Concentration fluctuations in nonisothermal reaction-diffusion systems

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In this paper a simple reaction-diffusion system, namely a binary fluid mixture with an association-dissociation reaction between the two components, is considered. Fluctuations at hydrodynamic spatiotemporal scales when a temperature gradient is present in this chemically reacting system are studied. First, fluctuating hydrodynamics when the system is in global equilibrium (isothermal) is reviewed. Comparing the two cases, an enhancement of the intensity of concentration fluctuations in the presence of a temperature gradient is predicted. The nonequilibrium concentration fluctuations are spatially long ranged, with an intensity depending on the wave number q. The intensity exhibits a crossover from a $\propto q^{-4}$ to a $\propto q^{-2}$ behavior depending on whether the corresponding wavelength is smaller or larger than the penetration depth of the reacting mixture. This opens a possibility to distinguish between diffusion- or activation-controlled regimes of the reaction by measuring these fluctuations. In addition, the possible observation of these fluctuations in nonequilibrium molecular dynamics simulations is considered. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2746326]

I. INTRODUCTION

Nonisothermal reaction-diffusion systems are important in industry, as most chemical process plants contain units where such processes take place.[1,2] These units, characterized by being out of global equilibrium, will experience hydrodynamic fluctuations. Such fluctuations arise in a nonisothermal system because the fluctuations of the velocity parallel to the temperature or concentration gradient couple, via the advection term in the balance laws, with the temperature and concentration fluctuations, similarly to the mode-coupling phenomena encountered in fluid mixtures in the absence of a chemical reaction.[3] Specifically, we shall consider chemically reacting fluid mixtures in thermal nonequilibrium steady states but sufficiently close to equilibrium so that macroscopic convection or turbulence is absent. It is to be expected that fluctuations in such nonequilibrium systems are spatially long range[4].

Long-range hydrodynamic fluctuations have not been discussed so far for these technically important systems, despite reports that stationary state operation of nonisothermal chemical reactors can be accidentally perturbed to show unstable behavior.[5] While some explanations have been proposed,[5] it may also be worthwhile to pursue a study of the hydrodynamic fluctuations in reactors of this kind, so as to learn about the relation between hydrodynamic fluctuations and Hopf bifurcations. This work is a first attempt in this direction, by deriving expressions for the concentration fluctuations in a chemical reaction in a temperature gradient. Thereby we hope to lay a basis for further analysis of chemical reactors along these lines, and to contribute to the understanding of their steady-state behavior. Reactor stability is crucial for good plant operation, especially in a development that goes in a direction of process intensification.[6] Despite important efforts, this is still not always understood, however.[5]

Nonequilibrium molecular simulations are useful for studies of transport properties, and this gives a second perspective to our analysis. Transport coefficients can be found from boundary-driven nonequilibrium molecular simulations or from equilibrium fluctuations via Green-Kubo relations. Hydrodynamic fluctuations in nonequilibrium molecular dynamics simulations have not been discussed so far with the purpose of finding transport properties of reaction-diffusion mixtures in a temperature gradient. In order to be able to take advantage of this theory, it is first necessary to find the simulation conditions when hydrodynamic fluctuations occur. For instance, what are the system dimensions that allow their observation? Can we expect to observe such fluctuations for all densities? Another purpose of the paper is also to discuss the theoretical results in view of recent nonequilibrium molecular dynamics simulations[7,8] on a system of this type.

Progress in this field may have been hampered by the absence of a suitable theory. In this paper we develop a theory to specify concentration fluctuations at hydrodynamic spatiotemporal scales, and discuss how they can be determined by light scattering and by molecular dynamics simulations. Light-scattering techniques are standardly used to find information on transport properties.

Insight into hydrodynamic fluctuations in nonisothermal reaction-diffusion systems may thus be valuable in an overall assessment of their importance on the macroscopic reactor

scale. But, we shall see that it may also be valuable for a search to establish new methods for transport-property determinations.

The paper is written in terms of a terminology that is common to chemists. We present the balance equations and the transport equations for a reversible chemical reaction with diffusion in a temperature gradient in Sec. II. The fluctuations in the mixture at equilibrium are described in Sec. III. An extension of the theory of fluctuations to nonequilibrium systems is presented in Sec. IV. In Sec. V we summarize the results and mention some perspectives, while discussing possible verifications of the predictions by experiments or simulations.

II. NONEQUILIBRIUM THERMODYNAMICS OF A CHEMICALLY REACTING FLUID MIXTURE

As a representative example we consider a reversible association-dissociation reaction, like in a mixture of atoms and molecules,

$$2A \rightleftharpoons A_2. \tag{1}$$

For the particular case of fluorine atoms and molecules, transport properties are known from nonequilibrium molecular dynamics simulations.[7,8] However, for our purpose the detailed intermolecular interactions are not relevant and we treat Eq. (1) as a model chemical reaction to develop a theory of nonequilibrium concentrations fluctuations that can be readily applied to any binary reaction-diffusion system.

A detailed treatment of nonequilibrium thermodynamics of chemically reacting fluid mixtures can be found in the monograph (Sec. XI.8) of de Groot and Mazur.[9] We basically adopt the same approach with some slight changes in notation. Nonequilibrium thermodynamics is based on the assumption of local thermodynamic equilibrium. The nonequilibrium molecular dynamics simulations of Xu *et al.*[7,8] have confirmed the validity of this assumption even in the presence of a substantial temperature gradient. However, as will become evident, one of the major findings of the present paper is that, although local equilibrium is valid for the local thermodynamic quantities, it is no longer valid for the fluctuations of these quantities around their local-equilibrium values. For instance, while fluctuations in equilibrium are generally short range except near critical points, fluctuations in nonequilibrium are always long range. Moreover, their intensity is much larger than what one would expect for equilibrium fluctuations corresponding to the local temperature and concentration. Hence, nonequilibrium fluctuations differ qualitatively from those in equilibrium states.

As usual in nonequilibrium thermodynamics, we shall start by reviewing the relevant balance laws, and then discuss the phenomenological relationships required to complete the nonequilibrium thermodynamics formulation of the problem.

A. Balance laws

The balance laws relevant to our problem are[4,9] balance of mass

$$\frac{\partial \rho_A}{\partial t} = -\nabla \cdot (\rho_A \mathbf{v} + \mathbf{J}_A) - \xi,$$

$$\frac{\partial \rho_{A_2}}{\partial t} = -\nabla \cdot (\rho_{A_2} \mathbf{v} + \mathbf{J}_{A_2}) + \xi, \tag{2}$$

balance of momentum

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) = -\nabla p - \nabla \cdot [(\rho \mathbf{v})\mathbf{v} - \Pi], \tag{3}$$

and balance of energy

$$\rho \frac{Du}{Dt} = -\nabla \cdot \mathbf{Q} - p \nabla \cdot \mathbf{v}$$

$$= \rho T \frac{Ds}{Dt} + \frac{p}{\rho}\frac{D\rho}{Dt} + \rho \mu_A \frac{Dc_A}{Dt} + \rho \mu_{A_2} \frac{Dc_{A_2}}{Dt}. \tag{4}$$

In the balance laws Eqs. (2)–(4), p is the pressure, and the mass density ρ of the mixture is obtained by adding the partial densities in mass per unit volume: $\rho = \rho_A + \rho_{A_2}$. The center of mass velocity is given by $\rho \mathbf{v} = \rho_A \mathbf{v}_A + \rho_{A_2} \mathbf{v}_{A_2}$. The symbols μ_A and μ_{A_2} represent the chemical potentials per unit mass of each component, u is the specific internal energy, and s is the specific entropy, while $c_A = \rho_A/\rho$ and $c_{A_2} = \rho_{A_2}/\rho$ represent the mass fractions of the two components of the mixture. Furthermore, the diffusion fluxes, $\mathbf{J}_A$ and $\mathbf{J}_{A_2}$, in the balance of mass Eq. (2), are related to the difference between the velocity of the component and the center of mass velocity; thus $\mathbf{J}_A = \rho_A(\mathbf{v}_A - \mathbf{v})$, and similarly for the diffusion of molecules.

We readily identify on the right-hand side (RHS) of the balance laws Eqs. (2) and (3) five fluxes. Three of them are vectors: the diffusion flux of atoms $\mathbf{J}_A$, the diffusion flux of molecules $\mathbf{J}_{A_2}$, and the energy flux $\mathbf{Q}$ (or total heat flux). Moreover, we have on the RHS of the mass balance Eq. (2) a scalar flux which is the chemical reaction rate ξ, in mass per unit volume and unit time. The last flux is the (deviatory) stress tensor Π, which appears on the RHS of the momentum balance Eq. (3) and is a second-order tensor. Finally, we note that in the balance of momentum Eq. (3), external forces (buoyancy) have been neglected, while in the balance of energy Eq. (4) we have neglected viscous heating. Moreover, in Eq. (4) we employ material time derivatives to simplify the notation.

Because we are considering a binary system, the two diffusion fluxes are not independent, since from their definition it follows that[9] $\mathbf{J}_A + \mathbf{J}_{A_2} = 0$. Therefore, if we add the two mass balance laws, we obtain $\partial_t \rho_A + \partial_t \rho_{A_2} = -\nabla \cdot (\rho \mathbf{v})$. Using these constraints, we express the set of balance laws in terms of the mass fraction of A_2, $c = c_{A_2}$, and temperature T as

$$\frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \nabla \rho + \rho \nabla \cdot \mathbf{v} = 0, \tag{5a}$$

$$\rho \left[\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c \right] = -\nabla \cdot \mathbf{J} + \xi, \tag{5b}$$

$$\rho\left[\frac{\partial \mathbf{v}}{\partial t}+(\mathbf{v}\cdot\nabla)\mathbf{v}\right]+\nabla p=\nabla\cdot\Pi, \tag{5c}$$

$$\rho c_p\left[\frac{\partial T}{\partial t}+\mathbf{v}\cdot\nabla T\right]-\alpha T\left[\frac{\partial p}{\partial t}+\mathbf{v}\cdot\nabla p\right]+\rho\Delta h\left[\frac{\partial c}{\partial t}+\mathbf{v}\cdot\nabla c\right]=-\nabla\cdot\mathbf{Q}, \tag{5d}$$

where c_p is the specific isobaric heat capacity of the mixture and α its thermal expansion coefficient. Here,

$$\Delta h=\mu_{A_2}-T\left(\frac{\partial \mu_{A_2}}{\partial T}\right)_{p,c}-\mu_A+T\left(\frac{\partial \mu_A}{\partial T}\right)_{p,c}=\Delta g-T\left(\frac{\partial \Delta g}{\partial T}\right)_{p,c}, \tag{6}$$

is the difference in specific enthalpy of the reaction, i.e., the difference in specific enthalpy between the two components of the mixture, with $\Delta g=\mu_{A_2}-\mu_A$ being the difference in specific Gibbs energy (or minus the affinity) between the two components. Equations (5a)–(5d) represent the balance laws expressed in terms of a single diffusion flux $\mathbf{J}=\mathbf{J}_{A_2}=-\mathbf{J}_A$, and have to be complemented with two equations of state, namely $\rho=\rho(T,p,c)$ and $\Delta g=\Delta g(T,p,c)$.

