Noncritical liquid mixtures far from equilibrium: The Rayleigh line

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In this paper we determine the contributions to the Rayleigh line for a noncritical binary liquid mixture in a temperature gradient using the technique of fluctuating hydrodynamics in a uniform-pressure approximation. The steady-state temperature gradient induces a steady-state concentration gradient in the liquid mixture. We predict a large enhancement to the Rayleigh line from concentration fluctuations that depends upon the square of the concentration gradient. The occurrence of two gradients within the liquid also gives rise to additional cross-coupling gradient contributions.

I. INTRODUCTION

In recent years the study of fluctuations in nonequilibrium steady-state systems has uncovered a rich variety of new phenomena. Reference 1 provides a good review of this field up to 1984. Recently, one of us (B.M.L.) observed the modifications to the Rayleigh line for a pure liquid subjected to a large stabilizing temperature gradient ∇T, where one finds an enhancement to the heat mode and the appearance of a new viscous mode;[2] both contributions to the time correlation function are found to depend upon $(\nabla T)^2/k^4$, where k is the scattering vector, as first predicted by Kirkpatrick, Cohen, and Dorfman[3] using mode coupling and kinetic theory and subsequently confirmed by Ronis and Procaccia[4] using fluctuating hydrodynamics. A very complete analysis of the correlation of fluctuations for a pure liquid in a temperature gradient, and which includes boundary effects, has recently been presented by Schmitz and Cohen.[5] In a future set of experiments Segrè, Gammon, and Sengers plan to study binary liquid mixtures removed far from equilibrium by a temperature gradient.[6] As an aid in choosing appropriate liquid mixtures and in analyzing the experimental results we calculate the modifications to the Rayleigh line for a noncritical binary liquid mixture in a temperature gradient using the technique of fluctuating hydrodynamics. For such a system the temperature gradient will induce a concentration gradient in the liquid mixture the *size* and *direction* of which will be determined by the thermal diffusion ratio. The Rayleigh line is enhanced by both temperature and concentration fluctuations while the presence of two gradients leads to cross-coupling terms between the gradients. There has been one previous theoretical study[7] of a system subjected to two dissipative fields—they considered the Brillouin lines for a pure liquid with imposed temperature and shear gradients; however, the cross-coupling effects here are expected to be small and perhaps unobservable.

The analysis in Sec. II, which most closely follows the work of Ronis and Procaccia,[4] is arranged as follows.

First, we present the general equations of hydrodynamics with the addition of random force terms. These equations are simplified by only retaining terms that are first order in the fluctuations; that is, we assume the system is far from any critical point or point of instability. Finally, the Rayleigh line is calculated explicitly for scattering vectors perpendicular to the gradients by adopting the simplifying approximations that pressure fluctuations are zero and that the Rayleigh line is determined to leading order by the temperature, concentration, and *transverse* velocity fluctuations;[8] the pressure and the longitudinal velocity fluctuations only contribute to the sound modes (Brillouin lines). This theory is applied to a 0.5-mole-fraction liquid mixture of benzene plus carbon tetrachloride. Enhancements of the order of 60 are observed for a scattering vector of 2000 cm^{-1} and temperature gradient of 100 K/cm.

II. THEORY

A consensus has been reached concerning the correct method for calculating the correlation of fluctuations for nonequilibrium steady-state systems; see, for example, Ref. 1. In the fluctuating hydrodynamics approach this involves the following steps: (a) One first writes down the nonlinear hydrodynamic equations that hold for the time evolution of the *average* hydrodynamic variables with appropriate boundary conditions; (b) random force terms are added to these hydrodynamic equations; the resulting equations describe the time evolution of the *instantaneous* hydrodynamic variables; (c) the dynamics of the fluctuations, for systems far from any instability or critical point, are described by determining the linearized equations in the fluctuations; and finally (d) the correlations in the fluctuations are calculated from these linearized equations by assuming that the random force correlations retain their local *equilibrium* value; this is because the random forces account for the very rapid localized molecular processes and on a molecular level the molecules are not influenced by the gradient.

