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Light-scattering measurements of nonequilibrium fluctuations in a liquid mixture

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We report results of small-angle Rayleigh-scattering experiments performed in an equimolar liquid mixture of toluene and *n*-hexane that is brought out of thermal equilibrium by the imposition of a stationary temperature gradient ∇T perpendicular to the scattering wave vector. The experiments demonstrate the presence of long-range nonequilibrium fluctuations in temperature, concentration, and momentum and confirm that the strength of these nonequilibrium fluctuations varies with $(\nabla T)^2/k^4$, where k is the wave number of the fluctuations. It is suggested that nonequilibrium Rayleigh scattering may provide an alternative technique for measuring Soret coefficients of liquid mixtures.

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I. INTRODUCTION

The theory of fluctuations in fluids that are in macroscopic thermal equilibrium is well established. Fluctuations in density that occur on hydrodynamic length and time scales can be probed experimentally by light scattering. The light-scattering spectrum of one-component fluids contains a central Rayleigh line, unshifted in frequency, resulting from fluctuations in entropy or temperature and whose decay rate is determined by the thermal diffusivity [1,2]. With the addition of a second component, local fluctuations in composition give rise to a second Rayleigh component, whose decay rate is determined by the mass diffusivity [3,4]. Measuring the linewidths of these Rayleigh components provides a useful method for determining thermal and mass diffusivities [5].

More recently, the theory of fluctuations has been extended to fluids in nonequilibrium steady states, as, e.g., reviewed by Schmitz [6]. Specifically, when a fluid is subjected to a stationary temperature gradient, long-range nonequilibrium fluctuations are present as originally found from mode-coupling theory [7] and subsequently from fluctuating hydrodynamics [8–11]. These nonequilibrium fluctuations arise from a coupling between microscopic velocity fluctuations and the macroscopic temperature gradient. The Rayleigh-line intensity is enhanced by the nonequilibrium thermal fluctuations and modified by a contribution from nonequilibrium viscous fluctuations. These theoretical predictions have been verified both qualitatively [12] and quantitatively [13,14] in a series of recent light-scattering experiments with liquid toluene.

In the present paper, we report results of Rayleigh-scattering experiments in a liquid mixture of toluene and *n*-hexane in the presence of a stationary temperature gradient. In anticipation of our experiments, the theory of nonequilibrium fluctuations was extended to fluid mixtures by Law and Nieuwoudt [15,16]. It is well known that a macroscopic temperature gradient ∇T induces in a fluid mixture a macroscopic concentration gradient ∇c [17,18]. Hence, the microscopic velocity fluctuations not only couple with the temperature gradient ∇T, but also with the concentration gradient ∇c. As a consequence, the Rayleigh spectrum will be modified by the presence of nonequilibrium thermal, viscous, and concentration fluctuations. All these nonequilibrium fluctuations are predicted to be proportional to $(\nabla T)^2$ and inversely proportional to the fourth power of the wave number k of the fluctuations. We have indeed observed these nonequilibrium fluctuations and we shall demonstrate that the experimental results are consistent with the theoretical predictions.

II. THEORY

The intensity of light scattered by fluctuations with wave vector $\mathbf{k}$ and frequency ω is proportional to the correlation function $\langle \delta n_{\mathbf{k},\omega} \delta n^*_{\mathbf{k},\omega} \rangle$, which is a measure of the fluctuations δn in the refractive index n. This correlation function can, in turn, be related to the correlation functions of the fluctuations δT and δc in the local temperature T and the local concentration c, so that the Rayleigh component of the scattered-light intensity of a liquid mixture is proportional to [4]

$$\langle \delta n_{\mathbf{k},\omega} \delta n^*_{\mathbf{k},\omega} \rangle = \left[\frac{\partial n}{\partial T}\right]^2_{p,c} \langle \delta T_{\mathbf{k},\omega} \delta T^*_{\mathbf{k},\omega} \rangle + \left[\frac{\partial n}{\partial c}\right]^2_{p,T} \langle \delta c_{\mathbf{k},\omega} \delta c^*_{\mathbf{k},\omega} \rangle + \left[\frac{\partial n}{\partial T}\right]_{p,c} \left[\frac{\partial n}{\partial c}\right]_{p,T} [\langle \delta T_{\mathbf{k},\omega} \delta c^*_{\mathbf{k},\omega} \rangle + \langle \delta T^*_{\mathbf{k},\omega} \delta c_{\mathbf{k},\omega} \rangle] , \tag{2.1}$$

where the derivatives of the refractive index with respect to T and c are to be taken at constant pressure p. In Eq. (2.1), we have neglected any contributions from pressure fluctuations, since they only contribute to the propagating Brillouin lines and not to the diffusive Rayleigh lines [15,16].

