside the brackets in Eq. (15) of Ref. [11]),

$$A_D = \frac{(\nabla c_0)^2}{\nu D}\left(\frac{\partial \mu}{\partial c}\right) + \frac{\beta g \nabla c_0}{\nu D}. \tag{28}$$

It is obvious from Eq. (28) that the contributions to the mode-coupling coefficients from the nonequilibrium enhancement coefficients $\hat{C}^{\mathrm{NE}}_{NM}(q_\parallel)$ vanish in equilibrium, $\nabla T_0 = 0$ (which implies $\nabla c_0 = 0$ if the nonequilibrium concentration fluctuations are induced by the Soret effect). However, it should also be noted that the first term on the RHS of Eq. (26) depends implicitly on the concentration gradient through the decay rates and the normalization constants $B_N(q_\parallel)$.

IV. HYDRODYNAMIC STRUCTURE FACTOR

Similarly to the treatment in previous papers [9,10], the concentration fluctuations autocorrelation may be related to a dynamic structure factor $S(\omega, q_\parallel, z, z')$ by

$$\left(\frac{\partial n}{\partial c}\right)^2 \langle \delta c^*(\omega, \mathbf{q}_\parallel, z)\cdot \delta c(\omega', \mathbf{q}'_\parallel, z')\rangle = S(\omega, q_\parallel, z, z')(2\pi)^3 \delta(\mathbf{q}_\parallel - \mathbf{q}'_\parallel)\delta(\omega - \omega'). \tag{29}$$

Note that in the large-Le approximation temperature fluctuations do not contribute to the structure factor. Substituting Eq. (18) with G_N given by (19) into Eq. (29), taking into account the definition (22) of the mode-coupling coefficients, we immediately obtain for the structure factor

$$S(\omega, q_\parallel, z, z') = \sum_{N,M=0}^{\infty} \frac{C_{NM}(q_\parallel)\Xi^*_N(q_\parallel, z)\Xi_M(q_\parallel, z')}{B^*_N(q_\parallel)B_M(q_\parallel)[-i\omega + \Gamma^*_N(q_\parallel)][i\omega + \Gamma_M(q_\parallel)]}. \tag{30}$$

By construction, Eq. (30) for the dynamic structure factor contains the effects of both gravity and confinement of the fluid layer. In this paper we are primarily interested in the static structure factor, $S(q_\parallel, z, z')$, which is $1/(2\pi)$ times the integral of $S(\omega, q_\parallel, z, z')$ over the frequency ω [21]. Hence, if we integrate Eq. (30) over the frequency, upon substitution of Eq. (26) for the mode-coupling coefficients, we obtain for the static structure factor

$$S(q_\parallel, z, z') = S_{\mathrm{E}}\left(\sum_{N=0}^{\infty} \frac{\beta g q_\parallel^2}{B_N(q_\parallel)}\Xi_N(q_\parallel, z)\Xi_N(q_\parallel, z') + \hat{S}_{\mathrm{NE}}(q_\parallel, z, z')\right) = S_{\mathrm{E}}[\delta(z - z') + \hat{S}_{\mathrm{NE}}(q_\parallel, z, z')], \tag{31}$$

where the enhancement of nonequilibrium concentration fluctuations is given by

$$\hat{S}_{\mathrm{NE}}(q_\parallel, z, z') = A_D \sum_{N,M=0}^{\infty} \frac{\hat{C}^{\mathrm{NE}}_{NM}(q_\parallel)\Xi_N(q_\parallel, z)\Xi_M(q_\parallel, z')}{B_N(q_\parallel)B_M(q_\parallel)[\Gamma_N(q_\parallel) + \Gamma_M(q_\parallel)]}. \tag{32}$$

In deducing Eqs. (31) and (32) use has been made of the fact that for the eigenproblem (7) under consideration, the decay rates are real numbers. As a consequence, both the normalization constants $B_N(q_\parallel)$ and the hydrodynamic modes $\Xi_N(q_\parallel, z)$ can be chosen to be real-valued functions, see Sec. V below. The summation contained in the second line of Eq. (31) can be elucidated by considering the two-dimensional vector function,

$$\mathbf{G}(z') = \begin{pmatrix} 0 \\ \delta(z - z') \end{pmatrix}. \tag{33}$$

For $z' \in [-L/2, L/2]$ the vector function (33) satisfies the boundary conditions (5), independently of the value of z. Hence, as we did in Eq. (18) for the fluctuating fields, the vector function (33) can be expanded in a series of right eigenfunctions by projection onto the set obtained by applying the differential operator $\mathcal{D}$ to the left eigenfunctions. Thus, for real hydrodynamic modes and provided that z is a point located inside the interval $[-L/2, L/2]$, we obtain

$$0 = \sum_{N=0}^{\infty} \frac{1}{B_N(q_\parallel)}\Xi_N(q_\parallel, z)V_N(q_\parallel, z'),$$

$$\delta(z - z') = \sum_{N=0}^{\infty} \frac{\beta g q_\parallel^2}{B_N(q_\parallel)}\Xi_N(q_\parallel, z)\Xi_N(q_\parallel, z'), \tag{34}$$

in accordance with the second line of Eq. (31). When $\nabla c_0 = 0$ (equilibrium) we have from Eq. (28) that $A_D = 0$, so that $\tilde{S}_{\mathrm{NE}}$ does not contribute to the static structure factor. Hence, Eq. (31) shows that the structure factor can be decomposed into the sum of an equilibrium and a nonequilibrium contribution. Furthermore, we confirm that the structure factor in equilibrium is not affected by boundary conditions, which is to be expected because the equilibrium structure factor is spatially short ranged (proportional to delta functions), and therefore cannot be affected by what happens at the boundaries.