Alternatively, we can express the set of working equations in terms of the molar concentration of molecules $[A_2]=\rho_{A_2}/M_{A_2}$, which is more customary in the chemical literature. This second approach implies modifications in Eqs. (5b) and (5d), which have to be expressed in terms of $[A_2]$, so that

$$\frac{\partial [A_2]}{\partial t}+\mathbf{v}\cdot\nabla[A_2]+[A_2]\nabla\cdot\mathbf{v}=-\nabla\cdot\mathbf{J}'+\xi', \tag{7a}$$

$$\rho c_p\frac{DT}{Dt}-\alpha T\frac{Dp}{Dt}+\Delta h M_{A_2}\left\{\frac{D[A_2]}{Dt}-\frac{[A_2]}{\rho}\frac{D\rho}{Dt}\right\}=-\nabla\cdot\mathbf{Q}, \tag{7b}$$

where the term $\Delta h M_{A_2}$ is the reaction enthalpy expressed in J/mol, $\mathbf{J}'=\mathbf{J}/M_{A_2}$ is the diffusion flux expressed in moles of molecules per m^2 and second, and similarly $\xi'=\xi/M_{A_2}$ the chemical reaction rate expressed in terms of moles produced per unit volume.

In principle, the hydrodynamic fluctuations can be analyzed on the basis of the full set of balance laws Eq. (5a)–(5d) once they are supplemented with the corresponding phenomenological relationships as described in Sec. II B. For the case of an isothermal global-equilibrium system, this procedure was adopted by Lekkerkerker and Laidlaw.[10] However, for the sake of simplicity, and to concentrate on the most salient physical features of our problem, we shall adopt first the incompressibility approximation. This approximation is commonly made in dealing with fluctuations and with the onset of convection in fluid mixtures in the absence of a chemical reaction.[4] In our particular case[11] the incompressibility approximation implies that we can neglect $\partial\rho/\partial t$ and $\nabla\rho$ in Eq. (5a), as well as the term containing the thermal expansion α in Eq. (5d), while the mass density everywhere in the equations can be identified with an average uniform value ρ_0. The incompressibility assumption is equivalent to the assumption, usually adopted in chemical kinetics,[12] that chemical reactions proceed at constant volume. Then, the balance laws relevant to our current problem reduce to

$$\nabla\cdot\mathbf{v}=0, \tag{8a}$$

$$\rho\left[\frac{\partial c}{\partial t}+\mathbf{v}\cdot\nabla c\right]=-\nabla\cdot\mathbf{J}+\xi, \tag{8b}$$

$$\rho\left[\frac{\partial \mathbf{v}}{\partial t}+(\mathbf{v}\cdot\nabla)\mathbf{v}\right]+\nabla p=\nabla\cdot\Pi, \tag{8c}$$

$$\rho c_p\left[\frac{\partial T}{\partial t}+\mathbf{v}\cdot\nabla T\right]+\rho\Delta h\left[\frac{\partial c}{\partial t}+\mathbf{v}\cdot\nabla c\right]=-\nabla\cdot\mathbf{Q}. \tag{8d}$$

In the alternative formulation in terms of molar concentration, the incompressibility approximation implies

$$\nabla\cdot\mathbf{v}=0, \tag{9a}$$

$$\frac{\partial [A_2]}{\partial t}+\mathbf{v}\cdot\nabla[A_2]=-\nabla\cdot\mathbf{J}'+\xi', \tag{9b}$$

$$\rho\left[\frac{\partial \mathbf{v}}{\partial t}+(\mathbf{v}\cdot\nabla)\mathbf{v}\right]+\nabla p=\nabla\cdot\Pi, \tag{9c}$$

$$\rho c_p\left[\frac{\partial T}{\partial t}+\mathbf{v}\cdot\nabla T\right]+M_{A_2}\Delta h\left\{\frac{\partial [A_2]}{\partial t}+\mathbf{v}\cdot\nabla[A_2]\right\}=-\nabla\cdot\mathbf{Q}. \tag{9d}$$

The product $M_{A_2}\Delta h$ in the RHS of Eq. (9d), with the help of Eq. (6), can be expressed as

$$M_{A_2}\Delta h=\mu'_{A_2}-T\left(\frac{\partial \mu'_{A_2}}{\partial T}\right)_{p,c}-2\mu'_A+2T\left(\frac{\partial \mu'_A}{\partial T}\right)_{p,c}, \tag{10}$$

where $\mu'_{A_2}=M_{A_2}\mu_{A_2}$ and $\mu'_A=M_A\mu_A$ are the chemical potentials of A_2 and A, respectively, in J/mol. Hence, the product $M_{A_2}\Delta h$ is the enthalpy of the chemical reaction Eq. (1), also in J/mol.

We conclude that, within the incompressibility assumption, the set of balance equations, whether formulated in terms of mass fractions or in terms of molar concentrations, has a completely parallel structure. The following developments can be translated from one language to the other just by replacing c with $[A_2]$, $\mathbf{J}$ with $\mathbf{J}'$, ξ with ξ', and by multiplying Δh everywhere by a factor M_{A_2}/ρ. We have chosen to use here version Eq. (8a)–(8d), but we emphasize that the other possibility is completely equivalent within our current approximations.

As usual, the RHS of the balance laws Eqs. (8a)–(8d) and (9a)–(9d) contains dissipative fluxes that need be related to the physical gradients in the system. This is considered next.

B. Phenomenological relationships

The complete nonequilibrium thermodynamic formulation of the system under study requires the consideration, in addition to the balance laws Eq. (5a)–(5d), of the entropy production rate $\dot{\mathcal{S}}$ of the system. This has been also evaluated by de Groot and Mazur[9] with the result

$$\dot{\mathcal{S}} = -\mathbf{Q}\cdot\frac{\nabla T}{T^2} + \Pi:\frac{(\nabla \mathbf{v})^{(s)}}{T} - \mathbf{J}_A\cdot\nabla\left(\frac{\mu_A}{T}\right) - \mathbf{J}_{A_2}\cdot\nabla\left(\frac{\mu_{A_2}}{T}\right) - \xi\frac{(\mu_{A_2}-\mu_A)}{T}, \tag{11}$$

where the superscript (s) indicates that only the symmetric part of the tensor of velocity derivatives contributes to $\dot{\mathcal{S}}$. The entropy-production rate in Eq. (11) has the typical structure linear in the dissipative fluxes. As is well known, the quantities multiplying each of the five fluxes in Eq. (11) are the corresponding *conjugate thermodynamic forces*. To set up the linear phenomenological laws and to facilitate the application to simulations, it is necessary to rewrite Eq. (11) in terms of independent fluxes,

$$\dot{\mathcal{S}} = -\mathbf{Q}\cdot\frac{\nabla T}{T^2} + \Pi:\frac{(\nabla \mathbf{v})^{(s)}}{T} - \mathbf{J}\cdot\nabla\left(\frac{\Delta g}{T}\right) - \xi\frac{\Delta g}{T}, \tag{12}$$

where we have introduced the notation $\Delta g=\mu_{A_2}-\mu_A$, for the reaction Gibbs energy of the chemical reaction Eq. (1).

Next, to obtain the equations of irreversible thermodynamics from the balance laws Eq. (8a)–(8d), one needs to introduce the linear phenomenological laws relating the fluxes to the gradients in terms of the appropriate Onsager coefficients or corresponding transport coefficients. Various formulations are possible and they are related to each other by a redefinition of the fluxes. The final hydrodynamic equations obtained [see Eqs. (19a) and (19b) below] do not depend on the choice of dissipative fluxes used to establish the phenomenological laws. We shall use as fluxes the tensor Π, the vectors $\mathbf{Q}$, $\mathbf{J}$, and the scalar ξ. Then, taking into account that the two vectorial heat and diffusive mass fluxes are coupled by virtue of the Curie principle, and assuming that the system is isotropic, one obtains for the linear phenomenological laws

$$\Pi_{ij} = \eta\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right), \tag{13a}$$

$$\mathbf{Q} = -L_{QQ}\frac{\nabla T}{T^2} - L_{QJ}\nabla\left(\frac{\Delta g}{T}\right), \tag{13b}$$

$$\mathbf{J} = -L_{JQ}\frac{\nabla T}{T^2} - L_{JJ}\nabla\left(\frac{\Delta g}{T}\right), \tag{13c}$$

$$\xi = -L_r\frac{\Delta g}{T}. \tag{13d}$$

Notice that in the phenomenological law Eq. (13a) for the stress tensor we have already introduced the assumption of a divergence-free (incompressible) fluid and expressed it in the common way, in terms of the shear viscosity η. As usual, we are assuming that due to their different tensorial character there is no coupling between the chemical-reaction rate and the heat and mass fluxes.[9] The phenomenological laws Eqs. (13b)–(13d) are written in terms of Onsager coefficients L_{QQ}, L_{JJ}, L_{QJ}, L_{JQ}, and L_r, which satisfy the Onsager relations $L_{QJ}=L_{JQ}$. For practical use, it is convenient to relate the Onsager coefficients to the well-known transport coefficients. In the case of the coupled phenomenological laws for $\mathbf{J}$ and $\mathbf{Q}$, this is achieved first by expressing the gradient in the reaction Gibbs energy in Eq. (13b) in terms of the diffusion flux $\mathbf{J}$, and then using the equation of state $\Delta g=\Delta g(p,T,c)$ in Eq. (13c) to write it explicitly in terms of pressure, temperature, and concentration gradients. This procedure yields

$$\mathbf{Q} = -\left[L_{QQ} - \frac{L_{JQ}^2}{L_{JJ}}\right]\frac{\nabla T}{T^2} + \frac{L_{QJ}}{L_{JJ}}\mathbf{J}, \tag{14a}$$

$$\mathbf{J} = -\{L_{QJ} - L_{JJ}\Delta h\}\frac{\nabla T}{T^2} - \frac{L_{JJ}}{T}\left(\frac{\partial \Delta g}{\partial p}\right)_{T,c}\nabla p - \frac{L_{JJ}}{T}\left(\frac{\partial \Delta g}{\partial c}\right)_{p,T}\nabla c, \tag{14b}$$

which, on comparing with the phenomenological equations for binary systems,[13]

$$\mathbf{Q} = -\lambda\nabla T + \left\{\Delta h + k_T\left(\frac{\partial \Delta g}{\partial c}\right)_{p,T}\right\}\mathbf{J}, \tag{15a}$$

$$\mathbf{J} = -\rho D\left\{\nabla c + \frac{k_T}{T}\nabla T + \frac{k_p}{p}\nabla p\right\}, \tag{15b}$$

allows us to express the Onsager coefficients in terms of the usual transport coefficients: a thermal conductivity λ, a mutual diffusion coefficient D, a dimensionless thermal diffusion ratio k_T, and a dimensionless barodiffusion ratio k_p. The resulting expressions are

$$D = \frac{L_{JJ}}{\rho T}\left(\frac{\partial \Delta g}{\partial c}\right)_{p,T},$$

$$\lambda = \frac{1}{T^2}\left[L_{QQ} - \frac{L_{QJ}^2}{L_{JJ}}\right],$$

$$\rho D T k_T = L_{QJ} - L_{JJ}\Delta h, \tag{16}$$

$$k_p = p\left(\frac{\partial \Delta g}{\partial p}\right)_{T,c}\left(\frac{\partial \Delta g}{\partial c}\right)_{p,T}^{-1}.$$