A concentration gradient develops in a liquid mixture that is subjected to a temperature gradient ∇T [17,18]. The magnitude of this concentration gradient ∇c is proportional to the Soret coefficient S_T, which is defined through the phenomenological relation

$$\nabla c = -\frac{k_T}{T}\nabla T = -S_T c(1-c)\nabla T \ , \qquad (2.2)$$

where k_T is the thermal-diffusion ratio, and c is the mass fraction of the heavier component 1, which in the present case will be toluene. It will be convenient to define

$$R_n \equiv -2c(1-c)\frac{\left[\dfrac{\partial n}{\partial c}\right]_{p,T}}{\left[\dfrac{\partial n}{\partial T}\right]_{p,c}} \ , \qquad (2.3)$$

so that $S_T R_n$ is a dimensionless number representing the ratio of the refractive-index gradients resulting from the concentration and temperature gradients.

The correlation functions appearing in (2.1) have been evaluated by Law and Nieuwoudt [15,16] for a liquid mixture subjected to a stationary temperature gradient. The light-scattering correlation function $C(\mathbf{k},t)$ is then obtained as the temporal Fourier transform of $\langle \delta n_{\mathbf{k},\omega}\delta n^*_{\mathbf{k},\omega}\rangle$ given by (2.1). The exact expression obtained by Law and Nieuwoudt is rather complicated, but, as justified in the Appendix, for the liquid mixture to be investigated it can be simplified to the sum of a positive heat-mode contribution, a negative viscous-mode contribution, and a positive concentration-mode contribution:

$$\begin{aligned} C(\mathbf{k},t) = C_B\{1 + C_0[(1+A_T)\exp(-D_T k^2 t) \\ - A_\nu \exp(-\nu k^2 t) \\ + \mathcal{R}(1+A_c)\exp(-Dk^2 t)]\} \ , \end{aligned} \qquad (2.4)$$

where C_B is an experimental background contribution that is always present in light-scattering experiments [13,14], while C_0 represents the strength of the heat-mode contribution in the absence of a temperature gradient. The decay rates of the three Rayleigh components are proportional to the thermal diffusivity D_T, the kinematic viscosity ν and the binary mass-diffusion coefficient D. For a typical liquid mixture like a mixture of toluene and n-hexane, the simplified expression (2.4) for the light-scattering correlation function is estimated to yield amplitudes accurate within a few percent, as discussed in the Appendix. The coefficient $\mathcal{R}$ in (2.4) determines the ratio of the scattering intensity from the concentration-mode and heat-mode fluctuations in the absence of a temperature gradient and is given by [19]

$$\mathcal{R} = \left[\frac{\partial \mu}{\partial c}\right]^{-1}_{p,T} \frac{c_{p,c}}{T} \frac{\left[\dfrac{\partial n}{\partial c}\right]^2_{p,T}}{\left[\dfrac{\partial n}{\partial T}\right]^2_{p,c}} \ . \qquad (2.5)$$

Here $c_{p,c}$ is the isobaric specific heat at constant concentration and $\mu = \mu_1 - \mu_2$, where μ_1 and μ_2 are the chemical potentials per unit mass of the two components of the mixture. The amplitudes A_T, A_ν, and A_c in (2.4) represent the relative contributions from the nonequilibrium fluctuations. These amplitudes are given by

$$\begin{aligned} A_T = A_T^* \frac{(\hat{\mathbf{k}}\times\nabla T)^2}{k^4} \ , \quad A_\nu = A_\nu^* \frac{(\hat{\mathbf{k}}\times\nabla T)^2}{k^4} \ , \\ A_c = A_c^* \frac{(\hat{\mathbf{k}}\times\nabla T)^2}{k^4} \ , \end{aligned} \qquad (2.6)$$

where $\hat{\mathbf{k}}$ is the unit vector in the direction of $\mathbf{k}$, while the coefficients A_T^*, A_ν^*, and A_c^* are related to the local thermophysical properties of the mixture by