As discussed in the Introduction, we are interested in consequences that might be observed in experiments. As extensively reviewed in previous papers [7,24], the total intensity of light scattered with scattering vector $\mathbf{q} = \{\mathbf{q}_\parallel, q_\perp\}$ is obtained upon integrating the static structure factor $S(q_\parallel, z, z')$ over the vertical variables, namely

$$S(\mathbf{q}) = S(q_\parallel, q_\perp) = \frac{1}{L}\int_{-L/2}^{L/2}\int_{-L/2}^{L/2} e^{-iq_\perp(z-z')} S(q_\parallel, z, z')\,dz\,dz'. \tag{35}$$

In practice, Eq. (35) is often used in the small-angle approximation, $q_\parallel \simeq q$, $q_\perp \simeq 0$, which is also the limit relevant for shadowgraphy [2,16]. Substituting Eq. (31) into Eq. (35) and performing the spatial integrals, we conclude that, in the small-angle limit, the experimental static structure factor can be expressed as

$$S(q) = S_{\mathrm{E}}[1 + \widetilde{S}_{\mathrm{NE}}(q)] \tag{36}$$

with the dimensionless nonequilibrium enhancement in the intensity of the concentration fluctuations given by

$$\begin{aligned}\widetilde{S}_{\mathrm{NE}}(q) &= \widetilde{S}_{\mathrm{NE}}(q_{\parallel} \simeq q, q_{\perp} \simeq 0) \\ &= \frac{A_D}{L}\sum_{N,M=0}^{\infty} \frac{\hat{C}^{\mathrm{NE}}_{NM}(q)X_N(q)X_M(q)}{B_N(q)B_M(q)[\Gamma_N(q)+\Gamma_M(q)]},\end{aligned} \tag{37}$$

where $X_N(q)$ are the result of the vertical integration of the concentration component of the hydrodynamic modes, see Eq. (44) below. Equation (37) is our final result for the present section. Before continuing with the calculation of the intensity of the nonequilibrium fluctuations, we need to evaluate the decay rates and hydrodynamic modes from the eigenproblem (7).

V. DECAY RATES AND HYDRODYNAMIC MODES

The decay rates and corresponding hydrodynamic modes (7) can be obtained by a procedure similar to that followed by Schmitz and Cohen [24] for a one-component fluid [16]. Thus, we start by searching for solutions to Eq. (7) that are proportional to $\exp(\widetilde{\lambda} z/L)$. From the corresponding secular equation, it is found that $\widetilde{\lambda}$ must be one of the six roots of the sixth-order algebraic equation

$$(\widetilde{q}^2 - \widetilde{\lambda}_j^2)^3 - \widetilde{\Gamma}(\widetilde{q}^2 - \widetilde{\lambda}_j^2)^2 - \widetilde{q}^2\,\mathrm{Rc} = 0, \tag{38}$$

where we use dimensionless decay rates $\widetilde{\Gamma} = \Gamma L^2/D$, a dimensionless wave number $\widetilde{q} = Lq$, and where we have introduced the "concentration" Rayleigh number, Rc, given by

$$\mathrm{Rc} = \frac{\beta g L^4 \nabla c_0}{\nu D} = \psi\,\mathrm{Le}\,\mathrm{Ra}, \tag{39}$$

with ψ being the separation ratio defined by Eq. (3), and Ra the traditional Rayleigh number [17]. In what follows we shall always consider the small-scattering-angle limit of our expressions, so that all wave vectors $\mathbf{q}$ will be restricted to the horizontal xy plane. Henceforward, we shall therefore drop the subscript "parallel" from the wave numbers.

In Eq. (38), the index $j = 0, \ldots, 5$ is used to enumerate the six $\widetilde{\lambda}$ roots for given values of $\widetilde{\Gamma}$ and of the other dimensionless parameters. Explicit expressions for $\widetilde{\lambda}_j^2(\widetilde{q}, \widetilde{\Gamma})$ are given by the formulas for the roots of a cubic equation, but these expressions are quite complicated and not very informative; therefore, we do not specify them here, although they have been used in some of the following calculations. Since Eq. (38) is quadratic in $\widetilde{\lambda}_j$, there are three roots with a positive real part and three roots with a negative real part. We choose the order of the roots in such a way that for $j = 0, 1, 2$ the real part of $\widetilde{\lambda}_j$ is positive. Because of the nature of the roots and the symmetry of the boundary conditions (9), the hydrodynamic modes $\mathbf{U}^{(\mathrm{R})}(q,z)$ possess a definite parity. It is advantageous to classify them in even $\mathbf{U}^{(\mathrm{R,E})}$ and odd $\mathbf{U}^{(\mathrm{R,O})}$ modes or eigenfunctions, with corresponding even $\Gamma^{(\mathrm{E})}(\widetilde{q})$ and odd $\Gamma^{(\mathrm{O})}(\widetilde{q})$ decay rates. Moreover, in view of the second and the third of the boundary conditions (9), we find it convenient to express the even right eigenfunctions as