In the following we will use the random forces as defined by Cohen, Sutherland, and Deutch[9] who calculated the correlations between the random forces for a binary liquid mixture in equilibrium. One can readily demonstrate that the nonlinear hydrodynamic equations as given by Landau and Lifshitz,[10] when supplemented by these random forces, are given by the following equations:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \ , \tag{1}$$

$$\rho \left[\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c \right] = -\nabla \cdot \mathbf{j} + \rho \nabla \cdot \mathbf{f} \ , \tag{2}$$

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

$$+ (\zeta + \tfrac{1}{3} \eta) \nabla (\nabla \cdot \mathbf{v}) + \nabla \cdot \mathbf{S} \ , \tag{3}$$

$$\rho T \left[\frac{\partial s}{\partial t} + \mathbf{v} \cdot \nabla s \right] = \sigma'_{ik} \frac{\partial v_i}{\partial x_k} - \nabla \cdot (\mathbf{q} - \mu \mathbf{j}) - \mathbf{j} \cdot \nabla \mu$$

$$- \rho T \left[\frac{\partial \mu}{\partial T} \right]_{p,c} \nabla \cdot \mathbf{f} + \nabla \cdot \mathbf{g} \ . \tag{4}$$

The mass diffusion flux $\mathbf{j}$ is

$$\mathbf{j} = -\rho D \left[\nabla c + \frac{k_T}{T} \nabla T + \frac{k_p}{p} \nabla p \right] \ , \tag{5}$$

while the heat diffusion flux q is

$$\mathbf{q} = \left[k_T \left[\frac{\partial \mu}{\partial c} \right]_{p,T} - T \left[\frac{\partial \mu}{\partial T} \right]_{p,c} + \mu \right] \mathbf{j} - \kappa \nabla T \ . \tag{6}$$

Here ρ is the mass density, c the mass concentration defined as the ratio of the mass of one component to the total mass of the fluid in a given volume element, $\mathbf{v}$ the velocity, s the entropy, T the temperature, p the pressure, μ the chemical potential, σ'_{ik} the viscosity stress tensor, η the shear viscosity, ζ the bulk viscosity, D the mass diffusion coefficient, k_T the thermal diffusion ratio, k_p the barodiffusion ratio, and κ the thermal conductivity. In the following, we neglect the temperature dependence and hence, correspondingly, the spatial dependence of the transport coefficients—this will be justified in a forthcoming publication. (Kirkpatrick, Cohen, and Dorfman[3] demonstrated that such an assumption was justified, at least for a *pure* liquid in a temperature gradient, for experimentally accessible scattering vectors and gradients.) The random forces $\mathbf{f}$, $\mathbf{S}$, and $\mathbf{g}$, as defined in Ref. 9, are, respectively, the random concentration flux, the random stress tensor, and the random flux for the variable $\phi = T - T_o \alpha_T p / C_p \rho_o$, where the subscript o denotes

mean value, α_T is the thermal expansion coefficient, and C_p is the heat capacity at constant pressure and concentration. The quantities ρ, c, $\mathbf{v}$, s, T, p, μ, $\mathbf{j}$, and $\mathbf{q}$ describe instantaneous hydrodynamic variables which can be separated into an average part plus a fluctuating part, for example, the instantaneous mass density is given by $\rho = \rho_o + \delta \rho$, where $\rho_o = \langle \rho \rangle$ is the average density and $\delta \rho$ is the density fluctuation with mean $\langle \delta \rho \rangle = 0$; $\langle \ \rangle$ denotes an ensemble average. We will assume that there is no convection in the system so that $\mathbf{v}_o = 0$.

The random forces $\mathbf{f}$, $\mathbf{g}$, and $\mathbf{S}$ have zero average value while their correlations retain their local equilibrium values. The correlations in the random forces are given explicitly in Eqs. (19)–(23) below.

