Shear-induced quench of long-range correlations in a liquid mixture

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A static correlation function of concentration fluctuations in a (dilute) binary liquid mixture subjected to both a concentration gradient and uniform shear flow is investigated within the framework of fluctuating hydrodynamics. It is shown that a well-known $|\nabla c|^2/k^4$ long-range correlation at large wave numbers k crosses over to a weaker divergent one at wave numbers satisfying $k<(\dot{\gamma}/D)^{1/2}$, while an asymptotic shear-controlled power-law dependence is found at much smaller wave numbers given by $k\ll(\dot{\gamma}/\nu)^{1/2}$, where c, $\dot{\gamma}$, D, and ν are the mass concentration, the rate of the shear, the mass diffusivity, and the kinematic viscosity of the mixture, respectively. The result will provide the possibility to observe the shear-induced suppression of a long-range correlation experimentally by using, for example, a low-angle light scattering technique.

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I. INTRODUCTION

Long-range correlations in a fluid far from equilibrium is one of the most salient features of nonequilibrium fluctuations [1–6]. Since the seminal discovery of the k^{-4} enhancement of the Rayleigh component of the structure factor in a fluid with a uniform temperature gradient by Kirkpatrick, Cohen, and Dorfman [7], where k is the wave number, algebraic decays of correlation functions have been found theoretically in a wide class of nonequilibrium systems [8–14]. The existence of such generic long-range correlations also have been confirmed in a series of the detailed light scattering experiments in pure liquids [15,16] and in binary mixtures [17]. Although the agreement between the theoretical studies and the experimental ones is sufficiently quantitative, it has been limited to relatively high wave number regions.

On the other hand, large-scale, long-time behavior of such nonequilibrium fluctuations is attracting much more attention in recent years [18]. Ultra-low-angle light scattering experiments performed by Vailati and Giglio [19] have revealed an impressive gravity-induced quench of the k^{-4} divergence of the Rayleigh line intensity at very small k range [20] in a binary mixture subjected to a uniform concentration gradient driven by the large Soret effect. So far as we know, this is the first experimental demonstration that true asymptotic behavior of a long-range correlation at large distances is qualitatively different from that predicted by the linear response theory at short distances.

However, from the theoretical point of view, the gravity-induced effect seems to be somewhat exceptional because it can be understood within the simple linear response theory. Generally speaking, a full nonlinear analysis of hydrodynamic equations is required for studying large-scale transport and fluctuation properties of a fluid [21]. Therefore, mainly because of its technical difficulty, studies beyond linear responses are rare in systems far from equilibrium so far. The only exception is a system undergoing uniform shear flow where effects of the shear advection can be treated in an analytic way [22–24]. It has been predicted theoretically that the density autocorrelation function and the density-momentum correlation function in a sheared compressible fluid exhibit much weaker divergent behavior in small wave number limits than the k^{-4} divergence found in large wave numbers [25]. A similar result has also been predicted for an incompressible fluid [26]. Nevertheless, it might be difficult to verify these predictions directly by using available experimental techniques, because the crossover length scales of these systems are so macroscopic.

The purpose of this paper is to emphasize effects of the shear upon long-range correlations which can allow an experimental confirmation. To this end, we consider a particularly simple system, a (dilute) low-molecular-weight binary mixture with imposed concentration and uniform shear gradients [27]. On the basis of fluctuating hydrodynamics approach [28], we calculate a static concentration autocorrelation function which contributes to the total intensity of the Rayleigh peak in a light scattering experiment. In Sec. II, hydrodynamic equations for the concentration and the velocity field are introduced with suitable random forces. We obtain general forms of space-time correlation functions of the hydrodynamic variables by solving the linearized equations around the steady state under imposed boundary conditions. In Sec. III, the static correlation function of concentration fluctuations is expressed in terms of a universal function which describes a shear-induced frustration of the long-range correlation. This function is numerically evaluated and is compared with asymptotic functions that are analytically derived. In Sec. IV, we provide a simple physical interpretation of our results. We also present rough estimations of the crossover length scales for a realistic fluid to suggest possible experimental verifications. Our conclusion is given in the last section.

II. MODEL AND ANALYSIS

A. Basic equations and approximations

The mass diffusion flux $\mathbf{j}$ generally depends not only on the concentration gradient ∇c but also on the temperature

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gradient ∇T and on the pressure gradient ∇p [28,29]. However, when the mass concentration c is small, the thermal diffusion ratio is expected to be rather small because it must vanish in a pure liquid [28]. We thus can safely neglect the term proportional to ∇T, as well as the term proportional to ∇p in the expression of $\mathbf{j}$ because we do not consider any gravity-induced effect. To make the analysis below as simple as possible, we further assume that the mixture is incompressible. Consequently, the only relevant hydrodynamic variables are the concentration c and the momentum $\rho\mathbf{v}$ of the mixture. The equations describing the time evolution of these variables supplemented by the suitable random forces are of the form [9,12,30]