$$\mathbf{U}^{(\mathrm{R,E})}(\widetilde{q},z) = \sum_{j=0}^{2} A_j(q,\Gamma) \begin{bmatrix} \dfrac{-\beta g L^2}{\nu}\dfrac{1}{\widetilde{\lambda}_j^2 - \widetilde{q}^2} \\ \dfrac{\widetilde{\lambda}_j^2 - \widetilde{q}^2}{\widetilde{q}^2} \end{bmatrix} \frac{\cosh(\widetilde{\lambda}_j z/L)}{\widetilde{\lambda}_j \sinh\left(\dfrac{1}{2}\widetilde{\lambda}_j\right)}, \tag{40}$$

with

$$A_j(\widetilde{q}, \widetilde{\Gamma}) = \frac{\widetilde{\Gamma} + \widetilde{\lambda}_j^2(\widetilde{q},\widetilde{\Gamma}) - \widetilde{q}^2}{3[\widetilde{\lambda}_j^2(\widetilde{q},\widetilde{\Gamma}) - \widetilde{q}^2] + 2\widetilde{\Gamma}}, \tag{41}$$

where $\widetilde{\lambda}_j(\widetilde{q}, \widetilde{\Gamma})$, $j = \{0,1,2\}$, are the three complex roots of Eq. (38) with positive real part. We note that the eigenfunctions (40) already satisfy the second and the third of the boundary conditions (9), since from (38) it follows that

$$\sum_{j=0}^{2} \frac{A_j}{\widetilde{\lambda}_j^2 - q^2} = \sum_{j=0}^{2} A_j(\widetilde{\lambda}_j^2 - \widetilde{q}^2) = 0. \tag{42}$$

It is worth mentioning that because of the parity of the functions in the vertical variable z, the same boundary conditions will be satisfied at $z = \frac{1}{2}L$ and at $z = -\frac{1}{2}L$. Hence, to satisfy all the boundary conditions we just need the first component of $\mathbf{U}_N^{\mathrm{R,E}}(q,z)$ to satisfy the first of Eqs. (9), which implies that

$$\sum_{j=0}^{2} \frac{\widetilde{\Gamma} + \widetilde{\lambda}_j^2(\widetilde{q},\widetilde{\Gamma}) - \widetilde{q}^2}{3[\widetilde{\lambda}_j^2(\widetilde{q},\widetilde{\Gamma}) - \widetilde{q}^2] + 2\widetilde{\Gamma}} \, \frac{\coth\left[\dfrac{1}{2}\widetilde{\lambda}_j(\widetilde{q},\widetilde{\Gamma})\right]}{\widetilde{\lambda}_j(\widetilde{q},\widetilde{\Gamma})[\widetilde{\lambda}_j^2(\widetilde{q},\widetilde{\Gamma}) - \widetilde{q}^2]} = 0. \tag{43}$$

Upon substitution of the three solutions $\widetilde{\lambda}_j(\widetilde{q}, \widetilde{\Gamma})$ of (38) with positive real part into Eq. (43), we obtain a complicated algebraic equation from which the decay rates of the even eigenfunctions can be determined. In general, this equation can only be solved numerically. Due to the periodicity of the hyperbolic cotangent, there is an infinite numerable set of solutions for the even eigenvalues, which we have been distinguishing by the subscript N: $\widetilde{\Gamma}_N^{(\mathrm{E})}(\widetilde{q})$.

The odd eigenfunctions have a structure similar to Eq. (40), but with the hyperbolic cosines replaced by hyperbolic sines in the numerator, and *vice versa* in the denominator. They automatically satisfy the second and the third of the boundary conditions (9). Imposing the first of the boundary conditions (9), we obtain a condition similar to Eq. (43), but with the hyperbolic cotangent in the numerator replaced by a hyperbolic tangent. Using a similar numerical procedure as used for calculating $\widetilde{\Gamma}_N^{(\mathrm{E})}(\widetilde{q})$, we can compute the set of odd decay rates $\widetilde{\Gamma}_N^{(\mathrm{O})}(\widetilde{q})$. We are not further interested here in the odd decay rates and hydrodynamic modes, because they will not contribute to the nonequilibrium amplitude of concentration fluctuations in the small-scattering-angle approximation (see below).

To determine the eigenfunctions completely, we need the normalization coefficients $B_N(\widetilde{q})$ defined by Eq. (17). Substituting Eq. (40) into Eq. (17) and performing the corresponding integrations, explicit expressions for the normalization coefficients in terms of $\tilde{\lambda}_j(q,\Gamma_N)$ and $\Gamma_N(\tilde{q})$ can be readily obtained. These expressions are long and complicated, so that we do not display them here although they shall be used in the following. Similarly, the mode-coupling coefficients $C_{NM}^{\mathrm{NE}}(q)$, defined by Eq. (27), can be obtained explicitly in terms of $\tilde{\Gamma}$ and $\tilde{\lambda}_j$; again the resulting expressions are long, we do not display them here, but they shall be used in the following.

