Nonequilibrium fluctuations in time-dependent diffusion processes

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A fluctuating hydrodynamics approach is presented for the calculation of the structure factor for *time-dependent* nonequilibrium diffusive processes in binary liquid mixtures. The hydrodynamic equations are linearized around the time-dependent macroscopic state given by the usual phenomenological diffusion equation. The cases of free diffusion, thermal diffusion, and barodiffusion are considered in detail. The results are used to describe the low-angle scattered intensity distributions from the time-dependent concentration profiles during the approach to steady state. The theoretical predictions are found to be in agreement with experimental data from thermal diffusion and free diffusion experiments. It is shown that in general the presence of nonequilibrium concentration fluctuations yields a substantial increase in the static structure factor over the equilibrium value, at least for the cases of free diffusion and thermal diffusion. As in the case of nonequilibrium fluctuations at steady state, the static structure factor displays a fast k^{-4} divergence at larger wave vectors k, and saturation to a constant value for k smaller than a critical wave vector k_{RO}. It is also shown that the static structure factor from a sedimenting mixture is actually temporarily lowered below the equilibrium value for k smaller than k_{RO}. As the steady state is approached, the structure factor loses any k dependence and it attains the equilibrium value. [S1063-651X(98)14910-3]

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I. INTRODUCTION

Equilibrium fluctuations in simple fluids and in binary mixtures have been studied very extensively in the past, mostly because the invention of the laser and the subsequent refinement of light scattering techniques have allowed thorough studies both of static and dynamic correlation properties of the fluctuations.

The behavior of the nonequilibrium fluctuations in a fluid under a steady stress condition has attracted much interest only fairly recently, the question being whether under stress the fluctuations retain the same correlation properties as in equilibrium. Particular attention has been dedicated to the study of the system consisting in a horizontal slab of fluid stressed by a steady stabilizing temperature gradient. Theoretical calculations, based on kinetic theories [1] and on fluctuating hydrodynamics [2–4], have shown that the fluctuations in this system are long range correlated, their static structure factor diverging as k^{-4} as the wave vector k goes to zero. The presence of long range correlations has been interpreted as a result of the coupling of velocity fluctuations with temperature and concentration fluctuations, due to the presence of macroscopic temperature and concentration gradients.

In a series of thorough experiments [5–8] Gammon, Law, Segrè, Sengers, and co-workers have measured the static structure factor of both simple fluids and binary mixtures stressed by a stationary thermal gradient, thus providing a neat quantitative check of the theoretical predictions. In order to measure the nonequilibrium static structure factor they used low-angle dynamic light scattering, which allowed them to get rid of the strong forward stray light, simply because it is not time correlated. By averaging a scattered intensity time autocorrelation function over a long period, they isolated the tiny fluctuating intensity on the top of the strong static stray intensity. Stray light can therefore be eliminated but at the expense of long measurement times. Consequently dynamic light scattering techniques are not suited to study time-dependent nonequilibrium fluctuations. This might partially explain why experimental studies of the time-dependent nonequilibrium fluctuations have been lacking until fairly recently.

In this paper we will show a simple way to obtain a theoretical description of time-dependent nonequilibrium fluctuations in diffusion processes. The description proceeds along the same fluctuating hydrodynamics guidelines of the stationary case. The main difference is that the fluctuating hydrodynamics equations are not linearized around a steady state, but instead around a macroscopic nonsteady state, whose time evolution can be obtained from the usual phenomenological diffusion equation. The time-dependent static structure factor can be obtained by supplementing the stationary structure factor with the phenomenological equations describing the time evolution of the macroscopic variables. In the following section we will derive the static structure factor of the nonequilibrium fluctuations which take place in a binary mixture where a time-dependent concentration gradient is present. We will explicitly consider the cases of free isothermal diffusion, of thermal diffusion, and of a gravitationally induced concentration gradient (barodiffusion). We will compare the results obtained for thermal diffusion and free diffusion with the data recently obtained by means of a unique ultra-low-angle static light scattering machine, which is able to measure the static intensity of the scattered light over a two decade range of angles, starting from $\theta = 2'$. This instrument allowed us to provide the first experimental evidence of the presence of long range correlated fluctuations during time-dependent diffusion processes [9,10].

It is already known that the presence of a stationary gravitationally induced concentration gradient (barodiffusion)

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does not produce any enhancement of the mean square amplitude of the fluctuations above the equilibrium value [11,12]. However, no predictions are available about the time evolution leading to the steady state (assuming a homogeneous, well mixed initial state). We will show that in this case the amplitude of the nonequilibrium fluctuations actually falls temporarily below the equilibrium value.

II. THE STRUCTURE FACTOR OF NONEQUILIBRIUM FLUCTUATIONS

The structure factor is the fundamental tool to describe fluctuations in a fluid. It is also most appropriate in this discussion since we will mainly describe scattering data.

In order to derive the structure factor of the time-dependent nonequilibrium concentration fluctuations we will use the fluctuating hydrodynamics (FH) approach [13]. Fluctuating hydrodynamics has been successfully used to describe nonequilibrium fluid systems at steady state [1–4,11,12,14].

We will now show that a time-dependent theory of nonequilibrium fluctuations in diffusion processes can be obtained by supplementing the FH equations with phenomenological equations describing the time evolution of the macroscopic state of a binary mixture. To simplify the problem we will neglect pressure fluctuations which contribute to Brillouin scattering only [14]. We will also neglect temperature fluctuations, so that the only relevant hydrodynamic variables are the density ρ, the concentration c, and the velocity $\mathbf{u}$ of the mixture. Moreover we will assume that the fluid is at rest. The hydrodynamic equations describing the mixture in the presence of gravity are then [12]

$$\frac{\partial c}{\partial t}+\mathbf{u}\cdot\nabla c=-\frac{1}{\rho}\nabla\cdot\mathbf{j}, \tag{1}$$

$$\frac{\partial \mathbf{u}}{\partial t}=-\frac{1}{\rho}\nabla p+\upsilon\nabla^2\mathbf{u}+\mathbf{g}, \tag{2}$$

where ρ is the mass density of the mixture, c is the weight fraction of the denser component, $\mathbf{j}$ is the mass flux, p is the hydrostatic pressure, υ the kinematic viscosity, and $\mathbf{g}$ the gravitational acceleration vector. The hydrodynamic variables c, ρ, and $\mathbf{u}$ fluctuate both in time and space around a certain average macroscopic value. As customary [13] we rewrite these variables as the sum of an averaged term and a fluctuating one:

$$c(\mathbf{x},t)=\langle c(\mathbf{x},t)\rangle+\delta c(\mathbf{x},t), \tag{3}$$

$$\rho(\mathbf{x},t)=\langle\rho(\mathbf{x},t)\rangle+\delta\rho(\mathbf{x},t)=\langle\rho(\mathbf{x},t)\rangle+\rho\beta\delta c(\mathbf{x},t), \tag{4}$$

$$\mathbf{u}(\mathbf{x},t)=\langle\mathbf{u}(\mathbf{x},t)\rangle+\delta\mathbf{u}(\mathbf{x},t)=\delta\mathbf{u}(\mathbf{x},t). \tag{5}$$

In writing Eq. (4) we have assumed that the only relevant density fluctuations are due to concentration fluctuations so that $\delta\rho=\rho\beta\delta c$, where $\beta=\rho^{-1}(\partial\rho/\partial c)_{p,T}$ (the thermal expansion effect is neglected because we have neglected temperature fluctuations). Moreover we have inserted in Eq. (5) the quiescent fluid hypothesis $\langle\mathbf{u}\rangle=\mathbf{0}$.