For a steady-state system $\partial \rho_o / \partial t = \partial c_o / \partial t = \partial s_o / \partial t = 0$ and $\mathbf{j}_o = 0$, that is, from Eq. (5),

$$\nabla c_o + \frac{k_T}{T} \nabla T_o = 0 \ , \tag{7}$$

where we have assumed that there are no significant pressure gradients and ∇c_o and ∇T_o denote the steady-state concentration and temperature gradients, respectively. The size and direction of the induced concentration gradient is determined by the steady-state condition, Eq. (7).

The next step towards calculating the correlations in the fluctuations, for a system far from any instability or critical point, is to determine the hydrodynamic equations that have been linearized in the fluctuations. For the continuity equation (1), using the thermodynamic relation

$$\delta \rho = \rho_o (\beta_p \delta p + \beta_c \delta c - \alpha_T \delta T) \ ,$$

where

$$\beta_p = \frac{1}{\rho_o} \left[\frac{\partial \rho}{\partial p} \right]_{T,c} \ ,$$

$$\beta_c = \frac{1}{\rho_o} \left[\frac{\partial \rho}{\partial c} \right]_{p,T} \ ,$$

$$\alpha_T = -\frac{1}{\rho_o} \left[\frac{\partial \rho}{\partial T} \right]_{p,c} \ ,$$

we find that

$$\beta_p \frac{\partial \delta p}{\partial t} + \beta_c \frac{\partial \delta c}{\partial t} - \alpha_T \frac{\partial \delta T}{\partial t} + \beta_c \delta \mathbf{v} \cdot \nabla c_o$$

$$- \alpha_T \delta \mathbf{v} \cdot \nabla T_o + \nabla \cdot \delta \mathbf{v} = 0 \ . \tag{8}$$

Similarly, the concentration equation (2), the momentum equation (3), and the heat transfer equation (4) become, respectively,

$$\rho_o \left[\frac{\partial \delta c}{\partial t} + \delta \mathbf{v} \cdot \nabla c \right] = -\nabla \cdot \delta \mathbf{j} + \rho_o \nabla \cdot \mathbf{f} \ , \tag{9}$$

$$\rho_o \frac{\partial \delta \mathbf{v}}{\partial t} = -\nabla \delta p + \eta \nabla^2 \delta \mathbf{v} + (\zeta + \tfrac{1}{3} \eta) \nabla (\nabla \cdot \delta \mathbf{v}) + \nabla \cdot \mathbf{S} \ , \tag{10}$$

and

$$\rho_o C_p \frac{\partial \delta T}{\partial t} - \alpha_T T_o \frac{\partial \delta p}{\partial t} - \rho_o T_o \left[\frac{\partial \mu}{\partial T}\right]_{c,p} \frac{\partial \delta c}{\partial t} + \rho_o C_p \delta \mathbf{v} \cdot \nabla T_o - \rho_o T_o \left[\frac{\partial \mu}{\partial T}\right]_{c,p} \delta \mathbf{v} \cdot \nabla c_o$$

$$= -\left[k_T \left[\frac{\partial \mu}{\partial c}\right]_{p,T} - T_o \left[\frac{\partial \mu}{\partial T}\right]_{p,c}\right] \nabla \cdot \delta \mathbf{j} + \kappa \nabla^2 \delta T + \rho_o D \left[\frac{\partial \mu}{\partial c}\right]_{p,T} \nabla c_o \cdot \left[\nabla \delta c + \frac{k_T}{T_o} \nabla \delta T + \frac{k_p}{p_o} \nabla \delta p\right]$$

$$- \rho_o T_o \left[\frac{\partial \mu}{\partial T}\right]_{p,c} \nabla \cdot \mathbf{f} + \nabla \cdot \mathbf{g} \ , \tag{11}$$

where we have used the thermodynamic relation

$$\delta_S = \frac{C_p}{T_o} \delta T - \frac{\alpha_T}{\rho_o} \delta p - \left[\frac{\partial \mu}{\partial T}\right]_{c,p} \delta c$$

in the heat equation (11), and where

$$-\nabla \cdot \delta \mathbf{j} = D \nabla \rho_o \cdot \left[\nabla \delta c + \frac{k_T}{T_o} \nabla \delta T + \frac{k_p}{p_o} \nabla \delta p\right] + \rho_o D \left[\nabla^2 \delta c + \frac{k_T}{T_o} \nabla^2 \delta T + \frac{k_p}{p_o} \nabla^2 \delta p\right] - \frac{2\rho_o D k_T}{T_o^2} \nabla T_o \cdot \nabla \delta T \ . \tag{12}$$