To conclude this section we discuss the result of the vertical integration of the concentration component of the hydrodynamic modes, which is also required for obtaining the nonequilibrium structure factor from Eq. (37). In this case the resulting expression can be simplified. Indeed, integrating vertically Eq. (40) for the even hydrodynamic modes and using the properties of the three roots $\tilde{\lambda}_j^2$ of Eq. (38), we find

$$X_N^{(\mathrm{E})}(\tilde{q}) = \int_{-1/2L}^{1/2L} \Xi_N^{(\mathrm{E})}(q,z)dz = \frac{2L}{\tilde{q}^2}\frac{\mathrm{Rc}}{\mathrm{Rc}-\tilde{q}^2(\tilde{\Gamma}_N^{(\mathrm{E})}-\tilde{q}^2)}. \tag{44}$$

In the case of the odd hydrodynamic modes, because of the parity of the vertical dependence it is obvious that $X_N^{(\mathrm{O})}(q)=0$. Consequently, as anticipated, the odd modes do not contribute to the static structure factor in the small-angle approximation, see Eq. (37). We shall not further discuss the odd modes in this paper.

Later, in Sec. VII, we shall pursue a numerical investigation of the decay rates and its dependence on Rc and $\tilde{q}$. But first we show in the next section how an analytical expression for these decay rates can be obtained in the limit of small q.

VI. PERTURBATIVE CALCULATION FOR SMALL WAVE NUMBERS

In the preceding section, we reduced the eigenvalue problem (7) to solving the set of two algebraic equations (38) and (43). Generally, this can only be done numerically. However, in the small-q limit (which turns out to be the most interesting case) analytical expressions can be obtained for the decay rates and hydrodynamic modes. From these expressions, the small-q limit of the normalization constants $B_N(q)$ and of the mode-coupling coefficients $C_{NM}(q)$ can in turn be obtained. Combining all that information, we shall be able to determine explicitly the amplitude of nonequilibrium fluctuations in that limit.

An extensive investigation of the small-q behavior of the even modes and decay rates solution of Eq. (7) shows that there exists first an infinite numerable set of solutions, that we shall refer to as "regular" modes. The main feature of the regular modes is that the corresponding decay rates reach a finite nonzero limit for $q\to 0$. However, in addition to the regular modes, one can identify a single slower mode whose corresponding decay rate is zero for $q\to 0$, independent of the Rayleigh number. Thus, the slowest mode is marginally stable and, as will be shown, completely determines the small-q behavior of the nonequilibrium structure factor. We discuss here the two types of modes separately.

A. Regular even modes

The regular even modes are characterized by both the decay rates and the square of the roots λ_j^2 of Eq. (38) being analytical functions for small values of q^2. They can be calculated by assuming that the decay rates admit a regular series expansion,

$$\tilde{\Gamma}(q) = \tilde{\Gamma}_0 + \tilde{\Gamma}_1 q + \tilde{\Gamma}_2 q^2 + \tilde{\Gamma}_3 q^3 + \tilde{\Gamma}_4 q^4 + \cdots , \tag{45}$$

and the same for the square of the roots of Eq. (38),

$$\tilde{\lambda}^2(q) = a_0 + a_1 q + a_2 q^2 + a_3 q^3 + a_4 q^4 + \cdots . \tag{46}$$

Substituting Eqs. (45) and (46) into Eq. (38), and cancelling terms with the same power of q, it is possible to express the coefficients a_i in terms of the coefficients $\tilde{\Gamma}_i$, so as to obtain

$$a_0 = \begin{bmatrix} 0 \\ 0 \\ -\tilde{\Gamma}_0 \end{bmatrix}, \quad a_1 = \begin{bmatrix} i\sqrt{\dfrac{\mathrm{Rc}}{\tilde{\Gamma}_0}} \\ -i\sqrt{\dfrac{\mathrm{Rc}}{\tilde{\Gamma}_0}} \\ -\tilde{\Gamma}_1 \end{bmatrix},$$

$$a_2 = 1 - \begin{bmatrix} \dfrac{i\tilde{\Gamma}_1}{2\tilde{\Gamma}_0}\sqrt{\dfrac{\mathrm{Rc}}{\tilde{\Gamma}_0}} - \dfrac{\mathrm{Rc}}{2\tilde{\Gamma}_0^2} \\ \dfrac{-i\tilde{\Gamma}_1}{2\tilde{\Gamma}_0}\sqrt{\dfrac{\mathrm{Rc}}{\tilde{\Gamma}_0}} - \dfrac{\mathrm{Rc}}{2\tilde{\Gamma}_0^2} \\ \tilde{\Gamma}_2 + \dfrac{\mathrm{Rc}}{\tilde{\Gamma}_0^2} \end{bmatrix}, \quad \ldots . \tag{47}$$