The averaged variables in Eqs. (3)–(5) depend both on space and time. We will assume that the time associated with changes in the macroscopic variables is much larger than those involved in the relaxation of the fluctuations. In this way the average values and the time Fourier transform can be calculated by integrating over the finite time needed to smooth out the fluctuations to zero [15]. During this time the macroscopic variables are assumed to be frozen. This assumption is consistent with our results because, as we will show later, the gravitational field determines an upper limit for the relaxation time of the fluctuations. In microgravity conditions the validity of the assumption could be seriously questioned.

To soften the notations, in the following we will drop the brackets from the averaged variables and we will not indicate the space-time dependence of both fluctuating and macroscopic variables.

By linearizing the equations around the macroscopic time-dependent state we obtain

$$\frac{\partial c}{\partial t}+\frac{1}{\rho}\nabla\cdot\mathbf{j}=-\frac{\partial\delta c}{\partial t}-\delta\mathbf{u}\cdot\nabla c-\frac{1}{\rho}\nabla\cdot\delta\mathbf{j}+\frac{1}{\rho}\beta\delta c\nabla\cdot\mathbf{j}+\nabla\cdot\mathbf{F}, \tag{6}$$

$$\frac{1}{\rho}\nabla p-\mathbf{g}=-\frac{\partial\delta\mathbf{u}}{\partial t}+\frac{1}{\rho}\beta\delta c\nabla p+\nu\nabla^2\delta\mathbf{u}+\frac{1}{\rho}\nabla\cdot\mathbf{S}, \tag{7}$$

where we have added terms containing the random forces $\mathbf{F}$ and $\mathbf{S}$, which describe the spontaneous onset of concentration and velocity fluctuations, respectively.

Equations (6) and (7) have to be complemented by phenomenological equations which describe the time evolution of the macroscopic state. In the steady-state theory these equations are $\partial c/\partial t=0$, $\partial\rho/\partial t=0$, which describe the time independence of mass-related variables, $\mathbf{u}=\mathbf{0}$, which stands for the absence of macroscopic convection, $\nabla\cdot\mathbf{j}=0$, which describes the absence of a net mass transfer in a layer of fluid, and $\nabla p=\rho\mathbf{g}$, which describes the hydrostatic pressure variation due to the gravitational field.

In the time-dependent theory we assume that the macroscopic concentration evolves in time according to the usual diffusion equation

$$\frac{\partial c}{\partial t}+\frac{1}{\rho}\nabla\cdot\mathbf{j}=0, \tag{8}$$

which describes the time evolution of the macroscopic concentration, once the dependence of the mass flux from hydrodynamic variables is prescribed. We still assume that macroscopic convection is absent and that a pressure gradient $\nabla p=\rho\mathbf{g}$ is present inside the mixture.

Moreover we assume that the gradients of the thermodynamic variables are small, so that we can neglect the spatial dependence of the thermophysical properties of the mixture [14]. Under these assumptions Eqs. (6) and (7) become

$$\frac{\partial\delta c}{\partial t}=-\delta\mathbf{u}\cdot\nabla c-\frac{1}{\rho}\nabla\cdot\delta\mathbf{j}+\frac{1}{\rho}\beta\delta c\nabla\cdot\mathbf{j}+\nabla\cdot\mathbf{F}, \tag{9}$$

$$\frac{\partial\delta\mathbf{u}}{\partial t}=\beta\mathbf{g}\delta c+\upsilon\nabla^2\delta\mathbf{u}+\frac{1}{\rho}\nabla\cdot\mathbf{S}. \tag{10}$$

Equations (9) and (10) have basically the same form of the equations found by Segrè and Sengers for a binary liquid mixture stressed by a steady temperature gradient under the action of the gravitational field [12]. However, these equations are now complemented by the diffusion equation (8), which describes how the ∇c term contained in Eq. (9) evolves in time, thus allowing determination of the spectrum of nonequilibrium fluctuations at different times during a diffusion process.

The term $\delta\mathbf{u}\cdot\nabla c$ in Eq. (9) represents a source term for the concentration fluctuations induced by velocity fluctuations. The term $\beta\mathbf{g}\delta c$ in Eq. (10) represents the opposite phenomenon, that is, the presence of velocity fluctuations induced by concentration fluctuations, due to the presence of the gravity force.

In order to calculate the correlation properties of the fluctuating variables we still have to specify the phenomenological relation which relates the mass flux $\mathbf{j}$ to the thermodynamic forces. In the general case where the slab of fluid is under the action of a stabilizing temperature gradient ∇T the mass flux is

$$\mathbf{j}=-\rho D\left(\nabla c+\frac{k_T}{T}\nabla T+\frac{k_p}{p}\nabla p\right), \tag{11}$$

where k_T is called the thermal diffusion ratio and k_p is the barodiffusion ratio [13]. The three gradient terms in parentheses describe the Fickean backflow, the Soret-induced flow, and the sedimentation flow, respectively. Each one of these terms can give rise to important modifications of the structure factor with respect to the thermodynamic equilibrium case. As we shall show, the results are quite unexpected, since the first two terms give rise to an enhancement, while the last actually depresses the mean square amplitude of the long wavelength fluctuations.

The thermal diffusion ratio k_T, the barodiffusion ratio k_p, and the osmotic compressibility $(\partial c/\partial\mu)_{p,T}$ depend on the concentration c of the mixture. Because of the small concentration gradient assumption previously formulated these dependencies are here neglected [14].

By linearizing Eq. (11) for small fluctuations we can now express the fluctuating part of $\mathbf{j}$ as a function of the hydrodynamic variables:

$$\nabla\cdot\delta\mathbf{j}=-\rho D\nabla^2\delta c+\beta\delta c\nabla\cdot\mathbf{j}+\beta\nabla\delta c\cdot\mathbf{j}-\rho\beta D\nabla\delta c\cdot\nabla c. \tag{12}$$

Only the first term on the right side of Eq. (12) is relevant to determine the correlation properties of the nonequilibrium fluctuations, as the second one will simplify with a similar term coming from Eq. (6), and the last two terms will cancel out during the following calculations.

In order to calculate the correlations of the fluctuating variables the spatial and temporal Fourier transforms of Eqs. (9) and (10) have to be evaluated. We will assume that the macroscopic temperature and concentration gradients are vertical (parallel to the z axis and to the gravitational acceleration $\mathbf{g}$) and that the wave vector $\mathbf{k}$ is perpendicular to these gradients. In this way the wave vector is restrained to the horizontal plane, and the spatial Fourier transform can be evaluated by transforming only the horizontal variables x and y. The space-time Fourier transform for the concentration fluctuations is thus

$$\delta c^{z,t}_{\mathbf{k},\omega}=\int dt\int dx\ dy c(\mathbf{x},t)\exp[i(\mathbf{k}\cdot\mathbf{x}-\omega t)] \tag{13}$$

and an analogous expression holds for the velocity fluctuations.

In Eq. (13) the variables $\mathbf{k}$ and ω in the lower label are used to describe the spectral properties of the nonequilibrium fluctuations, while the macroscopic state is identified by the variables in the upper label. The macroscopic variables are not affected by the temporal Fourier transform because, as we assumed before, the frequencies associated with them are much smaller than those associated with the fluctuations. This allows retaining the explicit temporal dependence of the macroscopic variables.