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

$$\frac{\partial \mathbf{v}}{\partial t}+(\mathbf{v}\cdot\boldsymbol{\nabla})\mathbf{v}=-\frac{1}{\rho}\boldsymbol{\nabla}p+\nu\nabla^2\mathbf{v}+\boldsymbol{\nabla}\cdot\mathbf{S}, \tag{2}$$

where the diffusion flux is given as $\mathbf{j}\cong-\rho D\boldsymbol{\nabla}c$, and the hydrostatic pressure p is determined from the incompressibility condition $\boldsymbol{\nabla}\cdot\mathbf{v}=0$. Here D is the mass diffusive coefficient, $\nu=\eta/\rho$ is the kinematic viscosity of the mixture (η the zero shear viscosity). The random forces $\mathbf{g}$ and $\mathbf{S}$ are the random concentration flux and the random stress tensor, respectively. The correlations of these random forces retain their local equilibrium values given by [6,8,9,28]

$$\langle g_i(\mathbf{r},t)g_j(\mathbf{r}',t')\rangle=2k_BT\rho^{-1}D\chi_c\delta_{ij}\times\delta^3(\mathbf{r}-\mathbf{r}')\delta(t-t'), \tag{3}$$

$$\langle S_{il}(\mathbf{r},t)S_{jm}(\mathbf{r}',t')\rangle=2k_BT\rho^{-1}\nu[\delta_{ij}\delta_{lm}+\delta_{im}\delta_{jl}-\tfrac{2}{3}\delta_{il}\delta_{jm}]\delta^3(\mathbf{r}-\mathbf{r}')\delta(t-t'), \tag{4}$$

and $\mathbf{g}$ is uncorrelated with $\mathbf{S}$. In the following, we assume that the osmotic compressibility $\chi_c=(\partial c/\partial\mu)_{p,T}$ and the mass diffusivity D are both independent of the concentration c, where μ is the chemical potential of the mixture [9,12,28]. This assumption may be valid when the gradient $|\boldsymbol{\nabla}c|$ is not sufficiently large. We note that the local equilibrium assumption in Eqs. (3) and (4) is justified from the fact that the random forces represent the fast and localized molecular process which cannot be affected by the macroscopic gradients of the hydrodynamic quantities.

B. Boundary conditions

Although we are primarily interested in the bulk fluctuation properties of the mixture, appropriate boundary conditions are required to specify a macroscopic steady state of the averaged thermodynamic quantities [6]. We adopt here the standard Lees-Edwards type boundary conditions [25,31], which can be written explicitly as

$$\mathbf{v}(x,y=\tfrac{1}{2}L,z)=\mathbf{v}(x-\dot\gamma Lt,y=-\tfrac{1}{2}L,z)+\dot\gamma L\hat{\mathbf{e}}_x \tag{5}$$

and

$$c(x,y=\tfrac{1}{2}L,z)=c(x-\dot\gamma Lt,y=-\tfrac{1}{2}L,z)+|\boldsymbol{\nabla}c|L, \tag{6}$$

where L is the linear system size of y direction that is parallel to both the concentration and shear gradient directions. It is also assumed that the system is infinitely large in all other directions. The statistically averaged, time-independent equations (1) and (2) under the imposed boundary conditions (5) and (6) have solutions

$$\langle\mathbf{v}(\mathbf{r})\rangle=\dot\gamma y\hat{\mathbf{e}}_x, \tag{7}$$

$$\langle c(\mathbf{r})\rangle=c_0+|\boldsymbol{\nabla}c|y, \tag{8}$$

where c_0 stands for the concentration in the $y=0$ plane. We have here chosen our coordinate frame whose origin is at rest by making use of the Galilean invariance. It is also easy to show that, within the present model, the average concentration profile (8) is linearly stable for a perturbation with any wave number under the imposed velocity profile (7) [32].

C. Linearized hydrodynamic equations around the steady state

Now let $c=\langle c\rangle+\delta c$ and $\mathbf{v}=\langle\mathbf{v}\rangle+\delta\mathbf{v}$ in Eqs. (1) and (2). We then obtain the linearized equations for fluctuations δc and $\delta\mathbf{v}=(\delta u,\delta v,\delta w)$ as

$$\frac{\partial}{\partial t}\delta c+\dot\gamma y\frac{\partial}{\partial x}\delta c=-|\boldsymbol{\nabla}c|\delta v+D\nabla^2\delta c+\theta, \tag{9}$$

$$\frac{\partial}{\partial t}\delta\mathbf{v}+\dot\gamma y\frac{\partial}{\partial x}\delta\mathbf{v}+\dot\gamma\delta v\hat{\mathbf{e}}_x=-\frac{1}{\rho}\boldsymbol{\nabla}\delta p+\nu\nabla^2\delta\mathbf{v}+\mathbf{f}, \tag{10}$$

where an equation for the pressure fluctuation follows from the divergence of the equation for $\delta\mathbf{v}$,

$$\nabla^2\delta p=-2\rho\dot\gamma\frac{\partial}{\partial x}\delta v+\rho\boldsymbol{\nabla}\cdot\mathbf{f}. \tag{11}$$