In Eq. (47) we have only displayed terms up to a_2, but for the following development, coefficients of the series (46) had to be calculated in terms of the $\tilde{\Gamma}_i$ up to a_4. Next, substituting Eq. (47) into Eq. (43), and expanding the resulting expression in powers of q, one observes that it is only possible to cancel the leading $O(q^{-2})$ term if the third root is $\tilde{\lambda}_3 \simeq 2i(N\pi + \mathrm{Rc}^2\,\tilde{q}^4/4096N^{10}\pi^{11})$, for integer N. This completely determines the first four coefficients of the series (45),

$$\tilde{\Gamma}_{N,0} = 4N^2\pi^2, \quad \tilde{\Gamma}_{N,1} = 0, \quad \tilde{\Gamma}_{N,2} = 1 - \frac{\mathrm{Rc}}{16N^4\pi^4},$$

$$\tilde{\Gamma}_{N,3} = 0, \quad \tilde{\Gamma}_{N,4} = \frac{\mathrm{Rc}(\mathrm{Rc}+16N^3\pi^4)}{512N^9\pi^{10}}, \tag{48}$$

for any integer $N=1,2,3,\ldots$. Substituting Eq. (48) into Eq. (45), we obtain for each N the series expansion for small q of the corresponding regular decay rate. As we anticipated, they form an infinite numerable set of real numbers and we use the index N to distinguish among them.

Next, substituting Eqs. (48) and (47) into Eq. (44) for $X_N^{(\mathrm{E})}(\tilde{q})$, as well as in Eq. (17) for the normalization constants and in Eq. (27) for the nonequilibrium mode-coupling coefficients, we can calculate the small-q limit of the contribution from these regular modes to the static structure factor, by substituting that information into Eq. (37). The result is a convergent series which, at most, is of order $O(q^2)$ for small wave numbers. This contribution will be negligible when compared to the contribution from the slowest mode discussed next, so we do not further elaborate on the regular modes here.

B. The slowest even mode

In addition to the infinite set of even modes discussed in the preceding section, we have identified another isolated even mode which is also a solution of the eigenproblem (7). This additional mode is characterized by a nonanalytic dependence of the decay rate for small values of the wave number, so that it can be expanded in powers of $q^{4/3}$ starting at power q^2. Specifically, it is possible to find a solution of the Eqs. (38) and (43) in the $q \to 0$ limit if we assume that the decay rate $\tilde{\Gamma}_0$ can be expanded as

$$\tilde{\Gamma}_0(q) = \tilde{\Gamma}_{0,1}q^2 + \tilde{\Gamma}_{0,2}q^{10/3} + \tilde{\Gamma}_{0,3}q^{14/3} + \tilde{\Gamma}_{0,4}q^6 + \cdots . \tag{49}$$

The square of the roots of Eq. (38) corresponding to the decay rate $\tilde{\Gamma}_0$ are to be expanded in a similar way, but starting at the power $q^{2/3}$, namely

$$\tilde{\lambda}^2(q) = b_0 q^{2/3} + b_1 q^2 + b_2 q^{10/3} + b_3 q^{14/3} + b_4 q^6 + \cdots . \tag{50}$$

Substituting Eqs. (49) and (50) into Eq. (38), and solving consistently in powers of q, one can express the coefficients of the series (50) in terms of those of the series (49), so that

$$b_0 = (-\mathrm{Rc})^{1/3}\begin{bmatrix} 1 \\ e^{i(2\pi/3)} \\ e^{i(4\pi/3)} \end{bmatrix}, \quad b_1 = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} - \frac{1}{3}\tilde{\Gamma}_{0,1},$$

$$b_2 = \frac{\tilde{\Gamma}_{0,1}^2}{9(-\mathrm{Rc})^{1/3}}\begin{bmatrix} 1 \\ e^{-i(2\pi/3)} \\ e^{-i(4\pi/3)} \end{bmatrix} - \frac{1}{3}\frac{\tilde{\Gamma}_{0,2}}{3}, \quad \ldots . \tag{51}$$

Notice that b_0 are the three complex cubic roots of minus the concentration Rayleigh number, Rc, and that the three components of b_1 are identical. Next, substituting Eqs. (49) and (50) with b_i given by (51), into Eq. (43) and expanding the resulting expression in powers of q, we find that one can cancel the leading $O(1)$-term if and only if

$$\tilde{\Gamma}_{0,1} = 1 - \frac{\mathrm{Rc}}{720} = 1 - \frac{\psi\,\mathrm{Le}\,\mathrm{Ra}}{720}. \tag{52}$$

Continuing the process, one can compute more terms of the series expansion (49) for $\tilde{\Gamma}_0(q)$. However, for our current purpose we stop here, since terms higher than the first will contribute to the nonequilibrium structure factor only in higher order (see below).

Using the information above, we now calculate the small-q expansion of the normalization coefficient. Substituting Eq. (40) for the hydrodynamic modes into the definition (17) of the normalization constant, performing the resulting integral and then expanding in series of q by using Eqs. (49)–(52), we obtain

$$B_0(q) \xrightarrow{q\to 0} \frac{\beta g}{L}\frac{4}{\tilde{q}^2} + O(q^2). \tag{53}$$

In a similar way, we can also compute the mode-coupling coefficient $C_{00}^{\mathrm{NE}}(q)$ in the small-q limit. Indeed, substituting Eq. (40) for the hydrodynamic modes into the definition (27) of the mode-coupling coefficient, performing the resulting integral and then expanding in series of q by using Eqs. (49)–(52), we obtain

$$C_{00}^{\mathrm{NE}}(q) \xrightarrow{q\to 0} D\frac{\beta^2 g^2}{L}\frac{\tilde{q}^2}{90} + O(q^{10/3}). \tag{54}$$

Of course, we must consider a possible coupling between the slowest mode and the regular modes described in the preceding section. However, it turns out that coupling contributions are of higher order in q, so that for the leading $q \to 0$ term for the amplitude of nonequilibrium fluctuations such cross coupling can be neglected. Hence, the small-q limit of the enhancement due to nonequilibrium fluctuations is simply given by the slowest mode, i.e., only the term $N=0$, $M=0$ in the series (37) is to be considered in the $q \to 0$ limit.