Moreover, since only the transverse velocity fluctuations contribute to the Rayleigh scattering [12], the transformed momentum equation can be projected in the direction perpendicular to $\mathbf{k}$ by means of the projection operator. Under these assumptions the Fourier-transformed equations are

$$\delta c^{z,t}_{\mathbf{k},\omega}(i\omega+Dk^2)=-\delta\mathbf{v}_{\mathbf{k},\omega}\cdot\nabla c(z,t)-i\mathbf{k}\cdot\mathbf{F}_{\mathbf{k},\omega}, \tag{14}$$

$$\delta\mathbf{v}^{z,t}_{\mathbf{k},\omega}(i\omega+vk^2)=\beta\delta c^{z,t}_{\mathbf{k},\omega}\mathbf{g}\cdot(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})-\frac{i}{\rho}\mathbf{k}\cdot\mathbf{S}_{\mathbf{k},\omega}\cdot(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}}), \tag{15}$$

where $\delta\mathbf{v}^{z,t}_{\mathbf{k},\omega}$ represents the transverse velocity fluctuation defined by

$$\delta\mathbf{v}^{z,t}_{\mathbf{k},\omega}=\delta\mathbf{u}^{z,t}_{\mathbf{k},\omega}\cdot(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}}). \tag{16}$$

By combining Eqs. (14) and (15) one readily obtains

$$\begin{aligned}\delta c^{z,t}_{\mathbf{k},\omega}&[(i\omega+Dk^2)(i\omega+vk^2)+\beta\mathbf{g}\cdot\nabla c(z,t)]\\&=-i(i\omega+vk^2)\mathbf{k}\cdot\mathbf{F}_{\mathbf{k},\omega}\\&\quad-\frac{i}{\rho}\mathbf{k}\cdot\mathbf{S}_{\mathbf{k},\omega}\cdot(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\nabla c(z,t).\end{aligned} \tag{17}$$

In order to calculate the correlation properties of the concentration fluctuations the correlation functions of the source terms $\mathbf{F}$ and $\mathbf{S}$ still have to be specified. We will assume that the correlations of these random forces retain their equilibrium values given by [16,14]

$$\langle F^i_{\mathbf{k},\omega}F^{*j}_{\mathbf{k}',\omega'}\rangle=\frac{k_BT}{8\pi^4\rho}D\left(\frac{\partial c}{\partial\mu}\right)_{p,T}\delta_{i,j}\delta(\mathbf{k}-\mathbf{k}')\delta(\omega-\omega'), \tag{18}$$

$$\begin{aligned}&\langle[\hat{\mathbf{k}}\cdot\mathbf{S}_{\mathbf{k},\omega}\cdot(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\nabla c][\hat{\mathbf{k}}\cdot\mathbf{S}^*_{\mathbf{k},\omega}\cdot(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\nabla c]\rangle\\&\quad=\frac{k_BT}{8\pi^4}\rho v|\nabla_c|^2,\end{aligned} \tag{19}$$

$$\langle F^t_{\mathbf{k},\omega}S^{*lm}_{\mathbf{k}',\omega'}\rangle=0. \tag{20}$$

By combining Eqs. (17)–(20) we obtain the correlation properties of the concentration fluctuations in a thin layer of mixture characterized by a macroscopic concentration gradient $\nabla c(z,t)$:

$$\langle \delta c^{z,t}_{\mathbf{k},\omega} \delta c^{*z,t}_{\mathbf{k},\omega} \rangle = \frac{k_B T}{8\pi^4 \rho} \left[\frac{(\omega^2 + v^2 k^4) D k^2 (\partial c/\partial \mu)_{p,T} + v k^2 |\nabla c(z,t)|^2}{|(i\omega + D k^2)(i\omega + v k^2) - [R(k)/R_c] v D k^4|^2} \right], \tag{21}$$

where $R(k)/R_c$ is given by

$$\frac{R(k)}{R_c} = -\frac{\beta \mathbf{g} \cdot \nabla c(z,t)}{v D k^4} \tag{22}$$

is a Rayleigh number ratio introduced in analogy with convective instabilities [11,12]. The Rayleigh number ratio is defined so that it is positive when the concentration profile is top-heavy (the concentration gradient points upwards), because this is the situation which leads to the onset of convective instabilities. As we are mainly interested in the stable situation where the gradient points downwards, in the following we will assume that $R(k)/R_c$ is negative.

It is interesting to calculate an approximate form for Eq. (21). The denominator of Eq. (21) can be factorized as $(\omega^2 + \omega_+^2)(\omega^2 + \omega_-^2)$, where the two roots are given by

$$\omega_\pm^2 = \frac{-k^4 v^2}{2} \left(-\left(1 + \frac{D}{v}\right)^2 + 2\left(1 - \frac{R(k)}{R_c}\right) \frac{D}{v} \pm \left\{ \left[\left(1 + \frac{D}{v}\right)^2 - 2\left(1 - \frac{R(k)}{R_c}\right) \frac{D}{v} \right]^2 - 4 \frac{D^2}{v^2} \left(1 - \frac{R(k)}{R_c}\right)^2 \right\}^{1/2} \right). \tag{23}$$

By assuming that $D/v \ll 1$ and that $-4DR(k)/(R_c v) \ll 1$ the two roots are $\omega_+^2 = D^2 k^4 (1 - R(k)/R_c)^2$ and $\omega_-^2 = v^2 k^4$, and Eq. (21) becomes

$$\langle \delta c^{z,t}_{\mathbf{k},\omega} \delta c^{*z,t}_{\mathbf{k},\omega} \rangle = \frac{k_B T}{8\pi^4 \rho} \left\{ \frac{D k^2 (\partial c/\partial \mu)_{p,T}}{\omega^2 + \{D k^2 [1 - R(k)/R_c]\}^2} + \frac{v k^2 |\nabla c(z,t)|^2}{[\omega^2 + (v k^2)^2](\omega^2 + \{D k^2 [1 - R(k)/R_c]\}^2)} \right\}. \tag{24}$$

The assumption $D/v \ll 1$ is valid for most binary liquid mixtures, as typical values for mixtures of organic fluids are $v \approx 10^{-3}$ cm^2/s and $D \approx 10^{-5}$ cm^2/s. The meaning of the assumption $-4DR(k)/(R_c v) \ll 1$ will be discussed later. The second term of Eq. (24), considered as a function of ω, is the product of two Lorentzian curves, whose width is given by $|\omega_+|$ and $|\omega_-|$. As we assumed that $-4DR(k)/(R_c v) \ll 1$, the Lorentzian of width $D k^2 [1 - R(k)/R_c]$ is much narrower than the one of width $v k^2$. By approximating the wider Lorentzian by its value at maximum the spectrum of the fluctuations becomes

$$\langle \delta c^{z,t}_{\mathbf{k},\omega} \delta c^{*z,t}_{\mathbf{k},\omega} \rangle = S^{z,t}(k) \frac{2D[1 - R(k)/R_c] k^2}{(\omega^2 + \{D[1 - R(k)/R_c] k^2\}^2)}, \tag{25}$$

where the static structure factor $S^{z,t}(k)$ is given by

$$S^{z,t}(k) = \frac{k_B T}{16\pi^4 \rho} \left[\left(\frac{\partial c}{\partial \mu} \right)_{p,T} \frac{1}{1 - R(k)/R_c} + \frac{|\nabla c(z,t)|^2}{v D k^4} \frac{1}{1 - R(k)/R_c} \right]. \tag{26}$$

The spectrum is therefore a Lorentzian with linewidth $D[1 - R(k)/R_c] k^2$. It is very instructive to see what is the value of the associated time constants for $-R(k)/R_c \gg 1$ and $-R(k)/R_c \ll 1$.