In deriving Eq. (12) for $-\nabla \cdot \delta \mathbf{j}$, we have assumed (i) all gradients are linear, that is, $\nabla^2 T_o = \nabla^2 c_o = 0$, (ii) all gradients are small, that is, we have only retained terms linear in the gradient, and (iii) we have used the steady-state equation (7).

The heat transfer equation (11) can be transformed into a more convenient form by eliminating $\nabla \cdot \delta \mathbf{j}$ using Eq. (9), then

$$\rho_o C_p \frac{\partial \delta T}{\partial t} - \alpha_T T_o \frac{\partial \delta p}{\partial t} - \rho_o k_T \left[\frac{\partial \mu}{\partial c}\right]_{p,T} \frac{\partial \delta c}{\partial t} + \rho_o C_p \delta \mathbf{v} \cdot \nabla T_o - \rho_o k_T \left[\frac{\partial \mu}{\partial c}\right]_{p,T} \delta \mathbf{v} \cdot \nabla c_o$$

$$= \kappa \nabla^2 \delta T + \rho_o D \left[\frac{\partial \mu}{\partial c}\right]_{p,T} \nabla c_o \cdot \left[\nabla \delta c + \frac{k_T}{T_o} \nabla \delta T + \frac{k_p}{p_o} \nabla \delta p\right] - \rho_o k_T \left[\frac{\partial \mu}{\partial c}\right]_{p,T} \nabla \cdot \mathbf{f} + \nabla \cdot \mathbf{g} \ . \tag{13}$$

The complete solution for this system of equations, Eqs. (8)–(10) and (13), is very algebraic and not particularly informative especially if one is principally interested in the Rayleigh line. We therefore specialize our treatment to the Rayleigh line using a uniform pressure approximation[11,12] (that is, $\delta p = 0$) where only the concentration, temperature, and *transverse* velocity fluctuate. We recently demonstrated[8] that for a pure liquid in a temperature gradient only the transverse velocity fluctuations contribute to the Rayleigh line to leading order; the longitudinal velocity fluctuations contribute to the Brillouin lines. This situation is not expected to be altered by the presence of a second liquid in a binary liquid mixture. If we also take the Fourier time and space transform and drop the subscript o, denoting mean value, we obtain the following equation for the concentration equation (9):

$$\delta c_{\mathbf{k},\omega} \left[i\omega + \frac{iD\mathbf{k} \cdot \nabla \rho}{\rho} + k^2 D\right] + \delta T_{\mathbf{k},\omega} \left[\frac{iDk_T}{\rho T} \mathbf{k} \cdot \nabla \rho - \frac{i2Dk_T}{T^2} \mathbf{k} \cdot \nabla T + \frac{k^2 Dk_T}{T}\right] = -i\mathbf{k} \cdot \mathbf{f}_{\mathbf{k},\omega} - \delta \mathbf{v}^t_{\mathbf{k},\omega} \cdot \nabla c \ , \tag{14}$$

where $\delta \mathbf{v}^t_{\mathbf{k},\omega}$ is the transverse velocity fluctuation. Similarly, the heat transfer equation (13) becomes

$$\delta c_{\mathbf{k},\omega} \left[-i\omega \rho k_T \left[\frac{\partial \mu}{\partial c}\right]_{p,T} + i\rho D \left[\frac{\partial \mu}{\partial c}\right]_{p,T} \mathbf{k} \cdot \nabla c\right] + \delta T_{\mathbf{k},\omega} \left[i\omega \rho C_p + k^2 D_T \rho C_p + \frac{i\rho D k_T}{T} \left[\frac{\partial \mu}{\partial c}\right]_{p,T} \mathbf{k} \cdot \nabla c\right]$$