Equations (14a), (14b), (15a), and (15b) are compatible, in the sense that the expression, obtained for k_T by identifying Eq. (14a) with Eq. (15a) is the same as obtained by identifying Eq. (14b) with Eq. (15b). It is interesting to note that the barodiffusion ratio is independent of the Onsager coefficients; it is an equilibrium property and not related to a dissipative process. Barodiffusion seems to be important only in geological problems, and is negligibly small for ordinary fluid mixtures. Hence, we neglect here barodiffusion, which means that we neglect the dependence of the specific Gibbs-energy difference on pressure in Eq. (14b), so that $\Delta g=\Delta g(T,c)$ only.

In the same way as the phenomenological coefficients for the energy and diffusion fluxes are related to the practical transport coefficients D, λ, and k_T, the coefficient L_r associated with the chemical reaction can be related to the rate constants used in chemical kinetics.[7,9,14] But, this relationship is not as straightforward as for the other transport coefficients, since several complications in chemical kinetics[12] need to be accounted for (concentrations units, distinction between reactions proceeding at constant volume or not, possibility of intermediate reaction steps, etc.). Hence, we prefer to use the Onsager coefficient L_r. In addition, we should note that the linear phenomenological law Eq. (13d) is only valid for small deviations from chemical equilibrium,[9] actually so small that many authors[15,16] doubt the practical usefulness of Eq. (13d) itself. In this respect we mention that, although this criticism may be valid, recent developments[17,18] have shown that by introducing an internal *mesoscopic* variable to describe the advancement of a chemical reaction, a linear phenomenological law similar to Eq. (13d) can be formulated in terms of that mesoscopic variable, thereby extending the validity of linear nonequilibrium thermodynamics (and its associated theory of fluctuating hydrodynamics, to be developed later in Sec. III) beyond those narrow classical limits. Therefore, in this paper we continue to assume the validity of Eq. (13d), keeping in mind that a mesoscopic extension[17] may be necessary. Such an extension is beyond our present scope here.

C. Hydrodynamic equations

Next, we substitute the phenomenological Eqs. (13a)–(13d) into the set of balance laws, Eqs. (8a)–(8d), so as to obtain the set of differential equations from which the spatiotemporal evolution of the velocity, the temperature, and the concentration of the mixture can be evaluated. If we neglect the dependence of the Onsager coefficients on pressure, concentration, or temperature, the hydrodynamic equations can be written as

$$\nabla\cdot\mathbf{v}=0,$$

$$\rho\left[\frac{\partial\mathbf{v}}{\partial t}+(\mathbf{v}\cdot\nabla)\mathbf{v}\right]=-\nabla p+\eta\nabla^2\mathbf{v},$$

$$\rho\left[\frac{\partial c}{\partial t}+\mathbf{v}\cdot\nabla c\right]=-L_{QJ}\nabla^2\left(\frac{1}{T}\right)+L_{JJ}\nabla^2\left(\frac{\Delta g}{T}\right)-\frac{L_r}{T}\Delta g,$$

$$\rho c_p\left[\frac{\partial T}{\partial t}+\mathbf{v}\cdot\nabla T\right]+\rho h\left[\frac{\partial c}{\partial t}+\mathbf{v}\cdot\nabla c\right]=-L_{QQ}\nabla^2\left(\frac{1}{T}\right)+L_{JQ}\nabla^2\left(\frac{\Delta g}{T}\right), \tag{17}$$

which, combined with the equation of state $\Delta g=\Delta g(p,T,c)$, constitute the hydrodynamic equations of the chemically reacting mixture under consideration.

Notice that the set of hydrodynamic equations, Eqs. (17), because of both the incompressibility assumption and the neglect of viscous heating, appears to separate into two pairs. The first pair of Eqs. (17) represents an ordinary hydrodynamic problem from which the velocity $\mathbf{v}$ and the pressure p can be calculated. These solutions then have to be substituted into the second pair of Eqs. (17), in particular the velocity, and a closed system is obtained from which concentration and temperature, in principle, may be evaluated.

It is usually advantageous to express the second pair of the hydrodynamic equations Eqs. (17) in terms of the ordinary transport coefficients: λ, D, k_T, instead of the Onsager coefficients L_{JJ}, etc. This can be achieved by inverting Eqs. (16) and substituting the result into Eqs. (17). Furthermore, it can be assumed that

$$\nabla^2\left(\frac{1}{T}\right)\simeq-\frac{1}{T^2}\nabla^2T,$$

$$\nabla^2\left(\frac{\Delta g}{T}\right)\simeq-\frac{\Delta g}{T^2}\nabla^2T+\frac{1}{T}\nabla^2(\Delta g)\simeq-\frac{1}{T^2}\left[\Delta g-T\left(\frac{\partial\Delta g}{\partial T}\right)_c\right]\nabla^2T+\frac{1}{T}\left(\frac{\partial\Delta g}{\partial c}\right)_T\nabla^2c, \tag{18}$$

where terms proportional to the square of gradients, like $(\nabla T)^2$, $(\nabla\mu)^2$, etc. have been neglected since they are second order in the dissipative fluxes as can be immediately seen by inverting the phenomenological relations Eq. (13a)–(13d). In addition, we recall that we are neglecting barodiffusion and, consequently, the dependence of the reaction Gibbs energy on the pressure; see Eq. (16). Then, substitution of Eq. (18) into the second pair of Eqs. (17), and use of the well-known transport coefficients give the hydrodynamic equations in their more classical form, namely

$$\frac{\partial c}{\partial t}+\mathbf{v}\cdot\nabla c=D\left\{\nabla^2c+\frac{k_T}{T}\nabla^2T\right\}-\frac{L_r}{\rho T}\Delta g, \tag{19a}$$

$$\frac{\partial T}{\partial t}+\mathbf{v}\cdot\nabla T=[a+D\varepsilon_D]\nabla^2T+\frac{DT}{k_T}\varepsilon_D\nabla^2c+\frac{L_r}{\rho}\Delta\tilde{h}\Delta g, \tag{19b}$$

where in the energy Eq. (19b) we have introduced the thermal diffusivity $a=\lambda/\rho c_p$, the dimensionless Dufour effect ratio

$$\varepsilon_D=\frac{k_T^2}{c_pT}\left(\frac{\partial\Delta g}{\partial c}\right)_{p,T}, \tag{20}$$

which measures the importance of the Dufour effect, and the dimensionless specific enthalpy of reaction, similar to Eq. (6),

$$\Delta\tilde{h}=\frac{\Delta h}{c_pT}. \tag{21}$$

The dimensionless specific enthalpy of reaction $\Delta\tilde{h}$ shows up multiplying the last term in the energy balance Eq. (19b); it thus causes a heating due to the chemical reaction. This term is important and cannot be neglected.

III. CONCENTRATION FLUCTUATIONS IN AN ISOTHERMAL CHEMICALLY REACTING MIXTURE

When the fluid mixture is in thermal equilibrium in the absence of a temperature gradient, the solution of the hydrodynamic Eqs. (17) is obviously given by zero velocity $\mathbf{v}=0$, uniform pressure, uniform temperature $T=T_0$, and uniform concentration c_0. This concentration c_0 is the solution of the chemical equilibrium equation $\Delta g(c,T_0)=0$. In this section we study small thermodynamic fluctuations around this simple equilibrium solution.

We have divided the material in this section in two parts. First, for the benefit of the reader, we review the theory of thermodynamic fluctuations, particularly the generic formulation in terms of the fluctuation-dissipation theorem. Then, we shall apply the general theory specifically to the case of an isothermal chemically reacting mixture.

A. Fluctuating hydrodynamics

Following the general guidelines of fluctuating hydrodynamics,[4] we formulate the stochastic version of the hydrodynamic Eqs. (19a) and (19b) by the following three-step procedure:

(1) The dissipative fluxes are affected by the random nature of molecular motion, so they must be considered as stochastic variables with a probability distribution to be specified below (for a global equilibrium state). As a consequence, both the temperature and the concentration also become stochastic variables whose spatiotemporal evolutions depend on the stochastic fluxes through Eqs. (5a)–(5d), as the balance laws Eqs. (5a)–(5d) continue to hold even in the presence of fluctuations.

(2) Because of stochastic phenomena, the phenomenological relationships Eqs. (13a)–(13d) are only valid on "average." This means, for instance, that when fluctuations are present, Eq. (13b) must be replaced by

$$\mathbf{Q}=-L_{QQ}\frac{\nabla T}{T^2}-L_{QJ}\nabla\left(\frac{\Delta g}{T}\right)+\delta\mathbf{Q}, \tag{22}$$

where $\delta\mathbf{Q}(\mathbf{r},t)$ is a random part of the energy flux, with mean value $\langle\delta\mathbf{Q}(\mathbf{r},t)\rangle=0$ when averaged over its functional probability distribution.

(3) To completely specify the probability distribution of the random fluxes [$\delta\mathbf{Q}(\mathbf{r},t)$ and the like], we need not only the first moment, but all the other moments of their probability distributions. When the system is in a global equilibrium state at a uniform temperature T_0, the probability distributions of the random fluxes are generated by a set of Gaussian stochastic processes. Hence, only the first and second moments are required to completely specify them. If we denote a generic random flux by $\delta J_k(\mathbf{r},t)$ (it could be any component of a tensorial flux, or a scalar flux), then its statistical properties (first and second moments) are

$$\langle\delta J_k(\mathbf{r},t)\rangle=0 \tag{23a}$$

$$\langle\delta J_k^*(\mathbf{r},t)\cdot\delta J_l(\mathbf{r}',t')\rangle=2k_BL_{kl}\delta(t-t')\delta(\mathbf{r}-\mathbf{r}'), \tag{23b}$$

where k_B is the Boltzmann constant and L_{kl} are the same phenomenological coefficients that appear in the linear phenomenological relationship between the fluxes J_k and J_l.