$$A_T^* = \left[\frac{c_{p,c}}{T(\nu^2 - D_T^2)}\right]\left[\frac{\nu}{D_T}\right]\{1 + S_T R_n(1 - D/D_T)\} \ , \qquad (2.7)$$

$$A_\nu^* = \left[\frac{c_{p,c}}{T(\nu^2 - D_T^2)}\right]\{1 + S_T R_n/2\}^2 \ , \qquad (2.8)$$

$$\begin{aligned} A_c^* = \left[\frac{R_n^2}{4\mathcal{R}}\right]\left[\frac{c_{p,c}}{T(\nu^2 - D^2)}\right]\left[\frac{\nu}{D}\right]S_T^2 \\ \times\{1 + 2D/D_T[1 + 2/(S_T R_n)]\} \ . \end{aligned} \qquad (2.9)$$

The amplitudes A_T, A_ν, and A_c of the nonequilibrium fluctuations vanish when $\nabla T = 0$. For $\nabla T \neq 0$, they reach their maximum values when the scattering wave vector $\mathbf{k}$ is perpendicular to ∇T; this is the configuration adopted in our experiments, so that $|\hat{\mathbf{k}}\times\nabla T| = |\nabla T|$. In the limit $c \to 0$ and, hence, $S_T \to 0$, $C(\mathbf{k},t)$ as given by (2.4) reduces to the light-scattering correlation function previously investigated for a one-component liquid in the presence of a temperature gradient [13,14]. The amplitudes A_T, A_ν, and A_c of all three nonequilibrium fluctuations are proportional to $(\nabla T)^2/k^4$.

The light-scattering correlation function $C(\mathbf{k},t)$ in the form given by (2.4) represents a sum of all hydrodynamic correlation functions appearing in (2.1). To gain some insight into the complicated structure of the expressions (2.7)–(2.9) for the amplitudes of the nonequilibrium fluctuations, we first note, as one might expect, that heat-mode and viscous-mode contributions originate from the temperature-temperature correlation function $\langle \delta T_{\mathbf{k},\omega}\delta T^*_{\mathbf{k},\omega}\rangle$, and concentration-mode contributions from the concentration-concentration correlation function $\langle \delta c_{\mathbf{k},\omega}\delta c^*_{\mathbf{k},\omega}\rangle$. The nonequilibrium amplitudes resultant from these two correlation functions are represented by the term of value unity in the curly brackets in Eqs. (2.7)–(2.9). It turns out, however, that important contributions also arise from the cross-correlation functions $\langle \delta c_{\mathbf{k},\omega} \delta T^*_{\mathbf{k},\omega} \rangle$ and $\langle \delta T_{\mathbf{k},\omega} \delta c^*_{\mathbf{k},\omega} \rangle$ in Eq. (2.1). They lead to the terms inside the curly brackets in Eqs. (2.7)–(2.9) that involve the product $S_T R_n$. From (2.7) and (2.8), we see that the nonequilibrium heat-mode and viscous-mode fluctuations will exhibit, for liquid mixtures with $S_T \neq 0$, an additional enhancement over the values previously found for a pure liquid. In addition, nonequilibrium concentration fluctuations with amplitude A_c should appear, which are absent in pure liquids. It was the purpose of the present investigation to observe these effects experimentally.

III. EXPERIMENT

The experimental arrangement and sample cell are identical to those used in our previous Rayleigh-scattering measurements of pure toluene in the presence of a temperature gradient [13,14]. To avoid any convection, the liquid layer is heated from above. The incident laser-light beam is in the direction antiparallel to the temperature gradient and the scattering wave vector $\mathbf{k}$ is located in the horizontal plane perpendicular to the temperature gradient. The light-scattering correlation function $C(\mathbf{k},t)$ is obtained by heterodyning the scattered light with residual stray light. Here we discuss only those aspects of the experiment that pertain specifically to measurements with a liquid mixture.