If $-R(k)/R_c \ll 1$, the time constant becomes $\tau_{\text{diff}} = 1/(D k^2)$, that is, the classical diffusion time constant. If $-R(k)/R_c \gg 1$ [but still smaller than $v/(4D)$], then the time constant is $\tau_{\text{grav}} = v k^2/(\beta g \nabla c)$. While the diffusion time constant decreases as $1/k^2$, we find that for $-R(k)/R_c \gg 1$ the time constant actually increases as k^2. As $R(k)/R_c = -\tau_{\text{diff}}/\tau_{\text{grav}}$, the transition between the two quite opposite regimes occurs when $R(k)/R_c = -1$, that is, in correspondence to the critical wave vector

$$k_{\text{RO}} = \left(\frac{\beta \mathbf{g} \cdot \nabla c}{v D} \right)^{1/4}. \tag{27}$$

For large values of k, $k > k_{\text{RO}}$, we are in the diffusive mode. This implies that concentration fluctuations decay because on the smaller length scales diffusion is a fast process. If we go to $k < k_{\text{RO}}$, we are considering fluctuations over length scales that are so large that other processes are more effective than diffusion in relaxing the fluctuations. What is actually happening is that a concentration fluctuation is associated to a density fluctuation and consequently a buoyancy force is generated. If the system is arranged with a built-in concentration gradient, then the fluctuation parcel will try to move to the layer where the density will be matched. It will also try to dispose of the excess concentration via diffusion, but the condition $-R(k)/R_c \gg 1$ implies that diffusion is slow in comparison with the buoyancy driven travel to the density-matching layer. The k_{RO} value then describes the longest wavelength at which a concentration fluctuation will predominantly decay via diffusion. Incidentally, at this wavelength the concentration fluctuation time constant attains its largest value, excitations at larger or smaller wavelengths decaying faster. For smaller-k values, buoyancy and drift to the density-matching layer is the winning mechanism for the relaxation of fluctuations.

We can now examine what is the physical meaning of the condition $-4DR(k)/(R_c v) \ll 1$, under which the previous

results have been obtained. If $-4DR(k)/(R_c v) \gg 1$, then the time needed by the viscosity force to act is so long that the motion of the parcel actually overshoots the density-matching layer, diffusion still playing an irrelevant role. So the fluctuations will become overstabilized, and the spectrum will split into the symmetric doublet characteristic of propagating fluctuations [11,12].

The static structure factor introduced with Eq. (26) describes the static transverse correlation properties of a thin, horizontal layer of mixture. To outline how the equilibrium static structure factor is modified in the nonequilibrium condition it is convenient to rewrite Eq. (26) as

$$S^{z,t}(k) = S_{\mathrm{eq}}\left[1 + \left(\frac{\nabla c(z,t)}{\nabla c_{\mathrm{grav}}} - 1\right)\frac{1}{1+[k/k_{\mathrm{RO}}(z,t)]^4}\right], \tag{28}$$

where

$$S_{\mathrm{eq}} = \frac{k_B T}{16\pi^4 \rho}\left(\frac{\partial c}{\partial \mu}\right)_{p,T} \tag{29}$$

is the equilibrium static structure factor and

$$\nabla c_{\mathrm{grav}} = -\frac{k_p}{p}\nabla p = \beta \mathbf{g}\left(\frac{\partial c}{\partial \mu}\right)_{p,T} \tag{30}$$

is the equilibrium concentration gradient induced by barodiffusion [13].

The first term of Eq. (28) represents the equilibrium contribution to the static structure factor while the second one represents a nonequilibrium contribution due to the presence of a macroscopic concentration gradient inside the mixture. The coupling of velocity fluctuations with concentration fluctuations due to the presence of the gradient determines the divergence of the nonequilibrium term as k^{-4} at wave vectors larger than k_{RO}. At smaller wave vectors the divergence is frustrated by the presence of the gravity force, and the nonequilibrium term rolls off to a constant value. Experimental evidence of the gravity-induced frustration of concentration fluctuations in a binary mixture under a steady temperature gradient was recently reported by our group [17].

The most remarkable feature of Eq. (28) is that the nonequilibrium term can lead to an enhancement or a depression of the equilibrium static structure factor, depending on the sign of the factor $\nabla c/\nabla c_{\mathrm{grav}} - 1$. This point will be discussed in more detail in Sec. IV B.

We would like to stress here that Eqs. (26) and (28) are valid under a great variety of conditions: they describe the static correlation properties in an equilibrium state, in a stationary nonequilibrium state, and in a nonequilibrium time-dependent state.

III. THE STATIC SCATTERED LIGHT

The static structure factor introduced with Eq. (26) describes the transverse correlation properties of the concentration fluctuations in a thin layer of a binary mixture. This structure factor can be best analyzed via light scattering. We will consider the scattering setup where the probe beam is aligned with the gravity acceleration. Since the angular distribution of the scattered intensity changes layer by layer, the overall scattering distribution results from a summation of the scattered intensity distributions from the individual layers. We will briefly outline how the superposition of the light coming from different layers of fluid contributes to the overall scattered intensity.

If we consider the light scattered at an angle θ with respect to the incident wave vector k_f we can define the transferred momentum wave vector k. In the case of Rayleigh scattering k is given by

$$k = \frac{4\pi n}{\lambda}\sin\frac{\theta}{2}, \tag{31}$$

where n is the index of refraction of the fluid and λ is the wavelength of the incoming beam.

In deriving the structure factor of the concentration fluctuations we have assumed that the wave vector k lies in the horizontal plane. As it is apparent from Eq. (31) this is approximately true only for small scattering angles, that is, the angles where substantial deviations of the nonequilibrium static structure factor from the equilibrium one are expected.

The spectral density of the light scattered with wave vector k and frequency ω onto a far detector at a distance R from the sample is [18]

$$I(k,\omega) = \frac{I_0 k_f^4}{16\pi^2 R^2 \varepsilon_0^2}\left(\frac{\partial \varepsilon}{\partial c}\right)^2_{p,T} S(k,\omega), \tag{32}$$

where I_0 is the intensity of the incident beam, ε_0 is the dielectric constant of the sample, and $S(k,\omega)$ is the overall dynamic structure factor defined by

$$S(k,\omega) = \langle \delta c_{k,\omega}\delta c^*_{k,\omega}\rangle. \tag{33}$$

This dynamic structure factor is different from that introduced with Eq. (25), since it is defined in terms of the three-dimensional spatial Fourier transform of the concentration fluctuations defined by

$$\begin{aligned}\delta c_{k,\omega} &= \int dz \int dx\, dy \int dt\ \delta c(\mathbf{x},t)\exp[i(\mathbf{k}\cdot\mathbf{x} - \omega t)] \\ &= \int dz\ \delta c^{z,t}_{k,\omega}.\end{aligned} \tag{34}$$

By assuming that fluctuations taking place in different layers are not correlated and by inserting Eq. (34) into Eq. (33) we obtain that the overall structure factor $S(k,\omega)$ is just the superposition of the structure factors due to different layers of fluid:

$$S(k,\omega) = \int dz \langle \delta c^{z,t}_{k,\omega}\delta c^{*z,t}_{k,\omega}\rangle. \tag{35}$$

By integrating Eq. (35) along the frequency axis we obtain the overall static structure factor:

$$S(k,t) = \int dz S^{z,t}(k). \tag{36}$$

It is convenient to introduce the overall nonequilibrium static structure factor

$$S_{\rm ne}(k,t)=S(k,t)-aS_{\rm eq}, \tag{37}$$

where a is the thickness of the sample. The nonequilibrium structure factor defined by Eq. (37) represents the excess contribution of the nonequilibrium fluctuations to the overall static structure factor, with respect to the equilibrium one.

IV. TIME-DEPENDENT DIFFUSION PROCESSES

In the following we will discuss the nonequilibrium time-dependent cases of free diffusion, thermal diffusion, and barodiffusion in a binary mixture. The features of the static structure factor will be presented and, when possible, compared with experimental results.

A. Free diffusion

A free diffusion process is usually arranged as follows [19]. Two miscible fluids are prepared so that they are separated by an initially sharp, horizontal boundary. As soon as the fluids are left in contact, a diffusive flow begins to transport mass across the interface so that the concentration in the neighborhood of the boundary begins to change. As time goes by, the thickness of the region involved in the concentration change grows. During a free diffusion process the concentration at the top and bottom of the sample is assumed to remain constant. This assumption is true in the case of unbounded diffusion, where two infinitely thick layers of fluid are allowed to diffuse one into each other. In practice the assumption is valid only during a given time interval after the beginning of the diffusion process, which depends on the vertical size of the vessel and on the mutual diffusion coefficient D. As soon as the concentration near the boundaries begins to change, the features of the macroscopic diffusion process cease to depend on the diffusion coefficient only, and they are influenced by the height of the vessel also.