Equation (23a) is just the definition of the fluctuating part of the random flux. Equation (23b) is the *fluctuation-dissipation theorem*, which gives the stochastic properties of the fluxes when the system is in a global equilibrium state.[13]

B. Equilibrium concentration and temperature fluctuations

Now, we elucidate how the general theory explained above applies to an isothermal chemically reacting binary mixture. First, we identify four independent random fluxes: the random stress tensor $\delta\Pi(\mathbf{r},t)$, the random energy flux $\delta\mathbf{Q}(\mathbf{r},t)$, the random diffusion flux $\delta\mathbf{J}(\mathbf{r},t)$, and, finally, the random chemical reaction rate $\delta\xi(\mathbf{r},t)$, the last one being a scalar.

The specification of the generic fluctuation-dissipation theorem Eq. (23b) for our system (when expressed in terms of the transport coefficients) becomes more compact if we redefine the energy flux by introducing an auxiliary random heat flux related to $\delta\mathbf{Q}(\mathbf{r},t)$ by

$$\delta\mathbf{Q}'(\mathbf{r},t)=\delta\mathbf{Q}(\mathbf{r},t)-\Delta h\delta\mathbf{J}(\mathbf{r},t). \tag{24}$$

With this auxiliary random heat flux, the fluctuation-dissipation theorem can be expressed in terms of the transport coefficients Eq. (16) as[4]

$$\langle\delta\Pi_{ij}^*(\mathbf{r},t)\cdot\delta\Pi_{kl}(\mathbf{r}',t')\rangle=2k_BT\eta[\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}]\delta(t-t')\delta(\mathbf{r}-\mathbf{r}'), \tag{25a}$$

$$\langle\delta Q_k'^*(\mathbf{r},t)\cdot\delta Q_l'(\mathbf{r}',t')\rangle=2k_BT^2\lambda\left[1+\frac{D}{a}\varepsilon_D\right]\delta_{kl}\delta(t-t')\delta(\mathbf{r}-\mathbf{r}'), \tag{25b}$$

$$\langle\delta J_k^*(\mathbf{r},t)\cdot\delta J_l(\mathbf{r}',t')\rangle=2k_BT\rho D\left(\frac{\partial\Delta g}{\partial c}\right)_{p,T}^{-1}\delta_{kl}\delta(t-t')\delta(\mathbf{r}-\mathbf{r}'), \tag{25c}$$

$$\langle\delta J_k^*(\mathbf{r},t)\cdot\delta Q_l'(\mathbf{r}',t')\rangle=2k_BT\rho Dk_T\delta_{kl}\delta(t-t')\delta(\mathbf{r}-\mathbf{r}'), \tag{25d}$$

$$\langle\delta\xi^*(\mathbf{r},t)\cdot\delta\xi(\mathbf{r}',t')\rangle=2k_BL_r\delta(t-t')\delta(\mathbf{r}-\mathbf{r}'). \tag{25e}$$

We recall that the Onsager coefficient for the stress tensor is proportional to $T\eta$, and note that the fluctuation-dissipation theorem for the random stress, written as in Eq. (25a), clearly shows the symmetry under permutation of indices: i by j, or k by l. Since the development in this section refers to a global equilibrium state of the mixture, all thermophysical properties in Eqs. (25a)–(25e) are to be evaluated at the equilibrium pressure p_0, equilibrium temperature T_0, and equilibrium concentration c_0.

Having formulated the fluctuation-dissipation theorem, we introduce two changes in the hydrodynamic equations, Eqs. (17). First we add the random part of the fluxes on the RHS of Eqs. (17). In addition, we split the thermodynamic fields in (uniform) equilibrium parts (p_0, T_0, and c_0), and random fluctuating parts: $\delta p(\mathbf{r},t)$, $\delta T(\mathbf{r},t)$, and $\delta c(\mathbf{r},t)$, which are driven by the random fluxes. Then, similarly to Eqs. (17), we obtain evolution equations for the thermodynamic fluctuations that include random forcing from the stochastic part of the fluxes. If we linearize the resulting equations, assuming that fluctuations around equilibrium are small, we can decouple (also because we are neglecting barodiffusion) the velocity and pressure fluctuations from the concentration and temperature fluctuations. As a consequence, we do not evaluate here the effect of the chemical reaction in the propagating sound modes, as discussed by other authors.[10,19] Thus, we only consider the coupled evolution equations for temperature and concentration fluctuations, for which we obtain the following set of stochastic partial differential equations:

$$\frac{\partial}{\partial t}\delta c = D\left\{\nabla^2\delta c + \frac{k_T}{T_0}\nabla^2\delta T\right\} - \frac{L_r}{\rho T_0}\delta(\Delta g) - \frac{1}{\rho}\nabla\cdot\delta\mathbf{J} + \frac{1}{\rho}\delta\xi, \tag{26a}$$

$$\frac{\partial}{\partial t}\delta T + T_0\Delta\tilde{h}\frac{\partial}{\partial t}\delta c = [a + D(\varepsilon_D + k_T\Delta\tilde{h})]\nabla^2\delta T + \frac{DT_0}{k_T}(\varepsilon_D + k_T\Delta\tilde{h})\nabla^2\delta c - \frac{1}{\rho c_p}\nabla\cdot\delta\mathbf{Q}. \tag{26b}$$

Alternatively, eliminating the concentration time derivative in the second equation using the first one, we obtain

$$\frac{\partial}{\partial t}\delta c = D\left\{\nabla^2\delta c + \frac{k_T}{T_0}\nabla^2\delta T\right\} - \frac{L_r}{\rho T_0}\delta(\Delta g) - \frac{1}{\rho}\nabla\cdot\delta\mathbf{J} + \frac{1}{\rho}\delta\xi, \tag{27a}$$

$$\frac{\partial}{\partial t}\delta T = [a + D\varepsilon_D]\nabla^2\delta T + \frac{DT_0}{k_T}\varepsilon_D\nabla^2\delta c + \frac{L_r}{\rho}\Delta\tilde{h}\delta(\Delta g) - \frac{1}{\rho c_p}\nabla\cdot\delta\mathbf{Q}' - \frac{T}{\rho}\Delta\tilde{h}\delta\xi. \tag{27b}$$

At this point we should comment that, according to the general approach described in Sec. III A, we are describing the stochastic nature of the chemical reaction through Langevin-type equations, Eqs. (26a), (26b), (27a), and (27b) above. There has been some debate in the literature on whether the use of a Langevin equation is correct for chemical reactions, or whether fluctuations in chemical reactions must always be described by a chemical master equation.[20–22] From a strictly microscopic point of view, we acknowledge that the proper theoretical framework to describe fluctuations in chemical reactions has to be based on the chemical master equation.[23] However, starting from the chemical master equation, through a Kramers-Moyal approximation combined with the system-size expansion proposed by Van Kampen,[24,25] it is possible to obtain a Fokker-Planck (or Langevin) equation which is approximately equivalent to the original chemical master equation.[23,26] It is known that this approximation scheme fails when there is a bistability in a system of chemical reactions,[26] so that the Langevin equation is only valid when there is a single stable solution to the deterministic kinetic equations, and when there are many particles per unit volume in the system. The second assumption (many particles in small volume elements) is equivalent to the approximations justifying hydrodynamics itself. In dealing with fluctuations at hydrodynamic spatiotemporal scales, we shall implicitly assume that the approximations leading to the chemical Langevin equation, Eqs. (26a), (26b), (27a), and (27b) above, are sufficiently well justified.

To solve the evolution equations, Eqs. (27a) and (27b), for the fluctuating fields, we need first to relate the fluctuations in the specific Gibbs-energy difference $\delta(\Delta g)$ in Eq. (26a) to temperature and concentration fluctuations. Since we are neglecting barodiffusion, the relevant relationship is simply

$$\delta(\Delta g) = \left(\frac{\partial\Delta g}{\partial c}\right)_T\delta c + \left(\frac{\partial\Delta g}{\partial T}\right)_c\delta T. \tag{28}$$

Next, substituting Eq. (28) into Eq. (26a), we obtain a closed system of differential equations for $\delta T(\mathbf{r},t)$ and $\delta c(\mathbf{r},t)$ that can be solved by the following procedure. First, since fluctuations in equilibrium systems are spatially short ranged, we do not need to account for boundary conditions. Therefore, the system of differential equations, Eqs. (26a) and (26b), can be solved by taking spatiotemporal Fourier transforms. This procedure yields:

$$\mathrm{G}^{-1}(\omega,q)\cdot\begin{pmatrix}\delta c(\omega,\mathbf{q})\\ \delta T(\omega,\mathbf{q})\end{pmatrix} = \mathbf{F}(\omega,\mathbf{q}), \tag{29}$$

where ω and $\mathbf{q}$ are the frequency and the wave vector of the fluctuations, respectively. Furthermore, we have introduced in Eq. (29) a matrix

$$\mathrm{G}^{-1}(\omega,q) = \begin{pmatrix} i\omega + Dq^2 + \frac{L_r}{\rho T_0}\left(\frac{\partial\Delta g}{\partial c}\right)_T & D\frac{k_T}{T_0}q^2 + \frac{L_r}{\rho T_0}\left(\frac{\partial\Delta g}{\partial T}\right)_c \\ T_0\Delta\tilde{h}i\omega + \frac{DT_0}{k_T}(\varepsilon_D + k_T\Delta\tilde{h})q^2 & i\omega + [a + D(\varepsilon_D + k_T\Delta\tilde{h})]q^2 \end{pmatrix}, \tag{30}$$

which is the inverse of the linear response operator for our system, and a vector of random forces

$$\mathbf{F}(\omega,\mathbf{q}) = \frac{-1}{\rho}\begin{pmatrix} iq_i\delta J_i(\omega,\mathbf{q}) - \delta\xi(\omega,\mathbf{q}) \\ ic_p^{-1}q_i\delta Q_i(\omega,\mathbf{q}) \end{pmatrix}, \tag{31}$$

where summation over repeated indices is understood. Now, the Fourier-transformed fluctuating fields can be simply evaluated by inversion of Eq. (30), so as to calculate the linear response function itself.