$$= i\rho k_T \left[\frac{\partial \mu}{\partial c}\right]_{p,T} \mathbf{k} \cdot \mathbf{f}_{\mathbf{k},\omega} - i\mathbf{k} \cdot \mathbf{g}_{\mathbf{k},\omega} - \rho C_p \delta \mathbf{v}^t_{\mathbf{k},\omega} \cdot \nabla T + \rho k_T \left[\frac{\partial \mu}{\partial c}\right]_{p,T} \delta \mathbf{v}^t_{\mathbf{k},\omega} \cdot \nabla c \ , \tag{15}$$

where the thermal diffusivity $D_T = \kappa / \rho C_p$. Velocity fluctuations are determined from the momentum equation (10), which in $\mathbf{k} - \omega$ space has the form

$$i\omega \delta \mathbf{v}_{\mathbf{k},\omega} = -\nu_t k^2 \delta \mathbf{v}_{\mathbf{k},\omega} - (\nu_1 - \nu_t) \mathbf{k}(\mathbf{k} \cdot \delta \mathbf{v}_{\mathbf{k},\omega}) - \frac{i\mathbf{k} \cdot \mathbf{S}_{\mathbf{k},\omega}}{\rho} \ , \tag{16}$$

where the longitudinal kinematic viscosity $\nu_1 = (\zeta + 4\eta/3)/\rho$ and the transverse kinematic viscosity $\nu_t = \eta/\rho$. To calculate the transverse velocity fluctuation $\delta \mathbf{v}^t_{\mathbf{k},\omega}$ one applies the projection operator $(1 - \hat{\mathbf{k}} \hat{\mathbf{k}})$ to (16)

$$\delta \mathbf{v}^t_{\mathbf{k},\omega} = (1 - \hat{\mathbf{k}} \hat{\mathbf{k}}) \cdot \delta \mathbf{v}_{\mathbf{k},\omega} = -\frac{i\mathbf{k} \cdot \mathbf{S}_{\mathbf{k},\omega} \cdot (1 - \hat{\mathbf{k}} \hat{\mathbf{k}})}{\rho(i\omega + k^2 \nu_t)} \ . \tag{17}$$

Here $\hat{\mathbf{k}}$ is the unit vector in the direction of the scattering vector $\mathbf{k}$.

The equations for the temperature and concentration fluctuations, Eqs. (14) and (15), simplify considerably if we only consider the case where the scattering vector $\mathbf{k}$ is *perpendicular* to the temperature and concentration gradients—this scattering geometry still retains the essential features of the calculation. From Eqs. (14), (15), and (17) we obtain the following 2×2 matrix equation for $\delta T_{\mathbf{k},\omega}$ and $\delta c_{\mathbf{k},\omega}$:

$$
\begin{bmatrix}
\dfrac{k^2 D k_T}{T} & i\omega + k^2 D \\[3mm]
\rho C_p(i\omega + k^2 D_T) & -i\rho\omega k_T\left[\dfrac{\partial\mu}{\partial c}\right]_{p,T}
\end{bmatrix}
\begin{bmatrix}
\delta T_{\mathbf{k},\omega} \\[2mm]
\delta c_{\mathbf{k},\omega}
\end{bmatrix}
$$

$$
=
\begin{bmatrix}
-\mathbf{k}\cdot\mathbf{f}_{\mathbf{k},\omega} + \dfrac{i\mathbf{k}\cdot\mathbf{S}_{\mathbf{k},\omega}\cdot(1-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\nabla c}{\rho(i\omega + k^2\nu_t)} \\[5mm]
i\rho k_T\left[\dfrac{\partial\mu}{\partial c}\right]_{p,T}\mathbf{k}\cdot\mathbf{f}_{\mathbf{k},\omega} - i\mathbf{k}\cdot\mathbf{g}_{\mathbf{k},\omega} - \dfrac{i\mathbf{k}\cdot\mathbf{S}_{\mathbf{k},\omega}\cdot(1-\hat{\mathbf{k}}\hat{\mathbf{k}})}{(i\omega + k^2\nu_t)}\cdot\left[k_T\left[\dfrac{\partial\mu}{\partial c}\right]_{p,T}\nabla c - C_p\nabla T\right]
\end{bmatrix} . \qquad (18)
$$