The typical initial condition of a free diffusion experiment is the step function concentration profile

$$c(z,0)=\begin{cases} c_1, & 0<z<h \\ c_2, & h<z<a \end{cases} \tag{38}$$

where h is the position of the initial boundary between the two fluids and a is the thickness of the two superimposed layers.

The evolution of the concentration profile during the free diffusion process, obtained by solving the diffusion equation with the initial condition (38), is [20]

$$c(\zeta,t)=c_0+\frac{2}{\pi}(c_1-c_2)\sum_j^{\infty}\frac{1}{j}\sin\left(\frac{j\pi h}{a}\right)\times\exp\left(-\frac{Dj^2\pi^2}{a^2}t\right)\cos(j\pi\zeta), \tag{39}$$

where $\zeta=z/a$ and $c_0=[c_1h+c_2(a-h)]/a$ is the concentration at the end of the diffusion process.

The time evolution of this concentration profile is shown in Fig. 1 for $D=1.5\times10^{-6}$ cm^2/s, $a=0.45$ cm, $h=a/2$, $c_1=0.75$, and $c_2=0.25$.

Equation (28) together with Eq. (39) solves the problem of finding the local static structure factor of the nonequilibrium time-dependent fluctuations which take place during a free diffusion process. Notice that the local structure factor depends on the specific layer of fluid and is characterized by the actual value of the local concentration gradient ∇c (∇c depends on the spatial coordinate z). In order to compare the theoretical results with low-angle static light scattering data, the overall nonequilibrium static structure factor, defined by Eq. (37), must be evaluated. We will assume that the concentration gradient present inside the fluid is much larger than that due to barodiffusion. The overall nonequilibrium static structure factor obtained by combining Eqs. (28) and (37) and normalized by its equilibrium value is given by

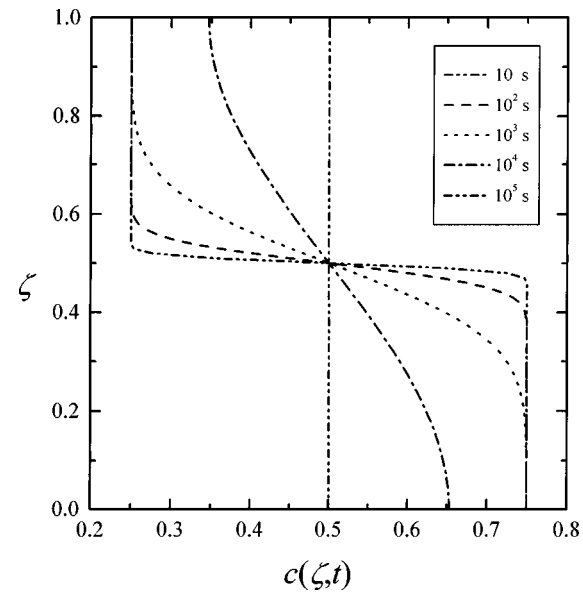

FIG. 1. Time evolution of the concentration profile plotted vs the normalized height ζ during a diffusion process. The horizontal and vertical axes are exchanged for convenience. The diffusion coefficient is $D=1.5\times10^{-6}$ cm^2/s, the thickness of the sample is $a=0.45$ cm. Initially two horizontal layers of the binary mixture at the uniform concentrations $c_1=0.75$ and $c_2=0.25$ are separated by a horizontal interface at the midheight $h=a/2$. In the early stages of the diffusion process the concentration at the boundaries $z=0$ and a does not change in time, as the diffusive remixing occurs only around the midheight. This is the free diffusion regime. When the concentration near the boundaries begins to change, then the system enters into the restricted diffusion regime.

$$\frac{S_{\rm ne}(k,t)}{aS_{\rm eq}}=\frac{1}{a}\int dz\left(\frac{\nabla c(z,t)}{\nabla c_{\rm grav}}-1\right)\frac{1}{1+[k/k_{\rm RO}(z,t)]^4}, \tag{40}$$

where in the free diffusive regime ∇c is given by [21]

$$\nabla c(z,t)=\frac{c_1-c_2}{\sqrt{4\pi Dt}}\exp\left[-\frac{(z-h)^2}{4Dt}\right]. \tag{41}$$

The nonequilibrium static structure factor calculated from Eq. (40) is plotted at different times in Fig. 2, where the parameters are the same used in Fig. 1 and $\beta=0.27$, $\upsilon=1.35$ cm^2/s, $(\partial c/\partial\mu)_{p,T}=7.7\times10^{-7}$ s^2/cm^2.

The nonequilibrium static structure factor experimentally measured by means of very-low-angle static light scattering during a free diffusion experiment and normalized by its

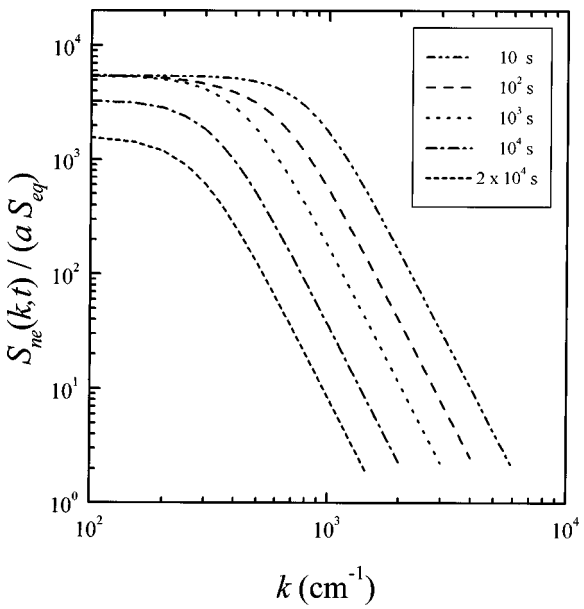

FIG. 2. Normalized overall nonequilibrium static structure factor calculated at different times during the diffusion process and plotted vs the wave vector k. The parameters correspond to those used in Fig. 1. At large wave vectors the structure factor displays the k^{-4} power law behavior characteristic of velocity-induced nonequilibrium concentration fluctuations. At smaller wave vectors the structure factor rolls off at a constant value because gravity inhibits the large wavelength fluctuations. The amplitude of the structure factor at small wave vector is initially constant and then suddenly drops. This amplitude is proportional to the concentration difference near the boundaries. As shown in Fig. 1, during the free diffusion regime this concentration difference is constant, and it changes rather sharply when the system enters the restricted diffusion regime.