We have now all the information required to compute the small-q limit of the dimensionless enhancement of nonequilibrium concentration fluctuations, $\tilde{S}_{\mathrm{NE}}(\tilde{q})$. We conclude that for fluctuations at small wave numbers (long wavelengths) it reaches a constant limit at $q \to 0$ given by

$$\tilde{S}_{\mathrm{NE}}(q) \xrightarrow{q\to 0} \frac{A_D L^4}{720\left(1 - \dfrac{\psi\,\mathrm{Le}\,\mathrm{Ra}}{720}\right)} + O(q^2). \tag{55}$$

Notice that there is a divergence in Eq. (55) for $\mathrm{Rc}=720$, or $\mathrm{Ra}=720/\psi\mathrm{Le}$. Therefore for that particular Rayleigh number the amplitude of the nonequilibrium fluctuations, calculated within the linear theory developed in this paper, grows without limit, suggesting the appearance of an instability. It is also interesting to note the difference between the small-q behavior predicted by Eq. (55) for the nonequilibrium structure factor of a binary mixture and what is obtained for a one-component fluid [7,8]. In the latter case, the amplitude of the nonequilibrium fluctuations at $\tilde{q} \to 0$ vanishes proportionally to $\tilde{q}^2$. We observe how different boundary conditions (vanishing field vs vanishing derivative of the field) correspond to different small-$\tilde{q}$ behavior of the amplitude of the nonequilibrium fluctuations.

VII. NUMERICAL CALCULATION FOR ARBITRARY WAVE NUMBERS

The results of the preceding section strictly refer to the limit $\tilde{q} \to 0$. As already mentioned, Eq. (55) indicates that the

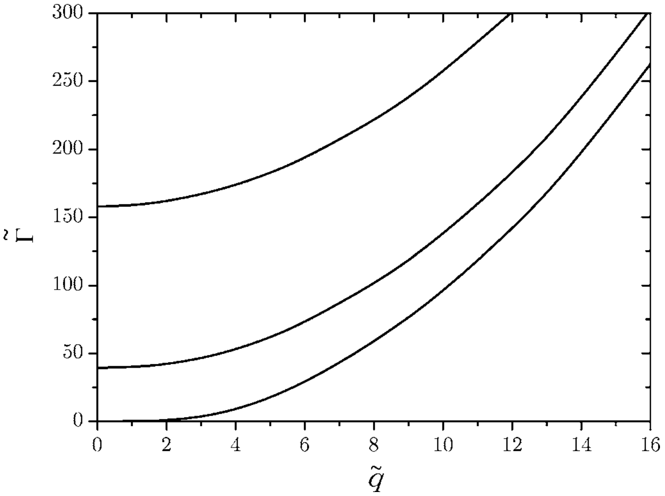

FIG. 1. Three lower even decay rates as a function of the wave number $\tilde{q}$ for Rc=700, which is close to the onset of convection (2.8%). The data have been obtained by solving numerically the set of algebraic equations (38) and (43).

system is only unstable for $\mathrm{Rc} \geqslant 720$. Thus, it would be possible by following the methods of Sec. IV, to calculate a nonequilibrium structure factor for $\mathrm{Rc} < 720$. However, a numerical computation is required to actually verify that there are indeed no problems for wave numbers other than $\tilde{q}=0$. In this section we present values for the decay rates as a function of $\tilde{q}$, calculated by solving the set of algebraic equations (38) and (43) numerically. From these values, we compute the nonequilibrium enhancement of concentration fluctuations, $\tilde{S}_{\mathrm{NE}}(\tilde{q})$, by use of Eq. (37).

Thus, we have evaluated numerically the decay rates $\tilde{\Gamma}(\tilde{q})$ for a range of wave numbers $\tilde{q}$ and concentration Rayleigh numbers Rc. As an example we show in Fig. 1 the results for the three lower decay rates and for Rc=700, which is close to the critical value $\mathrm{Rc}_c=720$. The lower curve in Fig. 1 corresponds to the slowest decay rate, whose small-q expansion is given by Eqs. (49) and (52). The two upper curves in Fig. 1 correspond to the two lower regular modes, so their small-q expansion is obtained by substituting Eq. (48) with $N=1$ and $N=2$ into Eq. (45). We observe in Fig. 1 that for Rc values close to, but below, the convective instability the decay rates have the global minimum at $q=0$. Also notice that, for $q \to \infty$, all the decay rates converge to a single $\tilde{\Gamma}=q^2$, as expected from the analysis of the Boussinesq Eqs. (1) in bulk fluid mixtures [11]. A consequence of the decay rates having the global minimum at $q=0$ is that the regular ones will always be positive, and the only worry about the stability of the system arises from the fact that the slowest rate is zero at $q=0$. Extensive numerical computations have convinced us that the aforementioned consequences for the stability of the system are valid for any Rc smaller than the critical $R_c=720$.