Here we introduced the random variables $\theta=\boldsymbol{\nabla}\cdot\mathbf{g}$ and $\mathbf{f}=\boldsymbol{\nabla}\cdot\mathbf{S}$. Equation (9) implies that the only y component of the velocity fluctuation δv can affect the dynamics of δc. Eliminating δp from Eq. (10) by using Eq. (11), we obtain the linearized hydrodynamic equations relevant to the present purpose of the form

$$\left(\frac{\partial}{\partial t}-\dot\gamma k_x\frac{\partial}{\partial k_y}\right)\delta c_{\mathbf{k}}(t)=-|\boldsymbol{\nabla}c|\delta v_{\mathbf{k}}(t)-Dk^2\delta c_{\mathbf{k}}(t)+\theta_{\mathbf{k}}(t), \tag{12}$$

$$\left(\frac{\partial}{\partial t}-\dot\gamma k_x\frac{\partial}{\partial k_y}\right)\delta v_{\mathbf{k}}(t)=-\left(\nu k^2-2\dot\gamma\frac{k_xk_y}{k^2}\right)\delta v_{\mathbf{k}}(t)+f_{\mathbf{k}}(t), \tag{13}$$

where the Fourier transform of an arbitrary function $\phi(\mathbf{r},t)$ is defined as

$$\phi(\mathbf{r},t)=\int\frac{d\mathbf{k}}{(2\pi)^3}\phi_{\mathbf{k}}(t)e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{14}$$

Note that the random variable in Eq. (13) is redefined by $f_{\mathbf{k}}(t)=\Sigma_j(\delta_{yj}-k_yk_j/k^2)f_{j\mathbf{k}}(t)$. This variable and $\theta_{\mathbf{k}}(t)$ satisfy the correlation properties given from Eq. (3) and Eq. (4) as

$$\langle\theta_{\mathbf{k}}(t)\theta_{\mathbf{k}'}(t')\rangle=2k_BT\rho^{-1}D\chi_ck^2(2\pi)^3\delta^3(\mathbf{k}+\mathbf{k}')\delta(t-t'), \tag{15}$$

$$\langle f_{\mathbf{k}}(t)f_{\mathbf{k}'}(t')\rangle=2k_BT\rho^{-1}\nu k_\perp^2(2\pi)^3\delta^3(\mathbf{k}+\mathbf{k}')\delta(t-t'), \tag{16}$$

and $\langle\theta_{\mathbf{k}}(t)f_{\mathbf{k}'}(t')\rangle=0$, where $k_\perp^2=k_x^2+k_z^2$.

The set of equations (12) and (13) are most easily solved by making a transformation to the local Lagrangian coordinate given by $\mathbf{r}'=\mathbf{r}-\dot\gamma yt\hat{\mathbf{e}}_x$ [10,22–24]. Applying the standard manipulation described elsewhere [24], we readily find the solutions of the form

$$\delta v_{\mathbf{k}}(t)=\int_0^\infty f_{\mathbf{k}(-s)}(t-s)G_{vv}(\mathbf{k},s)ds, \tag{17}$$

$$\delta c_{\mathbf{k}}(t)=\delta c_{\mathbf{k}}^{(0)}(t)-|\nabla c|\,\delta c_{\mathbf{k}}^{(1)}(t), \tag{18}$$

where

$$\delta c_{\mathbf{k}}^{(0)}(t)=\int_0^\infty\theta_{\mathbf{k}(-s)}(t-s)G_{cc}(\mathbf{k},s)ds, \tag{19}$$

and

$$\delta c_{\mathbf{k}}^{(1)}(t)=\int_0^\infty\delta v_{\mathbf{k}(-s)}(t-s)G_{cc}(\mathbf{k},s)ds. \tag{20}$$

Here $\mathbf{k}(t)$ is the time-dependent wave vector defined as

$$\mathbf{k}(t)=\mathbf{k}-\dot\gamma k_xt\hat{\mathbf{e}}_y, \tag{21}$$

and the Green's functions are given by

$$G_{\alpha\alpha}(\mathbf{k},t)=\exp\left(-\int_0^t\Gamma_{\alpha\alpha}(\mathbf{k}(-\tau))d\tau\right), \tag{22}$$

where $\Gamma_{cc}(k)=Dk^2$ and $\Gamma_{vv}(k)=\nu k^2-2\dot\gamma k^{-2}k_xk_y$.