In practice, $D_T/D \approx 30$, so that for longer delay times the photon-correlation function is only determined by the concentration fluctuations. The heat-mode and viscous-mode contributions are then studied by observing the photon-correlation function at shorter delay times. These heat-and viscous-mode contributions are investigated simultaneously, since $\nu/D_T \approx 6$. To analyze the longer-time and shorter-time correlation-function data, we decompose the expression (2.4) for $C(\mathbf{k},t)$ into

$$C(\mathbf{k},t) = C_{T,\nu}(\mathbf{k},t) + C_c(\mathbf{k},t) , \tag{3.1}$$

with

$$C_{T\nu}(\mathbf{k},t) = C_{B,T\nu}\{1 + C_{0,T\nu}[(1+A_T)\exp(-D_T k^2 t) - A_\nu \exp(-\nu k^2 t)]\} , \tag{3.2}$$

and

$$C_c(\mathbf{k},t) = C_{B,c}[1 + C_{0,c}(1+A_c)\exp(-Dk^2 t)] . \tag{3.3}$$

The subscripts $T\nu$ and c refer to the heat-viscous and concentration-mode contributions, respectively, and the equilibrium ratio $\mathcal{R}$ of the strength of the concentration fluctuations and the temperature fluctuations is

$$\mathcal{R} = \frac{C_{0,c}}{C_{0,T\nu}} . \tag{3.4}$$

When the correlator is set up to examine the slowly decaying concentration fluctuations, we eliminate any influence of the more quickly decaying temperature and viscous fluctuations by simply not analyzing the information contained in the early time channels. When we subsequently investigate the temperature and viscous fluctuations by measuring the photon-correlation function at earlier times, we need to correct for the contribution from the concentration fluctuations. This is illustrated in Fig. 1, where we show typical experimental photon-correlation data as a function of time with and without the contribution from the concentration fluctuations obtained for the liquid mixture with $\nabla T = 0$. The correction for the contribution from the concentration fluctuations is obtained by the following procedure. We first determine the correlation function $C_c(\mathbf{k},t)$ arising from the concentration fluctuations by measuring the photon-correlation function at a long-time scale. We then sample with the correlator the photon-correlation functions $C(\mathbf{k},t)$ at a short-time scale relevant for the temperature and viscous fluctuations and then take the difference

$$C_{T,\nu}(\mathbf{k},t) = C(\mathbf{k},t) - C_c(\mathbf{k},t) . \tag{3.5}$$

In principle, the wave number $\mathbf{k}$ can be determined from the scattering angle θ through the Bragg condition $k = 4\pi(n/\lambda)\sin(\theta/2)$, where λ is the wavelength of the laser light. However, as in our previous experiments with pure toluene [13,14], an alternate and more accurate procedure is to deduce k from the experimental correlation function obtained when the liquid sample is still in thermal equilibrium. For $\nabla T = 0$, the expressions (3.2) and (3.3) reduct to

$$C_{T\nu}(\mathbf{k},t) = C_{B,T\nu}[1 + C_{0,T\nu}\exp(-D_T k^2 t)] , \tag{3.6}$$

$$C_c(\mathbf{k},t) = C_{B,c}[1 + C_{0,c}\exp(-Dk^2 t)] . \tag{3.7}$$

Since we use a liquid mixture with a known mass diffusivity D, fitting the experimental long-time correla-

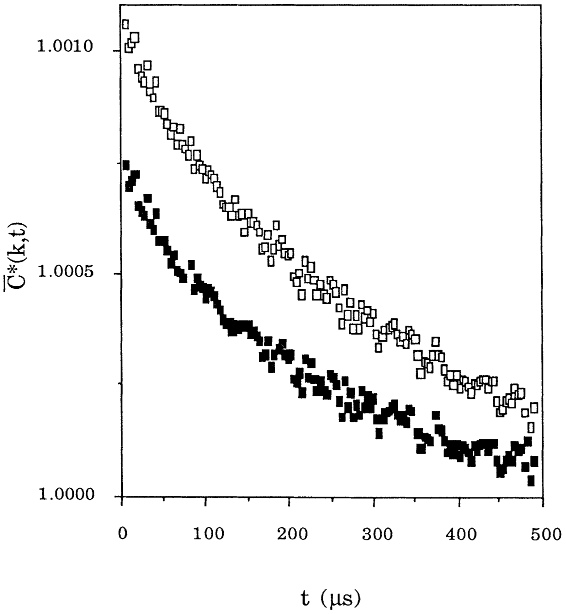

FIG. 1. Normalized experimental photon-correlation functions $\bar{C}^*(\mathbf{k},t) = \bar{C}(\mathbf{k},t)/C_B$ obtained for an equimolar mixture of toluene and n-hexane in thermal equilibrium ($\nabla T = \mathbf{0}$) at $k = 2341\ \text{cm}^{-1}$ without (□) and with (■) corrections for the concentration fluctuations.

tion function $C_c(\mathbf{k},t)$ obtained with $\nabla T=0$ yields k^2 in addition to $C_{B,c}$ and $C_{0,c}$. From the experimental correlation-function data obtained in thermal equilibrium at shorter times, we also find $C_{B,T\nu}$ and $C_{0,T\nu}$ and, hence, the ratio $\mathcal{R}=C_{0,c}/C_{0,T\nu}$.