In order to solve this equation for correlations between temperature and concentration fluctuations, one needs relations for the correlations in the random forces. From Ref. 9

$$
\langle f^i_{\mathbf{k},\omega} f^{j*}_{\mathbf{k}',\omega'}\rangle = \frac{k_B T D}{8\pi^4\rho\left[\dfrac{\partial\mu}{\partial c}\right]_{p,T}}\delta_{ij}\delta(\mathbf{k}-\mathbf{k}')\delta(\omega-\omega') ,
$$

$$
\qquad\qquad\qquad\qquad\qquad\qquad (19)
$$

$$
\langle g^i_{\mathbf{k},\omega} g^{j*}_{\mathbf{k}',\omega'}\rangle = \frac{1}{8\pi^4}k_B T^2\left[\frac{\rho D k_T^2}{T}\left[\frac{\partial\mu}{\partial c}\right]_{p,T} + \rho C_p D_T\right]
$$

$$
\times\delta_{ij}\delta(\mathbf{k}-\mathbf{k}')\delta(\omega-\omega') , \qquad (20)
$$

$$
\langle f^i_{\mathbf{k},\omega} g^{j*}_{\mathbf{k}',\omega'}\rangle = \frac{1}{8\pi^4}k_B T D k_T\delta_{ij}\delta(\mathbf{k}-\mathbf{k}')\delta(\omega-\omega') , \qquad (21)
$$

$$
\langle S^{ij}_{\mathbf{k},\omega} S^{lm*}_{\mathbf{k}',\omega'}\rangle = \frac{1}{8\pi^4}k_B T[\eta(\delta_{il}\delta_{jm} + \delta_{im}\delta_{jl})
$$

$$
+ (\zeta - \tfrac{2}{3}\eta)\delta_{ij}\delta_{lm}]
$$

$$
\times\delta(\mathbf{k}-\mathbf{k}')\delta(\omega-\omega') . \qquad (22)
$$

The random fluxes $\mathbf{f}$ and $\mathbf{g}$ are uncorrelated with the random stress tensor $\mathbf{S}$, that is,

$$
\langle f^i_{\mathbf{k},\omega} S^{lm*}_{\mathbf{k}',\omega'}\rangle = \langle g^i_{\mathbf{k},\omega} S^{lm*}_{\mathbf{k}',\omega'}\rangle = 0 . \qquad (23)
$$

Using Eqs. (19)–(21), one can readily show that

$$
\langle(\hat{\mathbf{k}}\cdot\mathbf{X}_{\mathbf{k},\omega})(\hat{\mathbf{k}}\cdot\mathbf{Y}^*_{\mathbf{k},\omega})\rangle = \langle X^i_{\mathbf{k},\omega}Y^{i*}_{\mathbf{k},\omega}\rangle , \qquad (24)
$$

where $\mathbf{X},\mathbf{Y} = \mathbf{f}$ or $\mathbf{g}$, while using Eq. (22) one can show that

$$
\langle[\hat{\mathbf{k}}\cdot\mathbf{S}_{\mathbf{k},\omega}\cdot(1-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\nabla U][\hat{\mathbf{k}}\cdot\mathbf{S}^*_{\mathbf{k},\omega}\cdot(1-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\nabla V]\rangle
$$

$$
= \frac{1}{8\pi^4}k_B T(\nabla U\cdot\nabla V)\rho\nu_t , \qquad (25)
$$

where ∇U, $\nabla V = \nabla T$ or ∇c.