D. Correlation functions

The space-time correlation function of the hydrodynamic fluctuations under the uniform shear is defined by [10]

$$\tilde C_{\alpha\beta}(\mathbf{k},t;\mathbf{k}',t')=\langle\phi_{\alpha,k}(t)\phi_{\beta,k'}(t')\rangle \tag{23}$$

for $(\alpha,\beta)=(c,v)$, where the angular bracket represents the statistical average with respect to the random variables θ and f. The function ϕ_α represents either δc or δv. Under the uniform shear condition, the system is invariant with respect to the temporal transformation, whereas it is not invariant with respect to the spatial transformations [10,23–25]. The time invariance property imposes the symmetry

$$\tilde C_{\alpha\beta}(\mathbf{k},t;\mathbf{k}',t')=\tilde C_{\alpha\beta}(\mathbf{k},t-t';\mathbf{k}',0). \tag{24}$$

This relation implies that it is sufficient to consider the function $\tilde C_{\alpha\beta}(\mathbf{k},t;\mathbf{k}',0)\equiv\tilde C_{\alpha\beta}(\mathbf{k},\mathbf{k}',t)$ for $t\geqslant0$ in the following calculations, without loss of generality [10].

Substituting Eqs. (17) and (18) into Eqs. (23) and using the properties of the random variables (15) and (16), we can derive the time correlation functions of the hydrodynamic modes. The calculations are somewhat lengthy, so we here give only the results:

$$\tilde C_{\alpha\beta}(\mathbf{k},\mathbf{k}',t)=C_{\alpha\beta}(\mathbf{k},t)(2\pi)^3\delta^3(\mathbf{k}+\mathbf{k}'(t)), \tag{25}$$

where

$$C_{vv}(\mathbf{k},t)=\frac{k_BT}{\rho}\frac{k_\perp^2}{k^2}\Bigg[G_{vv}(\mathbf{k},t)+2\dot\gamma G_{vv}^{-1}(\mathbf{k},t)\times\int_t^\infty(\hat k_x\hat k_y+\hat k_x^2s)G_{vv}^2(\mathbf{k},s)ds\Bigg], \tag{26}$$

$$C_{cc}(\mathbf{k},t)=\frac{k_BT}{\rho}\chi_c\Bigg[G_{cc}(\mathbf{k},t)+2|\nabla c|^2\frac{(\nu k_\perp^2)}{\chi_c}G_{cc}^{-1}(\mathbf{k},t)\times\int_0^\infty ds\frac{G_{cc}(\mathbf{k},s)}{G_{vv}(\mathbf{k},s)}\int_{\max(s,t)}^\infty ds'G_{vv}^2(\mathbf{k},s')\times\int_t^{s'}ds''\frac{G_{cc}(\mathbf{k},s'')}{G_{vv}(\mathbf{k},s'')}\Bigg], \tag{27}$$

and the cross-correlation function given by

$$C_{cv}(\mathbf{k},t)=-2\frac{k_BT}{\rho}|\nabla c|(\nu k_\perp^2)G_{vv}^{-1}(\mathbf{k},t)\times\int_0^\infty ds\frac{G_{cc}(\mathbf{k},s)}{G_{vv}(\mathbf{k},s)}\int_{\max(s,t)}^\infty ds'G_{vv}^2(\mathbf{k},s'). \tag{28}$$

Here the Green's functions are written explicitly as

$$G_{cc}(\mathbf{k},t)=e^{-Dk^2T(\hat{\mathbf{k}},t)}, \tag{29}$$

$$G_{vv}(\mathbf{k},t)=\tau(\hat{\mathbf{k}},t)e^{-\nu k^2T(\hat{\mathbf{k}},t)} \tag{30}$$

with

$$T(\hat{\mathbf{k}},t)=t+\dot\gamma\hat k_x\hat k_yt^2+\tfrac{1}{3}\dot\gamma^2\hat k_x^2t^3, \tag{31}$$

$$\tau(\hat{\mathbf{k}},t)=\frac{\partial}{\partial t}T(\hat{\mathbf{k}},t)=1+2\dot\gamma\hat k_x\hat k_yt+\dot\gamma^2\hat k_x^2t^2, \tag{32}$$

where $\hat{\mathbf{k}}=\mathbf{k}/|\mathbf{k}|$. In the derivations of Eqs. (26)–(28), we have made use of the identity $G_{\alpha\alpha}(\mathbf{k}(-t),s)=G_{\alpha\alpha}^{-1}(\mathbf{k},t)G_{\alpha\alpha}(\mathbf{k},s+t)$.

Although Eqs. (26)–(28) are rather complicated, the equal-time correlation functions have somewhat simpler

forms because of the recovery of the translational invariance with respect to the space. Setting $t=0$ in Eqs. (26)–(28), we obtain

$$C_{vv}(\mathbf{k})=\frac{k_BT}{\rho}\frac{k_\perp^2}{k^2}\left[1+2\dot{\gamma}\int_0^\infty dt(\hat{k}_x\hat{k}_y+\hat{k}_x^2t)e^{-2\nu k^2T(\hat{k},t)}\right], \tag{33}$$