As discussed in our previous publications [13,14], a complication arises, because the measurements are not obtained at a single value of the wave number k, but over a small range of k values due to the focusing of the beam in the sample and the finite size of about 0.1° of the collection angle. This effect is usually negligible in light-scattering experiments, but becomes significant here, first because of the small scattering angles needed for the observation of the nonequilibrium fluctuations, and second because the intensity of these nonequilibrium fluctuations varies with k^4. We account for this effect by convoluting the ideal correlation function (2.4) with a Gaussian beam profile [13,14,20]:

$$\bar{C}(k,t)=\frac{1}{Z}\int_{k-3\delta}^{k+3\delta}dk'\,C(k',t)\exp\left[-\frac{(k'-k)^2}{2\delta^2}\right] \qquad (3.8)$$

with

$$Z=\delta\sqrt{2\pi}\,\Phi(3\sqrt{2})\ , \qquad (3.9)$$

where k is now the average wave number and Φ the error function, while δ is a measure of the spread of experimental wave numbers, which is related to the collection-pinhole size. Hence the experimental correlation data are fit to (3.8), with Eqs. (3.1)–(3.3) substituted for $C(\mathbf{k},t)$. In the present experiments, we continued to use the same optical arrangement as in our most recent experiments with pure toluene, for which $\delta=140\ \mathrm{cm}^{-1}$ [14].

Typical normalized experimental correlation functions $\bar{C}^*(\mathbf{k},t)=\bar{C}(\mathbf{k},t)/C_B$ obtained for an equimolar mixture of toluene and n-hexane at $k=2341\ \mathrm{cm}^{-1}$ are shown in Fig. 2. The data labeled E correspond to the thermal-equilibrium state with $\nabla T=0$, and the data labeled N correspond to a nonequilibrium state with $|\nabla T|=63.3$ K/cm. The concentration-fluctuation data in Fig. 2(a) decay exponentially with time in accordance with Eq. (3.3). The nonequilibrium (N) correlation-function data associated with the thermal-viscous fluctuations in Fig. 2(b) show a deviation from a simple exponential decay at very short times because of the negative contribution from the viscous fluctuations similar to the behavior previously observed in a one-component liquid [13,14].

The selection of a liquid mixture for the experiment was based on the following considerations. We have shown previously that nonequilibrium fluctuations could readily be observed in liquid toluene, for which excellent agreement between theory and experiment was obtained [13,14]. Hence we preferred to continue that work by selecting a mixture with toluene as one of the liquid components. In order to compare the experimental results with the theoretical predictions, we need reliable values of the relevant thermophysical properties. Of particular importance is accurate information of the binary mass-diffusion coefficient D, since our experimental determination of the wave number k depends on its value. Furthermore, a large difference in refractive indices is necessary in order for the concentration fluctuations to be readily observable. For these reasons, we selected a liquid mixture of toluene and n-hexane. One would also like to choose a mixture with a large positive Soret coefficient S_T, but experimental information for the Soret coefficients of liquid mixtures is limited and frequently of very low accuracy [17]. We shall return to a discussion of the Soret effect in the following section.