Here, we are interested in the calculation of the autocorrelation function of the (Fourier-transformed) fluctuating fields, i.e., $\langle \delta c^*(\omega,\mathbf{q})\delta c(\omega',\mathbf{q}')\rangle$ for the concentration fluctuations, and $\langle \delta T^*(\omega,\mathbf{q})\delta T(\omega',\mathbf{q}')\rangle$ for the temperature fluctuations. To calculate these quantities, we need the correlations between the components of the random noise vector introduced in Eq. (31). These functions are conveniently expressed in terms of a correlation matrix $\mathrm{C}(q)$, defined by

$$\langle F_i^*(\omega,\mathbf{q})F_j(\omega',\mathbf{q}')\rangle = \frac{2k_\mathbf{B}T_0}{\rho}\left(\frac{\partial\Delta g}{\partial c}\right)_T^{-1} C_{ij}(q)(2\pi)^4\delta(\omega-\omega')\delta(\mathbf{q}-\mathbf{q}'). \tag{32}$$

By combining the definition Eq. (31) of the vector $\mathbf{F}(\omega,\mathbf{q})$ with the fluctuation-dissipation theorem, Eq. (25a)–(25e), we readily obtain for the correlation matrix

$$\mathrm{C}(q) = \begin{pmatrix} Dq^2 + \dfrac{L_r}{\rho T_0}\left(\dfrac{\partial\Delta g}{\partial c}\right)_T & \dfrac{DT_0}{k_T}(\varepsilon_D + k_T\Delta\tilde{h})q^2 \\ \dfrac{DT_0}{k_T}(\varepsilon_D + k_T\Delta\tilde{h})q^2 & \left[\dfrac{aT_0}{cp}\left(\dfrac{\partial\Delta g}{\partial c}\right)_T + \dfrac{DT_0^2}{k_T^2}(\varepsilon_D + k_T\Delta\tilde{h})^2\right]q^2 \end{pmatrix}. \tag{33}$$

Now we are in a position where we can evaluate the various correlation functions between the fluctuating fields. For instance, inverting Eq. (30), and using Eq. (32), we observe that the concentration fluctuations autocorrelation can be expressed in terms of a "structure factor" $S_{cc}(\omega,q)$ as

$$\langle \delta c^*(\omega,\mathbf{q})\delta c(\omega',\mathbf{q}')\rangle = S_{cc}(\omega,q)(2\pi)^4\delta(\omega-\omega')\delta(\mathbf{q}-\mathbf{q}'), \tag{34}$$

with

$$S_{cc}(\omega,q) = \frac{2k_BT_0}{\rho}\left(\frac{\partial\Delta g}{\partial c}\right)_T^{-1}\sum_{i,j=0}^{1} G_{1i}^*(\omega,q)C_{ij}(q)G_{1j}(\omega,q). \tag{35}$$

Inverting Eq. (30) for the inverse linear response function, we can obtain for the contribution $S_{cc}(\omega,q)$ of the concentration fluctuations to the dynamic structure factor

$$S_{cc}(\omega,q) = \frac{2k_BT_0}{\rho}\left(\frac{\partial\Delta g}{\partial c}\right)_T^{-1}\frac{\left[Dq^2 + \dfrac{c_p\varepsilon_DL_r}{\rho k_T^2}\right]\omega^2 + \Gamma_+(q)\Gamma_-(q)\left[(a+D\varepsilon_D)q^2 + \dfrac{c_p\Delta\tilde{h}^2L_r}{\rho}\right]}{[\omega^2+\Gamma_+^2(q)][\omega^2+\Gamma_-^2(q)]}. \tag{36}$$

If, similarly to Eq. (34), we introduce a contribution $S_{TT}(\omega,q)$ of the temperature fluctuations to the dynamic structure factor, we obtain

$$S_{TT}(\omega,q) = \frac{2k_BT_0^2}{\rho c_p}\frac{\left[(a+D\varepsilon_D)q^2 + \dfrac{c_p\Delta\tilde{h}^2L_r}{\rho}\right]\omega^2 + \Gamma_+(q)\Gamma_-(q)\left[Dq^2 + \dfrac{c_p\varepsilon_DL_r}{\rho k_T^2}\right]}{[\omega^2+\Gamma_+^2(q)][\omega^2+\Gamma_-^2(q)]}. \tag{37}$$

In Eqs. (36) and (37) the decay rates $\Gamma_\pm(q)$ of the fluctuations are given by

$$\Gamma_\pm(q) = \frac{1}{2}\left\{[a+D(\varepsilon_D+1)]q^2 + \frac{c_pL_r}{\rho k_T^2}(\varepsilon_D + k_T^2\Delta\tilde{h}^2)\right\}\left\{1 \pm \sqrt{1 - \frac{4q^2\left[aDq^2 + \dfrac{c_pL_r}{\rho k_T^2}(a\varepsilon_D + D(\varepsilon_D+k_T\Delta\tilde{h})^2)\right]}{\left[[a+D(\varepsilon_D+1)]q^2 + \dfrac{c_pL_r}{\rho k_T^2}(\varepsilon_D+k_T^2\Delta\tilde{h}^2)\right]^2}}\right\}. \tag{38}$$

To simplify Eqs. (36)–(38) we have used the fact that in chemical equilibrium $\Delta g=0$, so that the temperature derivative of Δg (minus the reaction entropy) is simply proportional to the reaction enthalpy Δh [see Eq. (6)] with $\Delta g=0$.

Equation (38) for the effects of the chemical reaction on the decay rates is rather long and complicated. An analysis of these decay rates for various ranges of the wave number q has been done by Lekkerkerker and Laidlaw.[10] Here, we consider some simplifications. A first possible approximation is to neglect the Dufour effect, which is a good assumption for

most ordinary liquid mixtures. However, neglecting the Dufour effect does not mean in our case to simply take the $\varepsilon_D \to 0$ limit of Eq. (38); although ε_D can indeed be very small, the dimensionless product $c_p L_r \varepsilon_D / \rho D q^2$ can be large depending on the rate of the chemical reaction and the wave number q. For this reason neglecting the Dufour effect leads only to a rather slight simplification of Eq. (38). However, we have found that a major simplification is obtained by adopting a large-Lewis-number approach (with $\mathrm{Le}=a/D$), which is also a good approximation for most ordinary liquid mixtures.[4] Indeed, taking the $\mathrm{Le} \to \infty$ limit of Eq. (38), we obtain

$$\Gamma_+(q) = D(\mathrm{Le} + \varepsilon_D)q^2 + \frac{c_p L_r}{\rho}\Delta\tilde{h}^2 + O(\mathrm{Le}^{-1}), \tag{39a}$$

$$\Gamma_-(q) = Dq^2 + \frac{L_r}{\rho T}\left(\frac{\partial \Delta g}{\partial c}\right)_T + \mathcal{O}(\mathrm{Le}^{-1}). \tag{39b}$$

If the chemical reaction is absent ($L_r \simeq 0$) and if the Dufour effect is negligible, we obtain from Eqs. (39a) and (39b): $\Gamma_+ \simeq aq^2$, $\Gamma_- \simeq Dq^2$, which are the well-known decay rates of the thermal and concentration fluctuations in a liquid mixture, respectively.[27,28] We have found that Eq. (39) gives a good representation of the decay rates $\Gamma_\pm(q)$ for reasonable liquid mixtures, except for $\Gamma_-(q)$ at very small wave numbers q, where it does not have the correct asymptotic limit. However, at such small wave numbers finite-size effects must be incorporated in the theory,[4] so that even Eq. (38) will need to be modified for small q. If we apply the same large-Lewis-number approximation to the dynamic structure factors Eqs. (36) and (37), it turns out that $S_{TT}(\omega,q)$ is $\mathcal{O}(Le^{-1})$, while $S_{cc}(\omega,q)$ is of $\mathcal{O}(1)$. Therefore, the intensity of the temperature fluctuations is negligible when compared to the intensity of concentration fluctuations, unless some particularity of the liquid mixture makes it otherwise (see below).

Notice in Eq. (38) as well as in Eqs. (39a) and (39b) that the decay rates of the fluctuations depend explicitly on the rate constant L_r. Hence, measuring these fluctuations by light scattering[4,27] or shadowgraphy[4,29,30] in a reacting mixture provides information about the rate constant of the reaction. For instance, Letamendia *et al.*[31,32] measured light scattering in various liquids with chemical equilibrium between two isomers. For these particular systems concentration fluctuations were not observable because the refractive indices of the two isomers are the same so that, in spite of large Le, only temperature fluctuations were observed. The experimental values obtained for the decay rate of the Rayleigh line at several scattering wave numbers q did agree well with Eq. (39a), with thermal diffusivity and rate constant obtained from independent sources.

Of particular interest here is the contribution of the concentration fluctuations to the static structure factor

$$S_{cc}(q) = \frac{1}{2\pi}\int_{-\infty}^{\infty} S_{cc}(\omega,q)d\omega, \tag{40}$$

which is related to the equal-time autocorrelation function of the concentration fluctuations as

$$\langle \delta c^*(t,\mathbf{q})\,\delta c(t,\mathbf{q}')\rangle = S_{cc}(q)(2\pi)^3\delta(\mathbf{q}-\mathbf{q}'). \tag{41}$$

Integrating Eq. (36) and using Eq. (38), we observe that the static structure factor $S_{cc}(q)$, in contrast to the dynamic structure factor $S_{cc}(\omega,q)$, does not depend on the wave number q of the fluctuations, and that it is simply given by the same result (inversely proportional to the osmotic compressibility) that would be obtained if chemical reactions were absent, namely[4,27,33]

$$S_{cc}(q) = \frac{k_B T_0}{\rho}\left(\frac{\partial \Delta g}{\partial c}\right)_T^{-1}. \tag{42}$$

Similarly for the temperature fluctuations, one finds

$$S_{TT}(q) = \frac{k_B T_0^2}{\rho c_p}. \tag{43}$$

The contribution from any cross correlation to the static structure factor is, as expected, zero. The results, Eqs. (42) and (43), depend crucially on the fact that $\Delta g = 0$, i.e., that the chemical reaction is in thermodynamic equilibrium everywhere in the system. We emphasize that the results [Eqs. (42) and (43)] for the static structure factor are obtained from the full expressions for the dynamic structure factor and the decay rates, without resorting to simplifications like neglecting the Dufour effect or assuming a large Lewis number.

From our present results, we reach the following conclusions:

(1) The static structure factors Eqs. (42) and (43) do not depend on the rate constant L_r and are the same as for a mixture without a chemical reaction. This is mainly a consequence of $\Delta g = 0$ everywhere; but can also be understood as a consequence of the Curie principle, i.e., because of their different tensorial character there is no thermodynamic coupling between the chemical reaction rate and the diffusive mass flux. In summary, while the dynamic structure factor contains information on the rate constant, such information is lost in the equal-time fluctuations. This feature has been noted previously in other chemically reacting systems,[4,27] where two active species are diluted in an inert "solvent" in the absence of temperature fluctuations.