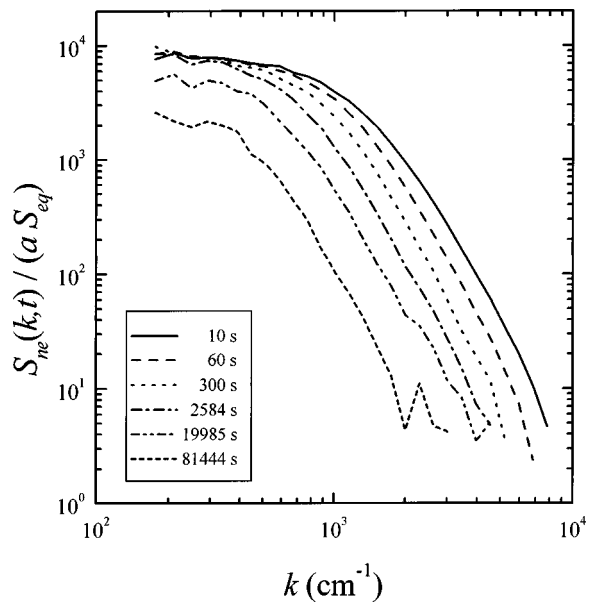

FIG. 3. Normalized overall nonequilibrium static structure factor measured by means of low-angle static light scattering. The structure factors are measured at different times during the diffusion process and plotted vs the wave vector k [10]. The sample is the binary mixture aniline-cyclohexane prepared at its critical concentration $c=0.47$. The mixture phase separates at $T_c-T=3$ K, where $c_1-c_2=0.5$, and the diffusive process is started by suddenly raising the temperature above the critical one at $T-T_c=1$ K. The parameters used in Figs. 1 and 2 correspond to the experimental situation described here, so that a quantitative comparison of the results is possible. The features of the structure factor closely mirror those of the calculated one shown in Fig. 2.

equilibrium value is plotted in Fig. 3 [10]. The values of the parameters in Fig. 2 correspond to the experimental conditions used during the measurement of the data in Fig. 3, so that a direct comparison is possible.

These data were taken by using a near-critical aniline-cyclohexane mixture. The mixture was prepared 3 °C below its critical temperature T_c, in its two-phase region, so as to obtain two macroscopic phases separated by a horizontal sharp boundary. A sudden temperature jump was then applied to bring the mixture 1 °C above T_c. After the temperature jump is applied the two macroscopic phases become completely miscible, and the free diffusion process starts.

The structure factor retains essentially the same features outlined before: the k^{-4} behavior for $k>k_{\mathrm{RO}}$, due to the coupling between velocity and concentration fluctuations, and a roll off to a constant value for smaller wave vectors, due to the restoring action of the buoyancy force.

There are a few features worth pointing out. Figures 2 and 3 show that initially the forward scattered intensity does not change in time. From Eq. (41) we can calculate the value of the nonequilibrium static structure factor for vanishingly small wave vectors:

$$\frac{S_{\mathrm{ne}}(0,t)}{aS_{\mathrm{eq}}}=\frac{c_1-c_2}{a\nabla c_{\mathrm{grav}}}-1, \tag{42}$$

where c_1 and c_2 are the concentrations at the top and bottom layers inside the sample. The term -1 on the right side of Eq. (42) becomes relevant only near equilibrium. Equation (42) explains why in Figs. 2 and 3 the scattered intensity extrapolated at zero angle is at first stationary and then suddenly drops. At first c_1-c_2 is constant because only a thin layer at the midheight of the mixture is involved in the diffusive process. The drop corresponds to the transition from the free diffusion regime to the restricted diffusion one, where the concentration near the boundaries is a time-dependent quantity [22]. During the free diffusion regime, the agreement between the low wave vector values of the structure factors shown in Figs. 2 and 3 is within 40%, which is satisfactory if one considers the uncertainty in reference data for $(\partial c/\partial\mu)_{p,T}$.

Figures 2 and 3 also show that the curves roll off at smaller wave vectors as time goes by. We can estimate how the roll off wave vector should evolve in time by assuming that its value is mostly determined by the midheight layer where the concentration gradient is maximum. From Eqs. (27) and (41) the time dependence of the roll off wave vector is

$$k_{\mathrm{ro}}=\left[\frac{\beta g}{\nu D}\frac{1}{\sqrt{4\pi Dt}}\right]^{1/4}=At^{-1/8}. \tag{43}$$

The exponent $-1/8$ is in fair agreement with the value -0.11 measured in the experiment described in Ref. [10], and the

measured value of the prefactor A is about 25% smaller than the value calculated by using Eq. (42) and reference data.

B. Thermal diffusion

When a temperature gradient is applied to a liquid mixture a macroscopic mass flux is induced [23]. This is the thermal diffusion or Soret effect. At steady state a macroscopic concentration gradient is produced such that the net diffusive mass flux **j** vanishes, the mass flow due to thermal diffusion being exactly balanced by the ordinary diffusion backflow. From Eq. (11) the steady-state Soret-induced concentration gradient in the absence of a gravitational field is

$$\nabla c_{\mathrm{Soret}} = -\frac{k_T}{T}\nabla T. \tag{44}$$

In the following we will assume that the sample is a horizontal layer of a binary mixture with $k_T > 0$ and that the temperature gradient is applied by heating the layer from above. This is the stable configuration that avoids the onset of convective instabilities.

Some theories [12,14] have recently described the nonequilibrium fluctuations in a mixture at steady state. The predictions of these theories have been checked by Sengers and co-workers [7,8]. However, so far no description has been provided for the nonequilibrium fluctuations during the transient after the application of the temperature gradient. For this purpose we can use Eq. (28), complemented by the solution of the diffusion equation (8), under the appropriate boundary and initial conditions. For a mixture initially at the uniform concentration c_0 and bounded by impermeable surfaces at $z=0$ and a these conditions are

$$c = c_0, \quad 0 \leqslant z \leqslant a, \quad t = 0 \tag{45}$$

and

$$\nabla c = \nabla c_{\mathrm{Soret}}, \quad z = 0, a, \quad t > 0. \tag{46}$$

The boundary conditions (46) arise from the fact that the concentration gradient must reach instantaneously its steady-state value in the layers where the mass flow is zero, as was pointed out by Archibald [19]. The diffusion equation with the boundary conditions (46) and the initial condition (45) can be solved by using the customary method of separation of variables [20] to obtain

$$c(\zeta,t) = c_0 + a\nabla c_{\mathrm{Soret}}\left\{\frac{1}{2} - \zeta - \frac{2}{\pi^2}\sum_{j=1}^{\infty}\frac{1}{j^2}[1-(-1)^j] \times \cos(j\pi\zeta)\exp\left(-\frac{j^2\pi^2 D}{a^2}t\right)\right\}. \tag{47}$$

In writing Eq. (47) we have assumed that the thermalization of the mixture is attained almost instantaneously with respect to the time needed to reach the steady concentration profile defined by Eq. (44). This assumption is valid for most mixtures, as a typical value of the thermal diffusivity is $D_T \approx 10^{-3}$ cm^2/s and the diffusion coefficient is usually smaller than 10^{-5} cm^2/s.

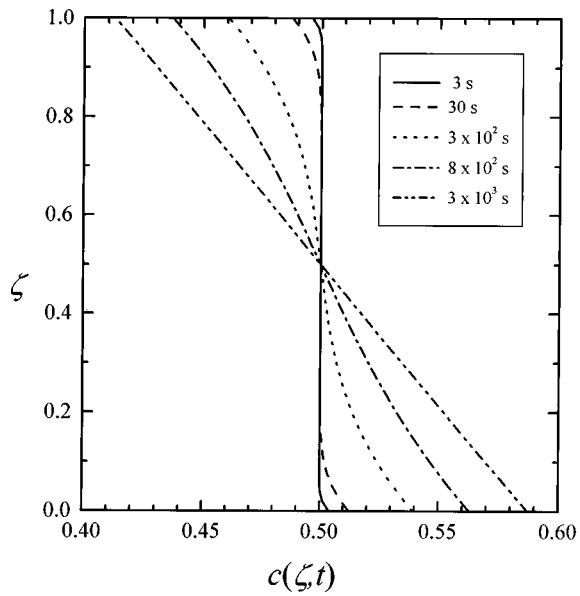

FIG. 4. Time evolution of the concentration profile plotted vs the normalized height ζ during a thermal diffusion process. The horizontal and vertical axes are exchanged for convenience. The initial concentration is $c_0 = 0.5$, the diffusion coefficient $D = 1.3\times10^{-6}$ cm^2/s, the temperature gradient $\nabla T = 160$ K/cm, the thermal diffusion ratio $k_T = 3.5$, and the temperature corresponds to $T = 315$ K. The concentration is initially uniform. As soon as the temperature gradient is applied, the concentration begins to change near the boundaries and the concentration gradient there attains instantaneously its steady-state value $\nabla c_{\mathrm{Soret}}$. At steady state a linear concentration profile is formed inside the sample.