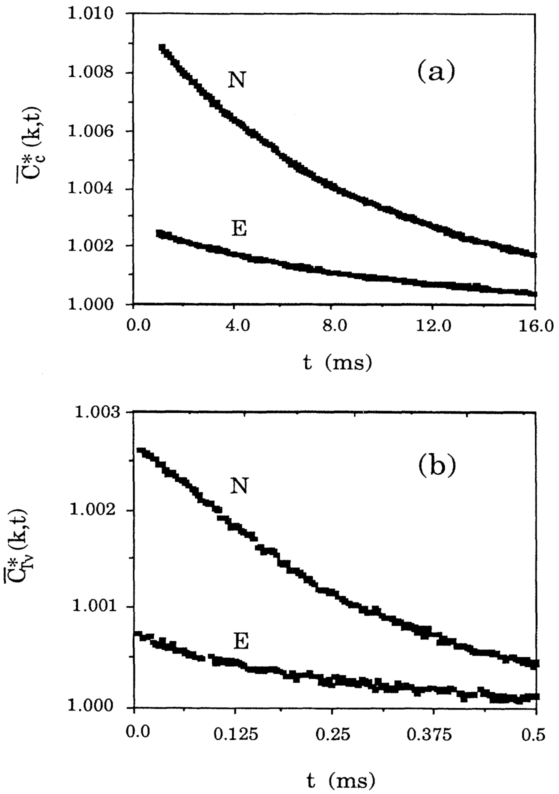

FIG. 2. Normalized experimental photon-correlation functions $\bar{C}_c^*(\mathbf{k},t)=\bar{C}_c(\mathbf{k},t)/C_{B,c}$ and $\overline{C_{T\nu}}^*(\mathbf{k},t)=\overline{C_{T\nu}}(\mathbf{k},t)/C_{B,T\nu}$ associated with the concentration fluctuations (a) and the temperature and viscous fluctuations (b) obtained for an equimolar mixture of toluene and n-hexane at $k=2341\ \mathrm{cm}^{-1}$. The data labeled E were obtained with $\nabla T=0$ and the data labeled N with $\nabla T=63.3$ K/cm. The data corresponding to the very early correlator sample times in (a), heavily influenced by the thermal fluctuations, are not shown.

IV. EXPERIMENTAL RESULTS

We have measured the scattered Rayleigh light of an equimolar mixture of toluene and n-hexane as a function of ∇T at five scattering angles ranging from 0.47° to 0.86° and corresponding to the wave numbers $k=1613$, 1983, 2190, 2341, and 2946 cm^{-1}. At each scattering angle, we would start with the liquid mixture in homogeneous thermal equilibrium at 25 °C. Then various values of the temperature gradient were applied by increasing and decreasing the temperatures of the upper and lower plate of the optical cell symmetrically, so that all experimental re-

TABLE I. Thermophysical properties of an equimolar toluene plus *n*-hexane liquid mixture at 25 °C.

Property	Value
Mass diffusivity[a]	$D = 2.757\times10^{-5}$ cm^2 s^{-1}
Thermal conductivity[b,c]	$\kappa = 0.1262$ W m^{-1}K^{-1}
Density[a]	$\rho = 747.8$ kg m^{-3}
Isobaric specific heat[b,d]	$c_{p,c} = 1.978$ kJ kg^{-1}K^{-1}
Thermal diffusivity[b]	$D_T = \kappa/\rho c_{p,c} = 0.854\times10^{-3}$ cm^2 s^{-1}
Shear viscosity[a]	$\eta = 372$ μPa s
Kinematic viscosity	$\nu = \eta/\rho = 4.975\times10^{-3}$ cm^2 s^{-1}
Refractive index[e]	$n = 1.433$
Refractive index derivative[f]	$\left[\frac{\partial n}{\partial T}\right]_{p,c} = -5.497\times10^{-4}$ K^{-1}
Refractive index derivative[f]	$\left[\frac{\partial n}{\partial c}\right]_{p,T} = 0.1206$
Osmotic compressibility[g]	$\left[\frac{\partial c}{\partial \mu}\right]_{p,T} = 118.1\times10^{-3}$ J^{-1} g
Rayleigh-factor ratio	$\mathcal{R} = \left[\frac{\partial c}{\partial \mu}\right]_{p,T} \frac{c_{p,c}}{T} \frac{\left[\frac{\partial n}{\partial c}\right]_{p,T}^2}{\left[\frac{\partial n}{\partial T}\right]_{p,c}^2} = 3.79$

[a] Reference [21].
[b] Denotes average of individual pure-component values.
[c] Reference [22].
[d] References [23,24].
[e] Reference [25].
[f] Reference [26].
[g] Reference [19,21].

sults correspond to the same average temperature of 25 °C. The equimolar mixture corresponds to a toluene mass fraction $c = 0.517$. Values of the relevant thermophysical properties of this mixture, needed for the interpretation of the experiments, are presented in Table I. The derivatives of the refractive index n with respect to temperature and concentration were especially determined in our laboratory for this purpose [26]. In principle, a temperature gradient induces spatial variations of the thermophysical properties as a function of height in the liquid sample. In our previous work with toluene, we have demonstrated that effects of such spatial variations of the thermophysical properties on the scattered light are very small, even when temperature gradients as large as 220 K/cm are applied [14]. Since the Soret coefficient of liquid mixtures can be sensitive to temperature [27], we limited the maximum value of the applied temperature gradient in the present experiments to 122.5 K/cm.