(2) Since the static structure factor S_{cc} does not depend on the wave number q, the fluctuations in equilibrium are spatially short ranged, even when a chemical reaction is present. Indeed, by substituting Eq. (42) into Eq. (41) and applying Fourier inverse transformations, we arrive at

$$\langle \delta c^*(\mathbf{r},t)\,\delta c(\mathbf{r}',t)\rangle = \frac{k_B T}{\rho}\left(\frac{\partial \Delta g}{\partial c}\right)_T^{-1}\delta(\mathbf{r}-\mathbf{r}'), \tag{44}$$

confirming that equal-time fluctuations are spatially short ranged (proportional to delta functions on hydrodynamic length scales).

IV. CONCENTRATION FLUCTUATIONS IN A NONISOTHERMAL CHEMICALLY REACTING MIXTURE

In the presence of a temperature gradient that is assumed to be stationary, the chemically reacting mixture will evolve to a nonequilibrium steady state. Our next goal is to evaluate the intensity of the fluctuations around such a nonequilibrium state. For this purpose we must first discuss the stationary solution. We follow here de Groot and Mazur[9] by considering the stationary state of a quiescent ($\mathbf{v}=0$) chemically reacting fluid mixture in a temperature gradient enclosed in a reservoir. Consequently, we are assuming the absence of any thermal convection. Since in our current development we are neglecting buoyancy, the quiescent solution will be always stable and convection shall not develop in our system.

A. The stationary solution

We assume the presence of a nonuniform temperature profile $T_0(x)$ in the x direction, such that at $x=0$ the temperature $T(0)=T_1$ and at $x=L$ the temperature $T(L)=T_2$. Just as de Groot and Mazur,[9] we consider the stationary solution with $\mathbf{v}=0$ and uniform pressure and with $\mathbf{J}=0$ at the boundaries of the reservoir at $x=0$ and $x=L$. The stationary temperature profile $T_0(x)$ and the stationary reaction Gibbs-energy profile $\Delta g_0(x)$ are then readily obtained by equating the left-hand side (LHS) of Eqs. (17) to zero,

$$0 = -L_{QJ}\nabla^2\left(\frac{1}{T_0}\right) + L_{JJ}\nabla^2\left(\frac{\Delta g_0}{T_0}\right) - L_r\frac{\Delta g_0}{T_0}, \tag{45a}$$

$$0 = -L_{QQ}\nabla^2\left(\frac{1}{T_0}\right) + L_{JQ}\nabla^2\left(\frac{\Delta g_0}{T_0}\right). \tag{45b}$$

For simplicity and following previous authors,[8,9] we assume that all Onsager coefficients are constants, independent of temperature and, hence, independent of position. In the chemical literature, nonisothermal reaction-diffusion systems like the one described by Eqs. (45a) and (45b) have often been considered in the context of reacting gases inside pores of a solid catalyst pellet.[34–37] In those studies, the temperature dependence of the rate constant L_r is not neglected, and an Arrhenius dependence,[36] or other more complicated nonlinear kinetic expressions[34,35,37] are assumed for $L_r(T)$. These approaches lead to a system of nonlinear coupled differential equations for the temperature and activity profiles that can be solved only numerically. Our present aim is to evaluate nonequilibrium fluctuations around the stationary solution of Eqs. (45a) and (45b), and those fluctuations (as discussed in detail later) depend only very slightly on whether the linear or nonlinear approach is used to solve Eqs. (45a) and (45b). For simplicity, we choose here to discuss the linear version of Eqs. (45a) and (45b), which yields analytic expressions for the temperature and activity profiles. This linear approximation can be relevant in parts of plug-flow reactors which operate close to chemical equilibrium. Indeed, plug-flow reactors have domains of this type when they are in the state of minimum entropy production.[37]

As already mentioned, the linear version of the problem Eqs. (45a) and (45b) was extensively reviewed by de Groot and Mazur,[9] on the basis of previous work by Meixner and Prigogine. We simply give the results in terms of our notation. They are

$$\frac{\Delta g_0(x)}{T_0(x)} = \frac{-\Delta T}{T_1}\frac{\rho D}{L_r}\frac{k_T\,\mathrm{Le}[\varepsilon_D + k_T\Delta\tilde{h}]}{d^2\tilde{Z}\varepsilon_D}\sinh\left[\frac{1}{d}\left(x-\frac{L}{2}\right)\right],$$

$$\frac{T_1T_2}{T_0(x)} = \bar{T} + \frac{\Delta T}{\tilde{Z}}\left\{\frac{\mathrm{Le}}{d}\cosh\left(\frac{L}{2d}\right)\left(x-\frac{L}{2}\right) + \frac{(\varepsilon_D + k_T\Delta\tilde{h})^2}{\varepsilon_D}\sinh\left[\frac{1}{d}\left(x-\frac{L}{2}\right)\right]\right\}, \tag{46}$$

where $\bar{T}$ represents the mean temperature $\bar{T}=(T_1+T_2)/2$ and $\Delta T=T_2-T_1$ the temperature difference between the two walls bounding the system. Furthermore,

$$\frac{1}{d^2} = \frac{L_rL_{QQ}}{L_{JJ}L_{QQ}-L_{JQ}^2} = \frac{L_r}{\rho DT}\left(\frac{\partial\Delta g}{\partial c}\right)_T\left[1+\frac{(\varepsilon_D+k_T\Delta\tilde{h})^2}{\mathrm{Le}\,\varepsilon_D}\right] = \frac{\phi^2}{L^2}\left[1+\frac{(\varepsilon_D+k_T\Delta\tilde{h})^2}{\mathrm{Le}\,\varepsilon_D}\right],$$

$$\tilde{Z} = \frac{2(\varepsilon_D+k_T\Delta\tilde{h})^2}{\varepsilon_D}\sinh\left(\frac{L}{2d}\right) + \mathrm{Le}\frac{L}{d}\cosh\left(\frac{L}{2d}\right). \tag{47}$$

The parameter d has units of length and is commonly referred to as the "penetration length" of the chemical reaction.[9] The dimensionless parameter ϕ in Eq. (47) has been used by Demirel[36] when solving the nonlinear (Arrhenius) version of Eq. (45a) and (45b). Except for corrections due to the Soret and Dufour effects, it can be interpreted as the ratio of the size of the system L to the penetration length d. Indeed, for the isothermal case (when Soret and Dufour effects are absent) if a concentration gradient is externally imposed the corresponding penetration length is simply given by $d=L/\phi$. Hence, Eq. (47) displays corrections to the penetration length due to the Soret and Dufour effects, similarly to recent work of Demirel[36] for the nonlinear regime. For a so-called "diffusion-controlled" process, ϕ is very large, so that the ratio d/L becomes very small. On the other hand, when d/L is large, we have an "activation-controlled" or, simply, an activated process. We have verified that in the large ϕ limit, the inverse temperature of Eq. (46) reduces to a linear profile like the one expected when there is no chemical reaction in the system.

For the calculation of nonequilibrium fluctuations in the next section, we shall actually need the stationary concentration gradient at the center of the layer. For this purpose we note that

$$\frac{dc}{dx} = T\left(\frac{\partial\Delta g}{\partial c}\right)_T^{-1}\left\{\frac{d(\Delta g/T)}{dx} - \left[\Delta g - T\left(\frac{\partial\Delta g}{\partial T}\right)_c\right]\frac{d(1/T)}{dx}\right\}. \tag{48}$$

Upon substitution of Eq. (46) into Eq. (48), we readily obtain for the concentration gradient at $x=L/2$

$$\nabla c_0|_{L/2} = -k_T \frac{\Delta T \overline{T}}{T_1 T_2} \frac{(\varepsilon_D + k_T \Delta\tilde{h})(\mathrm{Le} + \varepsilon_D + k_T \Delta\tilde{h}) - k_T \Delta\tilde{h}\ \mathrm{Le} \cosh\left(\frac{L}{2d}\right)}{2d(\varepsilon_D + k_T \Delta\tilde{h})^2 \sinh\left(\frac{L}{2d}\right) + \varepsilon_D\ \mathrm{Le}\ L \cosh\left(\frac{L}{2d}\right)}, \tag{49}$$

where the temperature $\overline{T}$ is identified with the average temperature of the layer, as used in the definition of the Dufour effect ratio and the dimensionless enthalpy of reaction. We shall again consider a large-Lewis-number approximation, for which we shall be specifically interested in the gradient at the middle of the cell in this limit. Taking the $\mathrm{Le} \to \infty$ limit of Eq. (49), we obtain

$$\nabla c_0|_{L/2} = -k_T \frac{\Delta T}{L} \frac{T}{T_1 T_2} \frac{1}{\varepsilon_D} \left[(\varepsilon_D + k_T \Delta\tilde{h}) \mathrm{sech}\left(\frac{L}{2d}\right) - k_T \Delta\tilde{h} \right], \tag{50}$$

which has to be compared with a uniform value $dc_0/dx = (-k_T/T)(\Delta T/L)$ that would be obtained if no chemical reaction were present in the system.

B. Nonequilibrium structure factor

We start the calculation of the nonequilibrium structure factor of the fluid by setting up the evolution equations for the thermodynamic fluctuations around the stationary solution described in the previous section. For this purpose we follow exactly the same generic procedure described in Sec. III for the isothermal case. Thus, we start from the balance laws in the form Eq. (8a)–(8d), and substitute in the RHS the thermodynamic fields by their stationary values (as described in Sec. IV A) plus some "fluctuation," for instance, $T(\mathbf{r},t) = T_0(x) + \delta T(\mathbf{r},t)$, $\mathbf{v}(\mathbf{r},t) = \delta\mathbf{v}(\mathbf{r},t)$, etc. Next, we perform a similar substitution in the phenomenological laws Eq. (13a)–(13d), *and* we add random fluxes $\delta\Pi$, $\delta\mathbf{Q}$, $\delta\mathbf{J}$, and $\delta\xi$, as was explained in more detail for the energy flux in Eq. (22). Finally, by substitution of these "random" linear phenomenological laws in the LHS of the balance laws, we obtain the fluctuating-hydrodynamics equations, from which the spatiotemporal evolution of the fluctuating thermodynamic variables may be initially computed.