For $\mathrm{Rc}>720$, there exists a range of wave numbers around $q=0$ for which the slowest decay rate is negative, see Eq. (52). Hence, in addition to $q=0$, there will be a second value of the wave number, $q=q_0$, for which the slowest decay rate is zero.

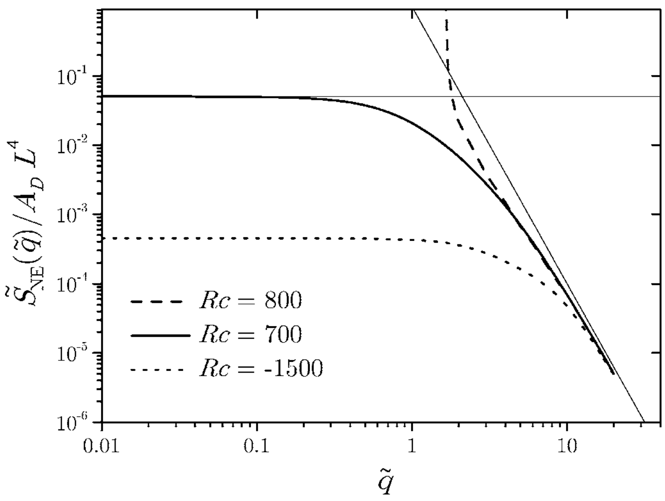

FIG. 2. Double logarithmic plot of the nonequilibrium enhancement of concentration fluctuations as a function of the dimensionless wave number $\tilde{q}$, for three values of the concentration Rayleigh number Rc as indicated. See main text for further explanations.

With the numerical values of the decay rates such as those presented in Fig. 1, the nonequilibrium enhancement of concentration fluctuations can be obtained from Eq. (37). We have performed an extensive numerical investigation of $\tilde{S}_{\mathrm{NE}}(q)$ for various values of the concentration Rayleigh number Rc. As an example of the results obtained, we show in Fig. 2 the normalized nonequilibrium enhancement [i.e., $\tilde{S}_{\mathrm{NE}}(\tilde{q})/A_D L^4$] as a function of the dimensionless wave number $\tilde{q}$ for three values of Rc. Notice in Fig. 2, that for the two Rc values lower than the critical $\mathrm{Rc}_c=720$ the nonequilibrium enhancement is a continuous function of the wave number, presenting a single global maximum at $\tilde{q}=0$. This means that the amplitude of nonequilibrium fluctuations is bounded independent of the wave number, confirming that the system is indeed stable in that range of Rc.

The two thin lines in Fig. 2 indicate the asymptotic limit for large q (i.e., $1/\tilde{q}^4$, see Ref. [11]) which is independent of Rc; and the asymptotic limit for $\tilde{q} \to 0$ [i.e., Eq. (55)] when Rc=700. These two asymptotic limits are known exactly. To compare them with the numerical results of this section, it should be taken into account that only a finite number of modes could be added to obtain the curves in Fig. 2 [actually, only the terms containing the first and the second decay rates in the double series (37) have been considered here]. As discussed in Sec. VI B, the exact $\tilde{q} \to 0$ limit of $\tilde{S}_{\mathrm{NE}}(\tilde{q})$ is given only by the contribution of the slowest mode, as is confirmed in Fig. 2, where the $q \to 0$ limit of the numerically computed structure factor coincides exactly with Eq. (55). However, to the $q \to \infty$ limit all modes contribute, and initially one needs to add an infinite number of modes to numerically reproduce the exact result of Ref. [11]. Having considered only a few modes the results displayed in Fig. 2 are still a little bit short ($\simeq 2\%$) of the exact $q \to \infty$ limit [11]. If more modes were added in the series (37), a better agreement would be obtained.

It is important to observe in Fig. 2 that for Rc=800, which is larger than the critical Rc_c, the amplitude of nonequilibrium concentration fluctuations diverges for $\tilde{q}_0$, which is the wave number (other than $\tilde{q}=0$) for which the slowest decay rate cancels. In the interval $[0,\tilde{q}_0]$, the amplitude of nonequilibrium concentration fluctuations calculated from Eq. (37) is negative, and cannot be displayed in the double logarithmic plot of Fig. 2. Of course, a negative value for $\tilde{S}_{\mathrm{NE}}(\tilde{q})$ is nonsense, and only reflects the failure of the linear theory developed in the present paper to describe fluctuations for $\mathrm{Rc}>720$. The development of a nonlinear theory of fluctuations, outside the scope of our present paper, is required to obtain meaningful results for the structure factor in this range of wave numbers and Rayleigh numbers.