$$C_{cc}(\mathbf{k})=\frac{k_BT}{\rho}\chi_c\left[1+2|\nabla c|^2\frac{(\nu k_\perp^2)}{\chi_c}\int_0^\infty dt\frac{e^{(\nu-D)k^2T(\hat{k},t)}}{\tau(\hat{\mathbf{k}},t)}\right.$$
$$\times\int_t^\infty dt'\,\tau^2(\hat{\mathbf{k}},t')e^{-2\nu k^2T(\hat{k},t')}$$
$$\left.\times\int_0^{t'}dt''\frac{e^{(\nu-D)k^2T(\hat{k},t'')}}{\tau(\hat{\mathbf{k}},t'')}\right], \tag{34}$$

and

$$C_{cv}(\mathbf{k})=-2\frac{k_BT}{\rho}|\nabla c|(\nu k_\perp^2)\int_0^\infty dt\frac{e^{(\nu-D)k^2T(\hat{k},t)}}{\tau(\hat{\mathbf{k}},t)}$$
$$\times\int_t^\infty dt'\,\tau^2(\hat{\mathbf{k}},t')e^{-2\nu k^2T(\hat{k},t')}. \tag{35}$$

Equations (33)–(35) together with Eqs. (31) and (32) are the main results of this section. The same result as Eq. (33) has also been derived for the simple fluid in Ref. [26]. Thus the correlation function between the momentum fluctuations is unaffected by the steady concentration gradient within the present analysis.

III. LONG-RANGE CORRELATIONS

We shall first examine the two limiting cases studied previously in Eqs. (33)–(35). At zero shear rate, Eqs. (33)–(35) are reduced to the form

$$C_{vv}(\mathbf{k})\to\frac{k_BT}{\rho}|\hat{\mathbf{k}}_\perp|^2, \tag{36}$$

$$C_{cc}(\mathbf{k})\to\frac{k_BT}{\rho}\chi_c\left[1+2|\nabla c|^2\frac{(\nu k_\perp^2)}{\chi_c}\int_0^\infty dte^{(\nu-D)k^2t}\right.$$
$$\left.\times\int_t^\infty dt'e^{-2\nu k^2t'}\int_0^{t'}dt''e^{(\nu-D)k^2t''}\right]$$
$$=\frac{k_BT}{\rho}\chi_c\left(1+\frac{|\nabla c|^2}{\chi_cD(\nu+D)}\frac{|\hat{\mathbf{k}}_\perp|^2}{k^4}\right), \tag{37}$$

$$C_{cv}(\mathbf{k})\to-2\frac{k_BT}{\rho}|\nabla c|(\nu k_\perp^2)\int_0^\infty dte^{(\nu-D)k^2t}\int_t^\infty dt'e^{-2\nu k^2t'}$$
$$=-\frac{k_BT}{\rho}\frac{|\nabla c|}{(\nu+D)}\frac{|\hat{\mathbf{k}}_\perp|^2}{k^2}. \tag{38}$$

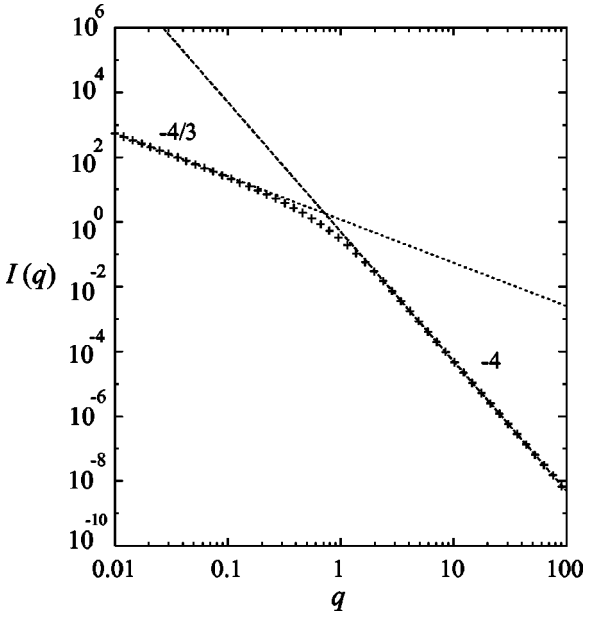

FIG. 1. Plots of numerically evaluated scaling function $I(q)$, where the momentum autocorrelation function is written in the form $C_{vv}(k,0,0)=\rho^{-1}k_BT[1+I(\xi_vk)]$. The dashed and dotted lines represent the asymptotic functions for large $q\gg1$ [Eq. (39)] and for small $q\ll1$ [Eq. (40)], respectively.