The concentration profiles obtained from Eq. (47) are plotted in Fig. 4 at different times during the transient. The curves in Fig. 4 correspond to $a = 0.1$ cm, $\nabla T = 160$ K/cm, $T = 315$ K, $D = 1.3\times10^{-6}$ cm^2/s, and $k_T = 3.5$. This choice of the parameters corresponds to the experimental situation that will be described shortly.

We use the same procedure outlined in the free diffusion case to calculate the overall nonequilibrium static structure factor via Eqs. (40) and (47). The results are plotted in Fig. 5 at different times (the parameters used are the same used in Fig. 4). The inset of Fig. 5 shows the structure factors rescaled by their value at $k=0$. From the inset it is apparent how the roll off wave vector varies within a very narrow range of values during the thermal diffusion process. Indeed the roll off position is dictated by the magnitude of the gradient. During the transient the gradient close to the boundaries is locked to the steady-state one. Due to the high gradient, these are the regions that contribute most to the structure factor and therefore are mainly responsible for the location of the roll off.

Figure 6 shows the static structure factor as determined by means of low-angle light scattering [9]. A 1 mm thick horizontal layer of a near-critical aniline-cyclohexane binary mixture was used to obtain these data. The mixture was kept about 12 K above T_c, in its one-phase region, and a symmetrical 16 K vertical temperature difference was suddenly applied across it (heating from above), so as to start the thermal diffusion process. The inset of Fig. 6 shows the scattering data rescaled by the forward scattered intensity. These scaled data confirm that the roll off position is almost sta-

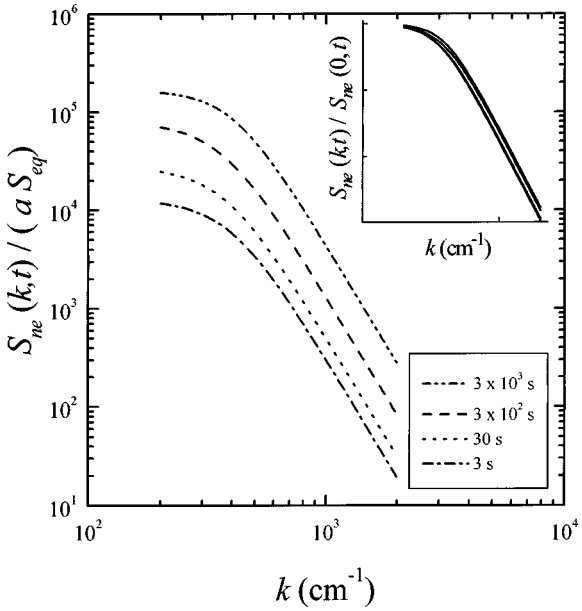

FIG. 5. Normalized overall nonequilibrium static structure factor calculated at different times during the thermal diffusion process and plotted vs the wave vector k. The parameters correspond to those used in Fig. 4. The curves retain the same features discussed in the free diffusion case: the k^{-4} power law behavior at large wave vector and the gravity-induced roll off at smaller wave vectors. However, in this case the roll off wave vector is almost stationary, as it depends on the magnitude of the concentration gradient near the boundaries, where the gradient attains its steady-state value almost instantaneously. This is best shown in the inset, where the structure factors are normalized by their small wave vector values. The parameters correspond to those used in Fig. 4.

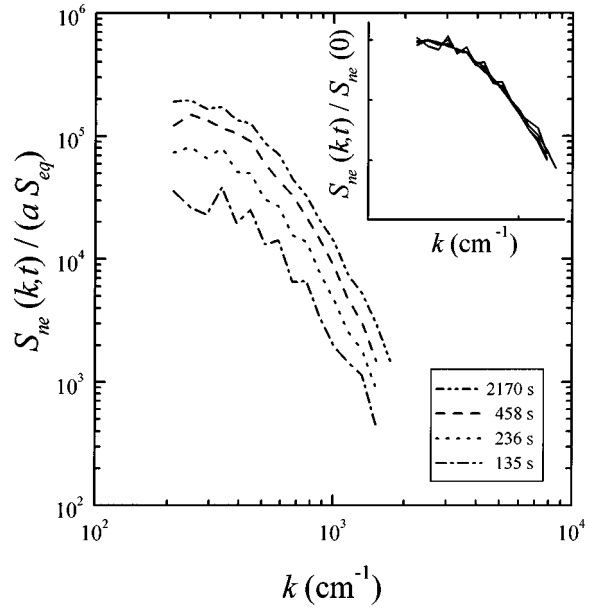

FIG. 6. Normalized overall nonequilibrium static structure factor measured at different times during the thermal diffusion process by means of low-angle static light scattering, and plotted vs the wave vector k [9]. The sample is the binary mixture aniline-cyclohexane prepared at its critical concentration $c=0.47$ and kept in its homogeneous state at $T-T_c=12$ K. The experiment is started by applying a steady temperature gradient to the mixture, so that a concentration gradient develops because of the Soret effect [23]. The inset shows the structure factors normalized by their value at $k=0$, and confirms that the roll off wave vector is almost stationary during the thermal diffusion process. The parameters used in Figs. 4 and 5 correspond to the experimental situation described here, so that a direct quantitative comparison is possible. The features of the structure factor closely mirror those of the calculated one shown in Fig. 5.

tionary. According to Eq. (42) the forward scattered intensity provides a measure of the difference of the concentration near the boundaries. By using Eqs. (42) and (47) we find that this concentration difference changes in time according to the law

$$\frac{S_{\rm ne}(0,t)}{aS_{\rm eq}}=\frac{\nabla c_{\rm Soret}}{\nabla c_{\rm grav}}\left[1-\frac{8}{\pi^2}\exp\left(-\frac{\pi^2 D}{a^2}t\right)\right]-1. \quad (48)$$

In writing Eq. (47) we have assumed that $t \gg a^2/(9\pi^2 D)$, so that the early stages of the thermal diffusion process can be neglected. Equation (48) is in good agreement with the experimental results presented in Ref. [9].

C. Barodiffusion: gravitationally induced concentration gradients

The static structure factor of a binary mixture in an equilibrium state is well known [24], and for ordinary fluids is completely featureless: the scattered intensity distribution is constant at all scattering angles.

In a mixture, gravity gives rise to sedimentation, a downward mass flow of the denser component. This creates a macroscopic concentration gradient, which in turn gives rise to a diffusive backflow. Eventually a stationary state is reached, where the two mass flows counterbalance each other. The gradient at steady state is given by Eq. (30). Large gradients are observed in solutions of macromolecules of large molecular weight M [M is proportional to $(\partial c/\partial\mu)_{p,T}$] or for smaller molecules under the action of a centrifuge. They are also large in the vicinity of critical points, where $(\partial c/\partial\mu)_{p,T}$ diverges. One might ask if the gravitationally induced concentration gradient gives rise to a coupling between velocity and concentration fluctuations. Segrè, Schmitz, and Sengers [11] showed that the presence of a steady gravitational gradient does not affect the static structure factor of a simple fluid and Segrè and Sengers [12] suggested that this should also hold true for a binary mixture. No predictions are available to describe what happens during the buildup of the sedimentation gradient, starting from a homogeneous state.

We will show that, at variance with the free diffusion and thermal diffusion cases, no enhancement of the fluctuations does occur during the transient, and indeed the fluctuations are depressed below the equilibrium value for excitation wave vectors smaller than the roll off one $k_{\rm RO}$.