For accurate Rayleigh-scattering measurements, it is imperative that the liquid sample be clean and free of any dirt. Since the liquid sample would invariably deteriorate somewhat in the course of time, especially after applying large temperature gradients, the optical cell was refilled with a clean, freshly filtered liquid sample every 24 h. The sample liquid came from a large (≈ 0.5 L) reservoir of equimolar toluene + *n*-hexane made by weighing out the individual components in the correct proportions.

The experimental concentration-fluctuation data $\overline{C}_c(\mathbf{k},t)$, obtained initially with $\nabla T = 0$, are fitted to Eq. (3.8) with Eq. (3.7) and with $D = 2.757\times10^{-5}$ cm^2 s^{-1} fixed at its known value [21] for the mixture. This procedure yields values of the coefficients $C_{B,c}$ and $C_{0,c}$ and of the scattering wave number k. We subsequently fit the experimental thermal-fluctuation data $\overline{C}_{T\nu}(\mathbf{k},t)$, obtained

TABLE II. Experimental results of the thermal diffusivity D_T, the Rayleigh-factor ratio $\mathcal{R}$, and the Soret coefficient S_T.

k (cm^{-1})	D_T[a] (10^{-3} cm^2 s^{-1})	$\mathcal{R}$[a]	S_T[b] (10^{-3} K^{-1})
1613	0.86±0.03	3.73±0.23	6.04±0.29
1983	0.83±0.03	4.02±0.23	6.23±0.24
2190	0.91±0.06	3.61±0.16	5.92±0.25
2341	0.83±0.03	3.84±0.15	6.09±0.23
2946	0.81±0.02	3.72±0.13	6.08±0.20
Average:	0.84±0.03	3.77±0.14	6.07±0.10

[a] From light-scattering measurements in thermal equilibrium.
[b] From intensity of nonequilibrium concentration fluctuations.

TABLE III. Nonequilibrium concentration-mode amplitude A_c.

∇T	k (cm^{-1})				
(K cm^{-1})	1613±85	1983±16	2190±38	2341±32	2946±11
44.72		2.48±0.14	1.43±0.02	1.08±0.03	0.53±0.02
63.25	9.3±0.4	3.90±0.20	3.61±0.04	2.30±0.06	0.97±0.04
77.46	16.2±0.3	6.96±0.12	5.29±0.05	3.75±0.07	1.47±0.02
89.44	20.7±0.6		6.32±0.20	4.80±0.21	1.98±0.06
100.00		11.1±0.2	7.44±0.06		2.22±0.08
122.47		17.6±0.3	10.50±0.20		3.74±0.08

with $\nabla T=0$, to Eq. (3.8) with Eq. (3.6), so as to obtain the coefficients $C_{B,T\nu}$ and $C_{0,T\nu}$ and the thermal diffusivity of the mixture. A normalization procedure, necessary to account for variations in the incident light intensity and of the local-oscillator strength, is applied to $C_{0,c}$ and $C_{0,T\nu}$ [13,28]. The Rayleigh-factor ratio $\mathcal{R}$ is readily found from (3.4) with the separately determined values of $C_{0,c}$ and $C_{0,T\nu}$. The experimental results thus obtained for the thermal diffusivity D_T and the Rayleigh-factor ratio $\mathcal{R}$ are presented in Table II. Our experimental values $D_T=(0.84\pm0.03)\times10^{-3}$ cm^2 s^{-1} and $\mathcal{R}=3.77\pm0.14$ are in good agreement with the values $D_T=0.85\times10^{-3}$ cm^{2}s^{-1} and $\mathcal{R}=3.79$ found from the literature, as shown in Table I.