Equation (36) is the standard result in thermal equilibrium [33]. In contrast to this, the second terms in Eq. (37) and Eq. (38) show the anomalous enhancements of the hydrodynamic fluctuations in the presence of the concentration gradient. These results were first predicted by Kirkpatrick *et al*. using mode coupling and kinetic theory [7] and subsequently confirmed by Ronis and Procaccia using fluctuating hydrodynamics [8]. On the other hand, in the limit of a small concentration gradient, Eqs. (37) and (38) converge to the equilibrium forms given by $C_{cc}(\mathbf{k})\to k_BT\chi_c/\rho$ and $C_{cv}(\mathbf{k})\to0$ regardless of the presence of the shear flow. However, the momentum-momentum correlation function becomes long ranged in this case because of the influence of the shear [6,8,10,25,26]. Two asymptotic forms in the selected direction of the wave vector $\mathbf{k}=(k,0,0)$ are given by [26]

$$C_{vv}(k,0,0)\sim\frac{k_BT}{\rho}\left(1+\frac{1}{2}\frac{\dot{\gamma}^2}{\nu^2k^4}\right) \tag{39}$$

for $k\xi_v\gg1$, and

$$C_{vv}(k,0,0)\sim\frac{k_BT}{\rho}\left(\frac{2}{3}\right)^{1/3}\Gamma\left(\frac{2}{3}\right)\frac{\dot{\gamma}^{2/3}}{\nu^{2/3}k^{4/3}} \tag{40}$$

for $k\xi_v\ll1$, where $\Gamma(x)$ is the Gamma function. The direct numerical evaluation of Eq. (33) is also shown in Fig. 1. The length scale which characterizes this crossover is introduced as

$$\xi_v=\sqrt{\frac{\dot{\gamma}}{\nu}}. \tag{41}$$

In the following, we shall focus our attention on the behavior of Eq. (34) for arbitrary magnitudes of the shear rate $\dot{\gamma}$ and the concentration gradient $|\nabla c|$. It is easy to show that Eq. (34) can be written in the form

$$C_{cc}(\mathbf{k}) = \frac{k_B T}{\rho}\chi_c\left(1+\frac{|\nabla c|^2}{\chi_c \dot{\gamma}^2}F(\mathbf{k}\xi_v)\right). \tag{42}$$

We here consider the case where the scattering wave vector $\mathbf{k}$ is perpendicular to the concentration gradient ∇c, i.e., $\mathbf{k}=\mathbf{k}_\perp=(k_x,0,k_z)$. This scattering geometry still holds all of the essential features of the nonequilibrium effects found in this system, and is actually the configuration adopted in most of the previous light scattering experiments [9,15–17,19]. The scaling function $F(\mathbf{q})$ in Eq. (42) in this geometry is given by

$$F(\mathbf{q}) = 2q^2\int_0^\infty \frac{ds}{1+\hat{q}_x^2 s^2} e^{(1-a)q^2\tilde{T}(\hat{\mathbf{q}},s)} \times \int_s^\infty ds'(1+\hat{q}_x^2 s'^2)^2 e^{-2q^2\tilde{T}(\hat{\mathbf{q}},s')} \times \int_0^{s'} \frac{ds''}{1+\hat{q}_x^2 s''^2} e^{(1-a)q^2\tilde{T}(\hat{\mathbf{q}},s'')}, \tag{43}$$

where $\tilde{T}(\hat{\mathbf{q}},t)=t+\frac{1}{3}\hat{q}_x^2 t^3$ and $a=D/\nu$ is the ratio of the mass diffusivity to the viscous diffusivity, which is usually much smaller than unity. As can be understood from Eq. (43), the effect of the shear is most likely to become evident in the particular direction of the wave vector given by $\mathbf{k}=(k,0,0)$. To simplify the analysis, we restrict our interest to the fluctuations in this direction. Because of this simplification, the asymptotic behavior for small $q=k\xi_v$ limit is easily found to be

$$F(q)\sim\left(\frac{3}{2}\right)^{2/3}\frac{\pi^2}{4}\Gamma\left(\frac{5}{3}\right)q^{-4/3}. \tag{44}$$

Equation (44) suggests that the enhancement of the nonequilibrium fluctuations is severely restricted in the long wavelength limit. On the other hand, the opposite asymptotic region, i.e., the short wavelength limit, is represented by $k\xi_c \gg 1$, where the second characteristic length scale ξ_c is given by

$$\xi_c = \sqrt{\frac{D}{\dot{\gamma}}} = a^{1/2}\xi_v \ll \xi_v . \tag{45}$$

It turns out that the asymptotic behavior of $F(k\xi_v)$ for $k\xi_c \gg 1$ has the same wave number dependence given by the second term in Eq. (37). This implies that thermal fluctuations of the hydrodynamic variables for $k\xi_c \gg 1$ are little affected by the shear and can dissipate purely thermally. Consequently, the static concentration autocorrelation functions in the two limiting cases of short and long wave numbers are written as