The static structure factor introduced with Eq. (28), and hence the scattered intensity, is given by the sum of the equilibrium term $(\partial c/\partial\mu)_{p,T}$ and a term accounting for nonequilibrium fluctuations. This last term, however, can be positive or negative, depending on the sign of the factor $\nabla c/\nabla c_{\rm grav}-1$.

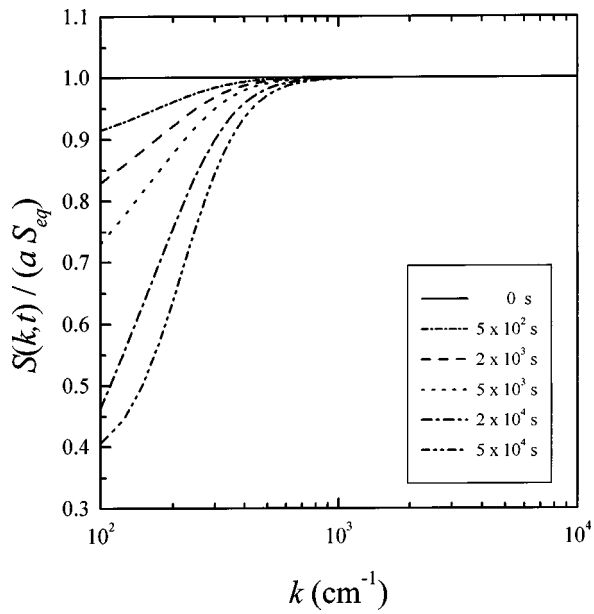

FIG. 7. Normalized overall structure factor calculated at different times during the early stages of a sedimentation process and plotted vs the wave vector k. At first the sample is at uniform concentration and the structure factor is flat. As sedimentation begins, the structure factor decreases below the equilibrium value at small wave vectors. The physical system modeled here corresponds to polystyrene particles with a radius of 100 nm immersed in water. The initial uniform concentration is $c_0=0.01$, the temperature $T=300$ K, the kinematic viscosity $\upsilon=0.01$ cm^2/s, the diffusion coefficient $D=2.2\times10^{-8}$ cm^2/s, $\beta=0.052$, and $(\partial c/\partial\mu)_{p,T}=10^{-3}$ s^2/cm^2.

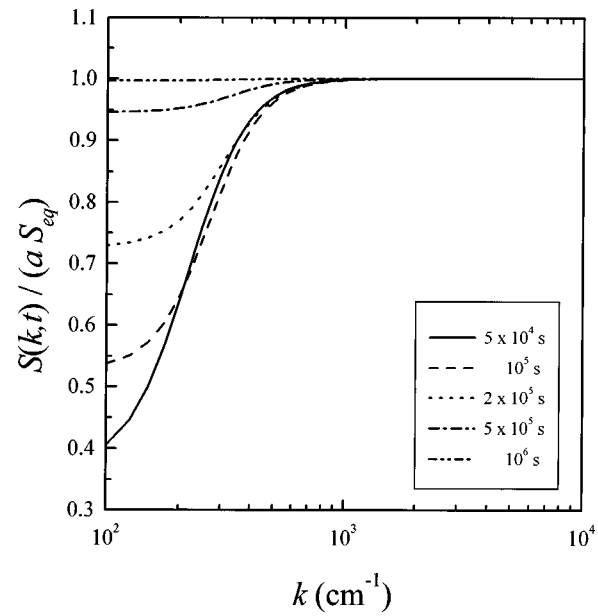

FIG. 8. Normalized overall structure factor calculated at different times during the intermediate and late stages of a sedimentation process and plotted vs the wave vector k. As the equilibrium state is approached the low-k depression in the structure factor gradually disappears. The physical system is the same depicted in Fig. 7.

If the system has reached the steady-state gradient value $\nabla c_{\rm grav}$, then one immediately recovers the result described by Segrè and Sengers [12], namely, the equilibrium structure factor is not modified by the presence of gravity. Notice that in the cases of free diffusion and thermal diffusion, the actual gradient ∇c is usually much larger than $\nabla c_{\rm grav}$, and this explains why the nonequilibrium fluctuations make the scattered intensity increase well above the equilibrium value. In the sedimentation case, however, if one starts with a homogeneous, well mixed state, the actual gradient will always be smaller than $\nabla c_{\rm grav}$, and therefore, quite unexpectedly, the amplitude of the nonequilibrium fluctuations will be smaller than the equilibrium one at small wave vectors.

We will present a calculation of the time evolution of the static structure factor from a sedimenting sample under realistic estimates. To do so, we first calculate the time-dependent concentration profiles in the same way outlined in the thermal diffusion case. The profiles have the same qualitative evolution of the ones shown in Fig. 4, the only differences being that the steady-state concentration gradient in Eqs. (46) and (47) used to calculate the profiles is now $\nabla c_{\rm grav}$, and that the time scales involved have changed, due to the different value of the diffusion coefficient.

Equation (28) together with Eqs. (36) and (47) solves the problem of finding the overall static structure factor for the sedimenting binary mixture. In Figs. 7 and 8 we show the calculated time evolution of the overall static structure factor normalized by its equilibrium value for a colloidal suspension of polystyrene particles in water ($r=100$ nm), starting from a homogeneous concentration condition. The initial concentration is $c_0=0.01$, the temperature $T=300$ K, the kinematic viscosity $\upsilon=0.01$ cm^2/s, the diffusion coefficient $D=2.2\times10^{-8}$ cm^2/s, $\beta=0.052$, and $(\partial c/\partial\mu)_{p,T}=10^{-3}$ s^2/cm^2. From Fig. 7 one can notice that indeed in the early phases of the process a depression in the structure factor below the equilibrium value develops at small wave vectors. Figure 8 shows that as the steady state is approached the structure factor tends to level off to the equilibrium value. One can also notice that the effect is not very pronounced and probably hard to measure in a real experiment.

V. SUMMARY AND CONCLUSIONS

We have presented an extension of the fluctuating hydrodynamics theory to the description of time-dependent nonequilibrium fluctuations. It is shown that under realistic assumptions, the theory already developed for steady-state nonequilibrium fluctuations can be used to account for the transient behavior by complementing the steady-state equations with those describing the evolution of the macroscopic concentration gradients. The role of velocity fluctuations as the principal mechanism leading to anomalously large concentration fluctuations is discussed together with the antagonizing effect due to spontaneous concentration fluctuations in the presence of gravitational acceleration. Three typical diffusion processes are considered, namely, free diffusion, thermal diffusion, and barodiffusion. The time evolution of the concentration gradients during the approach to steady state is recalled for the three cases, and a small section is dedicated to the calculation of the scattered intensity distribution from the liquid layers that host the gradients. The predictions are compared with experimental results from thermal diffusion and free diffusion experiments, and good agreement is found. In both cases the fluctuations do exhibit a pronounced

enhancement with respect to the equilibrium value during the transient to steady state. Quite different is the case of barodiffusion. It is predicted that during the transient, the mean square amplitude of the fluctuations is actually smaller than the equilibrium one, a result that is rather nonintuitive. We show that the presence of the gravitational gradient actually depresses the equilibrium fluctuations below their thermodynamic value in the early phases of the transient, since buoyancy actually ''hides away'' spontaneous fluctuations by drifting them along the gradient until they rest in a density-matching layer. This process is more effective at longer wavelength, and the calculated scattered intensity presents a hole around the main beam position. As the steady state is approached, the amplitude of the fluctuations gradually attains its thermodynamic value, and the scattered intensity becomes constant, in agreement with the existing theoretical predictions.

It is pointed out that the validity of the fluctuating hydrodynamic approach rests under the assumption that proper average quantities can be defined. This is the case for ground-based situations, where gravity actually prevents the amplitude of long wavelength fluctuations from diverging. Microgravity conditions might render this assumption quite questionable.

ACKNOWLEDGMENTS

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