From the matrix equation (18), the steady-state condition (7), and the correlation properties of the random forces, Eqs. (23)–(25), it is a tedious but nevertheless straightforward process to calculate the correlations in the temperature and concentration, which contribute to the Rayleigh line. For the correlations in the temperature one finds

$$
\langle\delta T_{\mathbf{k},\omega}\delta T^*_{\mathbf{k},\omega}\rangle|\Delta|^2 = \frac{1}{8\pi^4}k_B T^2\rho C_p k^2
$$

$$
\times[\omega^2(\mathcal{D} - D + D_T) + k^4 D^2 D_T]
$$

$$
+ \frac{1}{8\pi^4}\frac{k_B T k^2\nu_t\rho C_p^2}{(\omega^2 + k^4\nu_t^2)}|\nabla T|^2
$$

$$
\times(\omega^2 + k^4\mathcal{D}^2) . \qquad (26)
$$

Here Δ is the determinant of the 2×2 matrix appearing in Eq. (18). Therefore we find that

$$
|\Delta|^2 = \rho^2 C_p^2(\omega^2 + z_+^2)(\omega^2 + z_-^2) , \qquad (27)
$$

where the roots z_+ and z_- are given by

$$
\left.\begin{array}{c} z_+ \\ z_- \end{array}\right\} = \frac{k^2}{2}(D_T + \mathcal{D}) \pm \frac{k^2}{2}[(D_T + \mathcal{D})^2 - 4D_T D]^{1/2} \qquad (28)
$$

and

$$
\mathcal{D} = D\left[1 + \frac{k_T^2}{TC_p}\left[\frac{\partial\mu}{\partial c}\right]_{p,T}\right] . \qquad (29)
$$

Similarly, the correlation in the concentration fluctuations is given by

$$
\langle\delta c_{\mathbf{k},\omega}\delta c^*_{\mathbf{k},\omega}\rangle|\Delta|^2 = \frac{1}{8\pi^4}k_B T\rho C_p^2 k^2 D\left[\frac{\partial c}{\partial\mu}\right]_{p,T}
$$

$$
\times[\omega^2 + k^2 D_T(\mathcal{D} - D + D_T)]
$$

$$
+ \frac{1}{8\pi^4}\frac{k_B T k^2\nu_t\rho C_p^2}{(\omega^2 + k^4\nu_t^2)}|\nabla c|^2
$$

$$
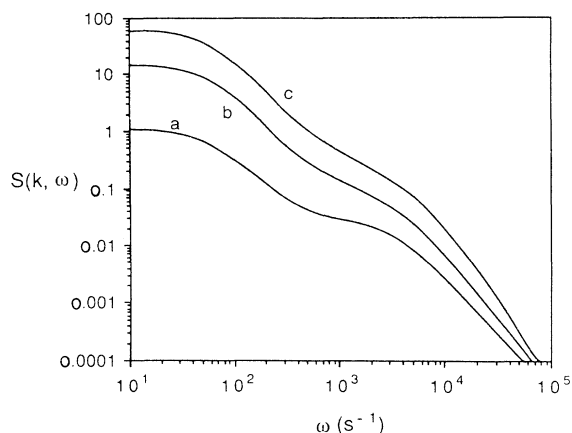\times[\omega^2 + k^2(D_T + \mathcal{D})^2] , \qquad (30)
$$

FIG. 1. Normalized dynamic structure factor for the binary liquid mixture benzene plus carbon tetrachloride for a mole fraction of 0.5 and scattering vector $k = 2000$ cm^{-1} in the configuration where the scattering vector is perpendicular to the temperature gradient. (a) Equilibrium structure factor normalized to 1 at $\omega = 0$. Nonequilibrium structure factor with (b) $\nabla T = 50$ K/cm and (c) $\nabla T = 100$ K/cm.