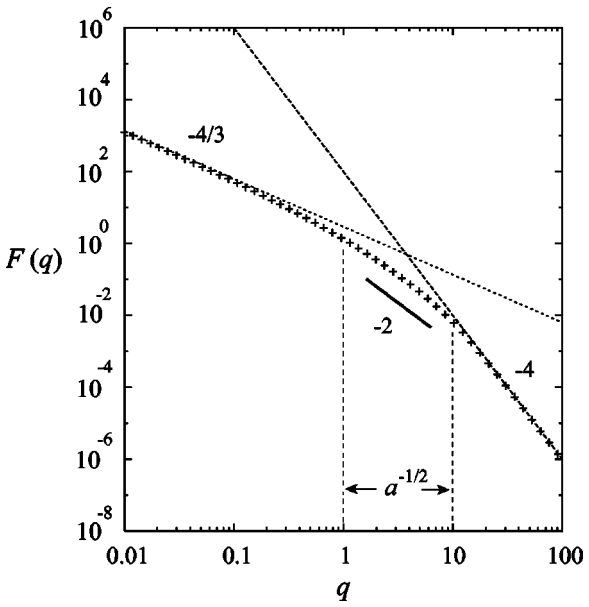

FIG. 2. The scaling function $F(k\xi_v)$ as a function of $q=k\xi_v$ obtained by the numerical integration of Eq. (43) for $\hat{q}_x=1$ and $a=0.01$. The lines are the asymptotic results derived analytically. Note that the crossover wave numbers given by $k\xi_v=1$ and $k\xi_c=1$ correspond to $q=1$ and $q=a^{-1/2}$, respectively.

$$C_{cc}(k,0,0)\sim\frac{k_B T}{\rho}\chi_c\left(1+\frac{|\nabla c|^2}{\chi_c D(\nu+D)k^4}\right) \tag{46}$$

for $k\xi_c \gg 1$, and

$$C_{cc}(k,0,0)\sim\frac{k_B T}{\rho}\chi_c\left(1+\frac{\alpha|\nabla c|^2}{\chi_c \nu^{2/3}\dot{\gamma}^{4/3}k^{4/3}}\right) \tag{47}$$

for $k\xi_v \ll 1$, where the numerical constant α is given by $\alpha=(\frac{3}{2})^{2/3}(\pi^2/4)\Gamma(\frac{5}{3})\approx 2.9$.

In Fig. 2, a numerically calculated scaling function $F(q)$ is plotted with the asymptotic functions for large and small q deduced from Eqs. (46) and (47), respectively. Although the intermediate region given by $\xi_v^{-1}<k<\xi_c^{-1}$ seems to have k^{-2} dependence, whether it is a true scaling regime or just a crossover is still unclear at present. Note, however, that this region is practically extended in a wide range of the wave numbers, which is typically given by $1<q<a^{-1/2}(\sim 10^2-10^3)$ due to the large asymmetry between the magnitude of the viscous and mass diffusivity. Therefore, we expect that this unclearness will be clarified by evaluating $F(q)$ for a much smaller a than that considered here ($a=10^{-2}$), though it cannot be done in the present study primarily because of the limitation of the numerical accuracy.

IV. DISCUSSION

As pointed out in a number of papers, the long-range correlation originates from the nondissipative coupling of

momentum fluctuations with concentration fluctuations through a macroscopic concentration gradient [7,8]. This is sometimes called a linear mode-coupling effect [10]. Following the discussions given in Refs. [34,35], let us suppose a small fluid element of linear size ξ in the mixture in the absence of the shear. This fluid portion is carried along the direction of the gradient by a spontaneously generated momentum fluctuation of its lifetime given by $\tau_v \sim \xi^2/\nu$. Because the surrounding fluid has a different average concentration, the large concentration difference persists for a time $\tau_c \sim \xi^2/D$ as it relaxes purely diffusively. Considering that $a = D/\nu \ll 1$, one can notice that a short-living, spontaneous momentum fluctuation can create a long-lasting, large-amplitude concentration fluctuation, which results in a long-range spatial correlation between concentration fluctuations in the steady state.

However, shear flow limits the size of such fluctuations significantly, because a sufficiently large fluctuation is drawn out and is even broken up by the shear before it disappears by the diffusion [22,23,25]. In our system, ξ_c and ξ_v correspond to the crossover length scale from the diffusion-dominated decay to the shear-dominated decay of concentration and momentum fluctuations, respectively. Because ξ_c is much smaller than ξ_v in practice, the overall behavior of $C_{cc}(\mathbf{k})$ is expected to have three distinctive wave number domains. They can be sketched as follows.

(I) When a small portion of mixture of linear size larger than ξ_v is carried along the direction of the gradient, it undergoes a dramatic shear deformation and becomes highly anisotropic. Because the lifetime of the concentration fluctuation is controlled by the shortest length scale of its spatial extent, this fluctuation dissipates thermally much faster than in a quiescent fluid. Thus the long-range correlation between concentration fluctuations is severely suppressed by the shear flow in this wave number region.

(II) When $\dot{\gamma}\tau_v \sim \xi^2/\xi_v^2 < 1$, a momentum fluctuation can displace a small parcel of fluid of size ξ without a notable shear deformation. However, if $\dot{\gamma}\tau_c \sim \xi^2/\xi_c^2 > 1$, the shear flow strongly affects the decay of this large-amplitude concentration fluctuation before it dissipates thermally. Then the decay of the fluctuation is still faster than in a quiescent fluid in this region, and the resulting correlation exhibits a weaker divergent dependence on the wave numbers k than on k^{-4}.