The generic procedure described above produces some complicated nonlinear equations and some approximations are *de rigueur*. First, some simplifications come from the observation that $T_0(x)$ and $\Delta g_0(x)$ are solutions of the stationary problem Eq. (45a) and (45b). Next, the most important simplification is obtained by linearizing the resulting expressions in the fluctuating fields. This approximation is justified if the fluctuations are "small." Previous work in nonreacting mixtures[4] shows that this is so when the stationary quiescent solution is stable, meaning that we are far from any instability like convection. Although we have not yet performed a complete and detailed analysis, we believe that our stationary solution Eq. (46) is always stable in the absence of buoyancy, and that we can safely linearize our evolution equations for the nonequilibrium fluctuations. After having linearized the equations, a further simplification can be obtained by taking a double curl of the fluctuating Navier-Stokes equation and using the divergence-free condition, $\nabla \cdot \delta\mathbf{v} = 0$. This procedure decouples the equations for the fluctuations in the y- and z components of the velocity from the temperature or concentration fluctuations. With all these simplifications, the fluctuating hydrodynamic equations (expressed in terms of the ordinary transport coefficients) read

$$\frac{\partial}{\partial t} \nabla^2 \delta v_x = \nu \nabla^2 (\nabla^2 \delta v_x) + \frac{1}{\rho} \{\nabla \times \nabla \times (\nabla \cdot \delta\Pi)\}_x, \tag{51a}$$

$$\frac{\partial}{\partial t} \delta c + \delta v_x \frac{dc_0}{dx} = D \left\{ \nabla^2 \delta c + \frac{k_T}{T} \nabla^2 \delta T \right\} - \frac{L_r}{\rho T} \delta(\Delta g) - \frac{1}{\rho} \nabla \cdot \delta\mathbf{J} + \frac{1}{\rho} \delta\xi, \tag{51b}$$

$$\frac{\partial}{\partial t} \delta T + \delta v_x \frac{dT_0}{dx} + T\Delta\tilde{h} \left[\frac{\partial}{\partial t} \delta c + \delta v_x \frac{dc_0}{dx} \right] = [a + D(\varepsilon_D + k_T \Delta\tilde{h})] \nabla^2 \delta T + \frac{DT}{k_T} (\varepsilon_D + k_T \Delta\tilde{h}) \nabla^2 \delta c - \frac{1}{\rho c_p} \nabla \cdot \delta\mathbf{Q}. \tag{51c}$$

It is interesting to compare Eqs. (51a)–(51c) with Eqs. (26a) and (26b) for the fluctuations around the equilibrium state. We notice that the main difference is that, because of the presence of nonvanishing stationary temperature and concentration gradients, in Eqs. (51b) and (51c) there appears a coupling (via the advection term in the balance laws) between the velocity fluctuations parallel to the gradient and the temperature or concentration fluctuations. Physically this is due to the fact that velocity fluctuations parallel to the stationary gradients do probe regions with different temperature or concentration values. As in the case of a nonisothermal nonreacting binary mixture,[4] this coupling is precisely the origin of an enhancement of the hydrodynamic fluctuations when the system is in a quiescent nonequilibrium steady state. In this paper we discuss fluctuations in nonequilibrium states that are quiescent. For situations very far from equilibrium, i.e., developed convection, nonlinear phenomena not covered by Eqs. (51a)–(51c) may appear. Our present analysis is for a system that is in local equilibrium, but far from global equilibrium.

Although nonequilibrium fluctuations can be directly evaluated from Eqs. (51a)–(51c), again a further simplification can be achieved by exploiting the fact that for dense fluids (liquids) the Lewis number $\mathrm{Le} = a/D$ is usually quite large. This is the same approximation used in Eqs. (39a) and

(39b) to simplify the expression for the equilibrium decay rates. For the nonequilibrium problem Eq. (51a)–(51c) the large-Lewis-number approximation was first proposed by Velarde and Schechter[38] so as to simplify the instability analysis when buoyancy effects are incorporated in the theory. The same approximation scheme also has been successfully used by some of us to study nonequilibrium concentration fluctuations induced by the Soret effect in a nonreacting binary mixture.[39,40] The most important consequence of this large-Lewis-number approximation is that temperature fluctuations can be ignored, and that only the coupling via the balance laws between concentration and velocity fluctuations needs to be considered. Indeed, in ordinary liquid mixtures concentration fluctuations usually dominate, and temperature fluctuations are more difficult to observe by the ordinary techniques like light scattering.[41–43] The same has been found from nonequilibrium molecular dynamics simulations.[44] Further details concerning this approximation scheme can be found in the relevant literature.[38,40] In the $\mathrm{Le}\to\infty$ limit the set of working Eqs. (51a)–(51c) reduces to

$$0=\nu\nabla^2(\nabla^2\delta v_x)+\frac{1}{\rho}\{\nabla\times\nabla\times(\nabla\cdot\delta\Pi)\}_z, \tag{52a}$$

$$\frac{\partial}{\partial t}\delta c+\delta v_x\,\nabla c_0|_{L/2}=D\nabla^2\delta c-\frac{L_r}{\rho T}\left(\frac{\partial\Delta g}{\partial c}\right)_{p,T}\delta c-\frac{1}{\rho}\nabla\cdot\delta\mathbf{J}+\frac{1}{\rho}\delta\xi. \tag{52b}$$

One further simplification has been performed in Eqs. (52a) and (52b), namely, we have identified the stationary concentration gradient that, initially, is an inhomogeneous position-dependent magnitude with its value at the center of the cell. This approximation simplifies enormously the calculation of the structure factor. Furthermore, it is consistent with having neglected throughout this paper the position dependence of all thermophysical properties of the mixture, such as the Onsager coefficients and, hence, the transport coefficients and the Lewis number. The influence of such nonlinearities in nonequilibrium fluctuations has been considered elsewhere,[3,45] and is negligible when nonequilibrium coupling between the fluctuating fields exists via the balance laws, as is the case here. We note that, with this approximation, the nonequilibrium structure factor will depend on the value of the concentration gradient at the center of the cell, and not on the detailed concentration profile $c_0(x)$. As a consequence, our final result will be only slightly sensitive to whether a linear or a nonlinear (numerical) approach is used to obtain the stationary solution of Eq. (46). For the same reason, our present results may also be applicable to some kinds of open systems[36] for which the stationary solution can still be represented by Eqs. (45a) and (45b) with $\mathbf{v}=0$, but with a nonvanishing diffusion flux $\mathbf{J}$ at the boundaries.

We shall not consider boundary conditions for the fluctuating fields in this paper. In general, fluctuations in fluids subjected to a temperature gradient at large wavelengths comparable to the size of the system are affected by the conditions at the boundaries.[46] However, boundary conditions are not needed to reproduce the proper asymptotic behavior of the nonequilibrium hydrodynamic fluctuations at small wavelengths (but still large enough to be in the hydrodynamic regime).[4,46] Deviations from our solution are expected for larger wavelengths due to confinement effects, but they are not considered in the present paper.

Thus, we take a full spatiotemporal Fourier transform of Eqs. (52a) and (52b), as we did in Eq. (29) for the equilibrium fluctuations. This procedure yields a linear set of algebraic equations that may be written in the usual form as

$$\mathrm{G}^{-1}(\omega,q)\cdot\begin{pmatrix}\delta v_x(\omega,\mathbf{q})\\ \delta c(\omega,\mathbf{q})\end{pmatrix}=\mathbf{F}(\omega,\mathbf{q})=\frac{1}{\rho}\begin{pmatrix}i\varepsilon_{0ni}q_n\varepsilon_{ijk}q_j[q_l\delta\Pi_{lk}(\omega,\mathbf{q})]\\ -iq_i\delta J_i(\omega,\mathbf{q})+\delta\xi(\omega,\mathbf{q})\end{pmatrix}, \tag{53}$$

where ω and $\mathbf{q}$ are the frequency and the wave vector of the fluctuations, respectively. In the expression of the vector of random forces $\mathbf{F}(\omega,\mathbf{q})$, summation over repeated indices is again understood, and in the first of the Levi-Civitta tensors, an index "0" appears because the actual random force corresponds to the x component of the vector between curly brackets in the RHS of Eq. (52a). The explicit expression of the inverse linear response function for the nonequilibrium fluctuations on the LHS of Eq. (53) is

$$\mathrm{G}^{-1}(\omega,q)=\begin{pmatrix}\nu q^4 & 0\\ \nabla c_0|_{L/2} & i\omega+Dq^2+\frac{L_r}{\rho T}\left(\frac{\partial\Delta g}{\partial c}\right)_T\end{pmatrix}. \tag{54}$$

The Fourier-transformed fluctuating fields can then be simply evaluated by inversion of Eq. (54). As in Sec. III B for the fluctuations in equilibrium, we are interested in the autocorrelation function of the (Fourier-transformed) concentration fluctuations, i.e., $\langle\delta c^*(\omega,\mathbf{q})\delta c(\omega',\mathbf{q}')\rangle$. For a calculation of this quantity, we need the correlations between the components of the random noise vector introduced in the RHS of Eq. (53). Again, these functions are conveniently expressed in terms of a correlation matrix $C(q)$, defined by

$$\langle F_i^*(\omega,\mathbf{q})F_j(\omega',\mathbf{q}')\rangle=\frac{2k_B\bar{T}}{\rho}\left(\frac{\partial\Delta g}{\partial c}\right)_T^{-1}C_{ij}(q)(2\pi)^4\delta(\omega-\omega')\delta(\mathbf{q}-\mathbf{q}'). \tag{55}$$

By combining the definition Eq. (53) of the vector $\mathbf{F}(\omega,\mathbf{q})$ with the fluctuation-dissipation theorem, Eq. (25a)–(25e), we readily obtain

$$C(q)=\begin{pmatrix}\nu\left(\frac{\partial\Delta g}{\partial c}\right)_T q_\parallel^2 q^4 & 0\\ 0 & Dq^2+\frac{L_r}{\rho T}\left(\frac{\partial\Delta g}{\partial c}\right)_T\end{pmatrix}, \tag{56}$$

where $q_\parallel^2=q_y^2+q_z^2$, with $q_\parallel$ being the component of the wave vector in the direction normal to that of the stationary concentration gradient.

In Eqs. (55) and (56) we are implicitly adopting the strong assumption that the fluctuation-dissipation theorem Eq. (25a)–(25e), initially valid only for fluctuations around

equilibrium states, will also hold *locally* in nonequilibrium steady states,[47] provided that the various thermophysical properties appearing in its formulation are identified with their local-equilibrium values. The physics behind such an extension of the fluctuation-dissipation theorem is that, even outside equilibrium the correlation between the components of the stochastic part of the fluxes continues to be short ranged and, thus, within a hydrodynamic theory, proportional to delta functions in space and time. The validity of such an extension of the fluctuation-dissipation theorem has been confirmed experimentally for (nonreacting) fluids in a temperature gradient.[4,42,48] In this same context, we also remind the reader that effects due to nonlinearities such as inhomogeneously correlated thermal noise[49] are completely negligible when there exists a coupling in nonequilibrium between fluctuating fields via the balance laws,[3] such as the one we found in Eq. (52a) and (52b).