VIII. CONCLUSIONS

In this paper we have shown that the Boussinesq equations for a binary fluid in the large-Le limit is a marginally stable problem, since there exists a decay rate $\Gamma_0(q)$ that is zero for $q\to 0$, independent of the Rc number. We have calculated the slope of $\Gamma_0(q)$ when $q\to 0$, and shown that it is negative for $\mathrm{Rc}>\mathrm{Rc}_c=720$. This fact foreshadows that the system will be unstable for $\mathrm{Rc}>\mathrm{Rc}_c$. However, in terms of a simple *deterministic* instability analysis it is impossible to decide whether the system is stable or not when $\mathrm{Rc}<720$ (or $\mathrm{Ra}<720/\psi\mathrm{Le}$ for positive ψ). Performing *stochastic* instability analysis, we have found that the amplitude of the nonequilibrium concentration fluctuations does indeed diverge at $q=0$ when $\mathrm{Ra}=720/\psi\mathrm{Le}$, see Eq. (55). This means that the nonequilibrium fluctuations grow without limit (in this simple linear approximation), confirming the existence of an instability. Most interestingly, our Eq. (55), complemented with numerical computation of the decay rates, shows that for $\mathrm{Ra}<720/\psi\mathrm{Le}$ the amplitude of nonequilibrium fluctuations is bounded for any q value, confirming that the system is indeed stable in this range of Ra numbers. The present work shows the advantage of performing a stability analysis in terms of stochastic instead of purely deterministic models. Again, as in the case of a one-component fluid [16], it is found that hydrodynamic instability is better understood as a divergence in the amplitude of the fluctuations rather than as the existence of a zero (or negative) decay rate. Our Eq. (55) also confirms previous results [10] suggesting that different kinds of boundary conditions correspond to different small-q behavior of $S_{\mathrm{NE}}(q)$.

The deterministic version of our problem has been recently considered by Ryskin *et al.* [13], who examined under which conditions the problem (7) admits $\Gamma=0$ as a solution, i.e., they performed a classical instability analysis. Ryskin *et al.* [13] showed that the linear stability of the binary Boussinesq problem in the weak diffusivity limit is equivalent to the linear stability of the one-component Bénard problem in the limit of very low-conductivity boundaries, studied long ago by Hurle *et al.* [27]. In those papers it was demonstrated that the system becomes unstable for a critical value of the control parameter $\mathrm{Rc}=720=6!$. Again, as in previous papers [8,16], we encounter that a hydrodynamic instability corresponds to a divergence in the nonequilibrium enhancement of the fluctuations. Interestingly, the problem studied here and in previous papers [13,27] is one of the few for which the instability condition can be obtained analytically for realistic boundary conditions.

We emphasize that the result (55) is exact, its validity will only be conditioned by the adequacy of the large-Le approximation (1) on which our calculation is based. The conditions for the validity of the large-Le approximation (1) to the Boussinesq equations have been extensively discussed in previous papers [11] (see also Ref. [12]), and it turned out to be applicable only to mixtures with positive separation ratio, $\psi>0$. For instance, it is well known that for mixtures with negative ψ the instability is oscillatory [12,28,29], a mechanism absent here because of the $\mathrm{Le}\to\infty$ approximation. In addition, it should be noted that, when heating from below a binary mixture with positive ψ and finite Le, it develops a convective instability at a nonzero q_c wave number. The fact that we found here the instability at zero wave number is also a consequence of the large-Le approximation. In spite of these shortcomings, we believe our Eq. (55) yields a good representation of the amplitude of large wavelength nonequilibrium concentration fluctuations mixtures with positive separation ratios, in particular when heated from above [11,12].

Equation (55) contains the effects of both gravity and confinement. It is interesting to compare it with the result obtained when gravity is the only mechanism quenching the fluctuations at small q, as studied elsewhere [11]. It turns out that the limit of $\tilde{S}_{\mathrm{NE}}(q)$ at $q\to 0$ when both gravity and confinement are accounted for is $(1-\mathrm{Rc})/(720-\mathrm{Rc})$ times the limit when only the quenching due to gravity is considered (what implicitly means that $\mathrm{Rc}<0$, since for positive Rc it is not possible to calculate a nonequilibrium structure factor considering only gravity effects). This ratio, for small Rc or in microgravity experiments, can be significantly different from unity.

It is also interesting to compare the exact result (55) for the intensity of the long-wavelength nonequilibrium concentration fluctuations with the equivalent one obtained on the basis of a Galerkin approximation and including temperature fluctuations, which is given by Eq. (55) of Ref. [10]. Remembering that the definition of Le employed in Ref. [10] is the inverse of the one employed here, we notice that the amplitude of long-wavelength fluctuations predicted in Ref. [10] diverges for a critical concentration Rayleigh number,

$$\mathrm{Rc}_c^{(\mathrm{G})}=\frac{\Lambda^6}{16}\coth^2\left(\frac{\Lambda}{2}\right)\simeq 725, \tag{56}$$

where $\Lambda\simeq 4.73$ is the wave number of the first of the Chandrasekhar's functions [10,17]. We thus find a very good agreement between the critical concentration Rayleigh number obtained here exactly ($\mathrm{Rc}=720$) and obtained previously [10] on the basis of a Galerkin approximation approximation.

We conclude this paper by a rather speculative comment. We have elucidated here how the consideration of thermal noise is crucial in the discussion of the stability of a binary fluid layer in the presence of a temperature gradient. Our present result suggests that stochastic forcing [14] should also be incorporated in an analysis of the stability of classical (isothermal) fluid flows [30]. Phenomena like a recently reported *energy amplification* in shear flows with stochastic forcing [31] must be somehow related to the *nonequilibrium enhancements* of the kind discussed in the present paper, that are also present in nonequilibrium states due to fluid shear [32,33]. The possible role of such processes in the initial path of transition to turbulence in plane shear flows has been recently acknowledged [34]. We plan to pursue this line of research in the future.

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