(III) When the size of a fluctuation is much smaller than ξ_c, the effect of the shear becomes rather weak because a thermal diffusive decay is faster than the shear deformation time scale; $\dot{\gamma}\tau_v \ll \dot{\gamma}\tau_c < 1$. Therefore the usual story for a quiescent fluid presented in the beginning of this section is fit for this regime.

Figure 2 shows that the deviation from the k^{-4} divergence becomes pronounced at the wave number $k_c \sim \xi_c^{-1}$. It should be emphasized that the presence of k_c is a clear evidence of the shear-induced suppression of the long-range correlation. Although the shear-controlled asymptote is confirmed only in the wave numbers smaller than $k_v \sim \xi_v^{-1}$, it may be impossible to verify this scaling experimentally because the length scale ξ_v is so macroscopic for relevant fluid parameters and experimentally feasible shear rates [25,26]. (For example, we can obtain $k_v \sim 1\ \mathrm{mm}^{-1}$ at most, for a typical value of the viscosity $\nu \sim 10^{-2}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$ and for a very high rate of the shear that is of the order of $10^4\ \mathrm{s}^{-1}$.) Contrary to this situation, a typical value of the diffusion coefficient $D \sim 10^{-6}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$ gives $k_c \sim 10^3\ \mathrm{cm}^{-1}$ even for a very small rate of the shear as $\dot{\gamma} \sim 1\ \mathrm{s}^{-1}$. Therefore, the wave number k_c, which characterizes the onset of the shear-induced frustration of the long-range correlation, is well covered by conventional low-angle light scattering methods, as well as the recently reported new optical technique [36].

There have been developed some experimental techniques to produce a macroscopic concentration gradient in a fluid, such as utilizing a diffusive remixing process of a mixture [35] or making use of a large Soret effect driven by a steady temperature gradient [19,37]. Although it is far beyond our ability to guess about, the latter method might be more favorable with respect to the compatibility with the shear flow, as well as the spatial uniformity and the temporal stationarity of the concentration gradient. When the large Soret effect is expected, however, temperature fluctuations should be taken into account, because the cross-correlation between concentration and temperature fluctuations makes an important contribution to the Rayleigh scattering [9,17]. The dynamic structure factor in that case is composed of various contributions from the correlations between the concentration, temperature, and momentum fluctuations, and then the third length scale $\xi_T = (D_T/\dot{\gamma})^{1/2}$ should enter into the theory, where D_T is the thermal diffusivity of the mixture. However, the whole spectrum can be separated using photon correlation spectroscopy when the decay times between T-T and c-c fluctuations differ by several orders of magnitude [9]. This condition is actually satisfied for most mixtures, because a typical value of the thermal diffusivity D_T is about $10^{-3}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$ while a mass diffusivity D is usually smaller than $10^{-5}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$ [12].

V. CONCLUSION

In this paper, using fluctuating hydrodynamics, we have studied the fluctuation properties in a (dilute) binary mixture with imposed uniform concentration and shear gradients. It is demonstrated that the static concentration autocorrelation function has three distinctive wave number regions. The length scales which characterize the crossovers between different regimes are given as $\xi_c \sim (D/\dot{\gamma})^{1/2}$ and $\xi_v \sim (\nu/\dot{\gamma})^{1/2}$, respectively. In particular, shear strongly suppresses the k^{-4} divergence for $k\xi_c < 1$, while the asymptotic shear-controlled behavior is found analytically in the smallest wave numbers satisfying $k\xi_v \ll 1$. It is worth noting that the shear-induced quench of the long-range correlation may be experimentally observable. The experimental system we are envisaging here is, for example, a suitably chosen dilute aqueous colloidal suspension. If we choose $D = 2 \times 10^{-7}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$, $\nu = 8 \times 10^{-3}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$, and $D_T = 10^{-3}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$ as typical values of the kinetic and transport coefficients [37], we find

$k_c \sim 10^3$ cm^{-1} for very small shear rate as $\dot{\gamma} \sim 1$ s^{-1} and $k_c \sim 10^4$ cm^{-1} for $\dot{\gamma} \sim 10^2$ s^{-1}. This simple estimation suggests that the quenched spectrum of the spatial long-range correlation by the shear flow is well covered by a low-angle light scattering experiment. In addition, the total intensity under the central peak at the wave number $k \sim k_c$ is about 10^2 times larger than that in the equilibrium if one assumes $\chi_c \sim 10^{-6}$ s^2 cm^{-2}, $|\nabla c| \sim 0.1$ cm^{-1}, and $\dot{\gamma} \sim 1$ s^{-1}. We expect that this property makes an experimental verification easier. Experimental and numerical verifications of the proposed effects will also become an important test for the applicability of fluctuating hydrodynamics to a fluid in a coupled-nonequilibrium steady state.

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