Inverting Eq. (54) and substituting the result into Eq. (35) (with the matrices G and C appropriate to the nonequilibrium case), we obtain

$$S_{cc}(\omega,\mathbf{q}) = \frac{2k_B\bar{T}}{\rho}\frac{D\left(\frac{\partial\Delta g}{\partial c}\right)_T^{-1}q^2+\frac{L_r}{\rho T}}{\omega^2+\left[Dq^2+\frac{L_r}{\rho T}\left(\frac{\partial\Delta g}{\partial c}\right)_T\right]^2} \times\left\{1+\frac{q_\parallel^2\left(\frac{\partial\Delta g}{\partial c}\right)_T(\nabla c_0|_{L/2})^2}{\nu q^4\left[Dq^2+\frac{L_r}{\rho T}\left(\frac{\partial\Delta g}{\partial c}\right)_T\right]}\right\}, \tag{57}$$

where the concentration gradient at the center of the cell is given by Eq. (50) in the large-Lewis-number approximation. We observe in Eq. (57) that the decay rate of nonequilibrium concentration fluctuations is the same as the decay rate of equilibrium concentration fluctuations, which in the large-Lewis-number approximation was given by Eq. (39b). This is a generic feature of nonequilibrium fluctuations, namely, that in first approximation for sufficiently large wave numbers the decay rate of the fluctuations is the same, while the intensity of the fluctuations is strongly affected by the nonequilibrium constraints.[4] However, inclusion of the effects of buoyancy and of boundary conditions does modify the decay rate at small wave numbers.[4]

To obtain the total intensity of the nonequilibrium concentration fluctuations we integrate $S_{cc}(\omega,q)$ over the frequency ω in accordance with Eq. (40), obtaining the static structure factor $S_{cc}(q)$. In terms of a dimensionless wave number $\tilde{q}=qL$,

$$S_{cc}(\mathbf{q}) = S_{cc}^{(E)}\left\{1+\tilde{S}_{cc}^{(\mathrm{NE},0)}\frac{\tilde{q}_\parallel^2}{\tilde{q}^4\left[\tilde{q}^2+\frac{L^2}{d^2}\right]}\right\} = S_{cc}^{(E)}\left\{1+\tilde{S}_{cc}^{(\mathrm{NE},0)}\frac{\tilde{q}_\parallel^2}{\tilde{q}^4[\tilde{q}^2+\phi^2]}\right\}, \tag{58}$$

where $S_{cc}^{(E)}$ is the equilibrium structure factor given by Eq. (42), and where $\tilde{S}_{cc}^{(\mathrm{NE},0)}$ is a normalized nonequilibrium enhancement of concentration fluctuations,

$$\tilde{S}_{cc}^{(\mathrm{NE},0)} = \frac{(\nabla c_0|_{L/2})^2}{\nu DL^4}\left(\frac{\partial\Delta g}{\partial c}\right)_T. \tag{59}$$

Our final results, Eqs. (57) and (58), exhibit the typical structure of nonequilibrium fluctuations, containing a nonequilibrium enhancement which explicitly depends on the wave number $\mathbf{q}$, showing that the equal-time nonequilibrium concentration fluctuations become spatially long ranged. We recall that $S_{cc}(q)$ is again related to the equal-time concentration fluctuations correlation function by Eq. (41).

We find that the nonequilibrium enhancement exhibits a crossover from the well-known q^{-4} dependence observed in nonreacting liquid mixtures[4] to a q^{-2} dependence for smaller wave numbers. The q^{-2} behavior is the one typically found when studying long-range nonequilibrium fluctuations in isothermal reacting mixtures, as discussed by several authors.[4,23,50] The crossover from a q^{-4} (nonisothermal nonreacting) to a q^{-2} (nonequilibrium but isothermally reacting) behavior occurs at wave numbers of the order

$$\tilde{q}_{\mathrm{CO}}^2 \simeq \frac{L^2}{D}\frac{L_r}{\rho T}\left(\frac{\partial\Delta g}{\partial c}\right)_T \simeq \frac{L^2}{d^2} = \phi^2, \tag{60}$$

which is closely related to the inverse of the penetration length of the stationary solution as given by Eq. (47). As mentioned by de Groot and Mazur,[9] the penetration depth d in liquid mixtures typically varies from 0.01 to 1 cm. As an illustration, we present in Fig. 1 a plot of the dimensionless nonequilibrium enhancement of the concentration fluctuations as a function of the dimensionless wave number. The plot is for $d=0.1$ cm and $L=0.2$ cm, which is a typical experimental value for the height of an optical cell;[51] thus, the dimensionless parameter $\phi=2$. Figure 1 shows a clear crossover from the asymptotic q^{-4} dependence at larger wave numbers (unaffected by the chemical reaction) to a q^{-2} dependence for smaller wave numbers.

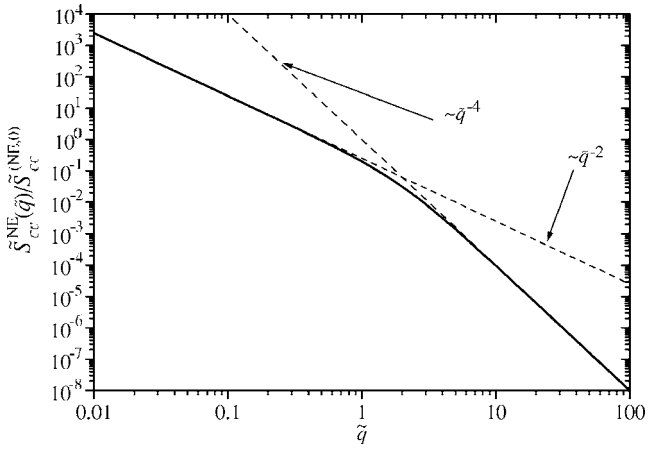

FIG. 1. Dimensionless enhancement of nonequilibrium concentration fluctuations as a function of dimensionless wave number, $\tilde{q}=qL$, for parameter $\phi=2$ (diffusion-controlled reaction). The crossover from the asymptotic q^{-4} dependence to q^{-2} dependence at smaller wave numbers is evident.

V. DISCUSSION AND CONCLUSIONS

We have mentioned in the Introduction that reactor stability may be affected by nonequilibrium hydrodynamic fluctuations. It is now clear from the above derivations that an activation controlled reactor, where this is relevant, can experience large fluctuations in the direction perpendicular to the transport direction of a tubular reactor. This may at certain conditions trigger a local bifurcation. A quantitative discussion of this issue requires an analysis of a more complicated reaction system, however, and is premature at the moment. In this section we only mention some consequences of our findings for experiments (light scattering and shadowgraphy) and for nonequilibrium molecular dynamics simulations. They shall be discussed separately below, along with a summary of the main findings.

A. Light scattering and shadowgraphy

We have seen above that the theory of hydrodynamic fluctuations can provide information about the transport coefficients D and L_r from measurements of the structure factor $S(\omega,q)$. This can be done by light scattering. The concentration fluctuations then give D from Eq. (59), and the coefficient L_r from Eq. (60).

We also predict an enhancement of the intensity of concentration fluctuations in the presence of a temperature gradient. The intensity of the fluctuations depends on the wave number q, and exhibits a crossover from q^{-4} to q^{-2} behavior. The crossover occurs when the wavelength is of the order of the penetration depth d. For wavelengths smaller than d a q^{-4} behavior will be observed and for wavelengths larger than d a q^{-2} behavior is expected (see Fig. 1). Small values of d correspond to diffusion-controlled processes and large values of d correspond to activated processes. Hence, by studying the wave-number dependence of the nonequilibrium concentration fluctuations it would in principle be possible to distinguish between a diffusion-controlled process and an activated process. This is a central issue in reactor engineering.[1] The actually feasibility of observing the crossover from q^{-4} to q^{-2} behavior will depend on the magnitude of the penetration depth. When the penetration depth is a mesoscopic length, the crossover can be observed by light scattering. When the penetration depth is a macroscopic length (as it often is[9]) shadowgraphy would be needed.[4,29] However, for a quantitative interpretation of experimental shadowgraphs, we shall need to also consider the effects of buoyancy and of the boundary conditions on the fluctuations.[4]

Our theory can also provide a way to probe whether chemical equilibrium has been reached in the temperature gradient. A mixture where the reactants and products are in chemical equilibrium has $\Delta g=0$. This condition may hold true also in a volume element exposed to a temperature gradient.[8] Such a volume element will then show q^{-2} behavior, while a volume element with the same mixture, but without chemical equilibrium, will show q^{-4} proportionality. Light scattering and/or shadowgraphy may in this manner serve as a process on-line tool to probe the progress of a chemical reaction.

B. Nonequilibrium molecular simulations

Molecular simulations are convenient tools for transport-coefficient determinations. It is therefore interesting to see whether this technique can also be used to determine hydrodynamic fluctuations. Clearly, one has to resort to nonequilibrium simulations to study the fluctuations considered here.

The nonequilibrium molecular simulations reported earlier[7,8] were not done in a manner that allows verification of the structure factors predicted here. The transport processes in that work[7,8] were described as one-dimensional processes, while sampling of the data for the present purpose must be done in the direction perpendicular to this direction. This can be seen from Eqs. (57) and (58), which explicitly contain $q_{\|}$. A first step in the direction of probing hydrodynamic fluctuations by nonequilibrium molecular simulations must include calculations of correlations in the direction normal to the direction of the temperature and concentration gradients.

The nonequilibrium enhancement of the concentration fluctuations caused by an externally imposed temperature gradient is proportional to the ratio $(\nabla T)^2/q^4$. The value of the proportionality constant[42,51] is around 10^{10} K^{-2} cm^{-2}. In molecular dynamics simulations the wave number of the observable fluctuations is limited by the size of the system, so that $q_{\min}\simeq 2\pi/L$. Therefore, we conclude that in order to have an observable nonequilibrium enhancement (of about 10%), the size of the system has to be at least $L_{\min}\simeq 2000/\Delta T$ nm, with ΔT being the temperature difference imposed between the two thermostats. For a typical temperature gradient, $\Delta T/L=10^8$ K/m, and a box with dimensions $4\times 4\times 8$ nm, one has to increase one of the lengths in a direction normal to the transport direction by a factor of 250, making this length 1000 nm or 1 micron. For condensed densities of around 7 particles per cubic nanometer, this means that simulations have to be performed with about 250 000 particles.

Another important factor is the time that the simulations have to run to observe nonequilibrium fluctuations. This time has to be several times the decay rate of the fluctuations. The decay time of nonequilibrium fluctuations is the same as in equilibrium; thus, for binary mixtures concentration fluctuations decay with $\Gamma\simeq Dq^2$, Eq. (39b). For a system of 200 nm size and for $D\simeq 10^{-5}$ cm^2 s^{-1}, this time will be around several μs.

To run simulations with several hundred thousand particles over tens of μs is not completely unreasonable, given the current calculation capabilities. The possibility to observe nonequilibrium fluctuations may be a good motivation to perform these very large-scale molecular simulations.

The transition we predict from q^{-4} to q^{-2} behavior in the presence of a chemical reaction will be more difficult to observe by nonequilibrium molecular dynamics than the asymptotic q^{-4} variation.

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