while the correlation between temperature and concentration fluctuations is given by

$$[\langle \delta T_{k,\omega} \delta c^*_{k,\omega} \rangle + \langle \delta T^*_{k,\omega} \delta c_{k,\omega} \rangle]|\Delta|^2$$

$$= \frac{1}{4\pi^4} k_B T \rho C_p k^2 D k_T (\omega^2 - k^4 D D_T)$$

$$+ \frac{1}{4\pi^4} \frac{k_B T k^2 v_t \rho C_p^2}{(\omega^2 + k^4 v_t^2)} (\nabla T \cdot \nabla c)[\omega^2 + k^4 \mathcal{D}(D_T + \mathcal{D})] .$$

$$(31)$$

Finally, the dynamic structure factor for the Rayleigh line, which determines the light scattering properties of the medium, is obtained from the usual formula

$$S(k,\omega) = \left[\frac{\partial \epsilon}{\partial T} \right]^2_{p,c} \langle \delta T_{k,\omega} \delta T^*_{k,\omega} \rangle$$

$$+ \left[\frac{\partial \epsilon}{\partial c} \right]^2_{p,T} \langle \delta c_{k,\omega} \delta c^*_{k,\omega} \rangle$$

$$+ \left[\frac{\partial \epsilon}{\partial c} \right]_{p,T} \left[\frac{\partial \epsilon}{\partial T} \right]_{p,c} [\langle \delta T_{k,\omega} \delta c^*_{k,\omega} \rangle$$

$$+ \langle \delta T^*_{k,\omega} \delta c_{k,\omega} \rangle] , \quad (32)$$

where the temperature and concentration correlation functions are given in Eqs. (26), (30), and (31). In the absence of any gradients, the dynamic structure factor $S(k,\omega)$ reduces to the equilibrium form for a binary liquid mixture;[9,12] while for a one-component system in a temperature gradient we retrieve the structure factor determined previously for a pure liquid in a temperature gradient.[3,4]

In Fig. 1 we plot the structure factor, Eq. (32), for a 0.5-mole-fraction liquid mixture of benzene and carbon tetrachloride at a scattering vector $k = 2000$ cm^{-1}. The equilibrium dynamic structure factor (curve a) has been normalized to 1 at $\omega = 0$. For this liquid mixture the scattering is dominated by concentration fluctuations. Curves b and c in Fig. 1 show the enhancement to the structure factor for temperature gradients of 50 and 100 K/cm, respectively, where we have used the thermal diffusion ratio from Tyrrell[13] in order to calculate the corresponding concentration gradient. We have plotted the structure factor on a log-log graph to demonstrate that the temperature-temperature correlations at large frequencies ($\omega \sim 10^5$ s^{-1}) are also enhanced in a temperature gradient as expected, although for this liquid mixture not to the same extent as the concentration-concentration correlations.

III. CONCLUSION

In this paper we have solved for the Rayleigh line of a noncritical binary liquid mixture in the presence of a temperature gradient using fluctuating hydrodynamics. The temperature gradient induces a concentration gradient in the liquid mixture—the magnitude and direction of this concentration gradient is determined by the thermal diffusion ratio. The temperature-temperature, concentration-concentration, and temperature-concentration correlations, which contribute to the Rayleigh line, are calculated for scattering vectors perpendicular to the gradient using a uniform pressure approximation. The theory is applied to the specific liquid mixture benzene and carbon tetrachloride for a mole fraction of 0.5, where an enormous enhancement to the Rayleigh line was observed from concentration fluctuations—this is the simplest case to study experimentally, that is, where the concentration fluctuations dominate the temperature fluctuations. A slightly more interesting, but necessarily more complex, situation is where the temperature and concentration contributions to the Rayleigh line are of similar magnitudes; here the cross-coupling gradient terms will become important. The experimental system we are envisaging is either a pair of index matched liquids or a suitably chosen dilute solution. The whole spectrum with its various contributions to the dynamic structure factor should be separable using photon correlation spectroscopy because the decay times between T-T and c-c fluctuations differ, in general, by two orders of magnitude. Quantitative comparison with theory will require an accurate determination of the thermal diffusion ratio.

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