We now turn our attention to the correlation-function data $\bar{C}_c(\mathbf{k},t)$ and $\bar{C}_{T\nu}(\mathbf{k},t)$, obtained in the presence of a temperature gradient and fitted to Eq. (3.8), with Eqs. (3.2) and (3.3) substituted for $C_c(\mathbf{k},t)$ and $C_{T\nu}(\mathbf{k},t)$. With the values of $C_{0,c}$ and $C_{0,T\nu}$ found from the scattering in thermal equilibrium, and with $\nu=4.975\times10^{-3}$ cm^2 s^{-1}, $D=2.757\times10^{-5}$ cm^2 s^{-1}, and $D_T=0.854\times10^{-3}$ cm^2 s^{-1} fixed at their known values for an equimolar mixture of toluene and n-hexane [21], only the background contributions $C_{B,c}$ and $C_{B,T\nu}$ and the amplitudes A_c, A_T, and A_ν of the nonequilibrium fluctuations are treated as adjustable coefficients. In all cases, the fits yielded standard χ^2 values close to unity, confirming that the experimentally observed correlation functions indeed decay with the three relaxation times associated with the heat-mode, viscous-mode and concentration-mode fluctuations.

The experimental results obtained for the amplitudes A_c, A_T, and A_ν are presented in Tables III–V. The errors quoted in these tables represent standard deviations when the results from the fits are averaged over four to six individual correlation-function measurements taken with correlator sample times of ≈ 3 μs for the heat-viscous modes, and ≈ 90 μs for the concentration mode. Only data are included for which no sign of convection was observed. An attempt was made to measure the light scattering for each angle at the same ten values of the temperature gradient ∇T. Because of slight variations, of the order 0.1 K, in the temperature of the lower plate, sometimes a small correction of up to a few percent was needed to convert the measurements to the desired nominal value of ∇T.

The amplitude A_c represents the strength of the nonequilibrium concentration fluctuations relative to the intensity of the concentration fluctuations in thermal equilibrium. Similarly, the amplitudes A_T and A_ν represent the strength of the nonequilibrium thermal and viscous fluctuations relative to the intensity of the thermal fluctuations in thermal equilibrium. From Eq. (2.6), we note that the amplitudes should be proportional to $(\nabla T)^2/k^4$. The experimental amplitudes A_c, A_T, and A_ν are plotted as a function of $(\nabla T)^2/k^4$ in Fig. 3 for the smaller values of ∇T and in Fig. 4 for the larger values of ∇T. The experimentally observed intensities of the nonequilibrium fluctuations indeed do vary with $(\nabla T)^2/k^4$.

The values of the coefficients $A_c^*=A_c k^4/(\nabla T)^2$, $A_T^*=A_T k^4/(\nabla T)^2$, $A_\nu^*=A_\nu k^4/(\nabla T)^2$ deduced from our experimental data for each wave number k are presented in Table VI, and we find

$$(A_c^*)_{\text{expt}}=(1.78\pm0.02)\times10^{10}\ \text{K}^{-2}\,\text{cm}^{-2}\ , \tag{4.1}$$

$$(A_T^*)_{\text{expt}}=(2.60\pm0.05)\times10^{10}\ \text{K}^{-2}\,\text{cm}^{-2}\ , \tag{4.2}$$

$$(A_\nu^*)_{\text{expt}}=(0.453\pm0.026)\times10^{10}\ \text{K}^{-2}\,\text{cm}^{-2}\ . \tag{4.3}$$

TABLE IV. Nonequilibrium heat-mode amplitude A_T.

∇T	k (cm^{-1})				
(K cm^{-1})	1613±85	1983±16	2190±38	2341±32	2946±11
44.72		3.80±0.11	1.64±0.06	1.60±0.03	0.61±0.02
63.25	12.4±0.5	6.12±0.23	4.51±0.24	3.66±0.04	1.40±0.08
77.46	23.9±1.0	10.7±0.2	7.11±0.07	5.59±0.18	2.00±0.03
89.44	31.0±1.0		9.27±0.10	7.05±0.67	2.67±0.06
100.00		16.7±0.4	10.7±0.4		3.21±0.08
122.47		26.1±0.3	15.0±0.5		5.16±0.17

TABLE V. Nonequilibrium viscous-mode amplitude A_v.

∇T	k (cm^{-1})				
(K cm^{-1})	1613±85	1983±16	2190±38	2341±32	2946±11
44.72		0.61±0.05	0.26±0.06	0.27±0.06	0.06±0.02
63.25	2.03±0.16	1.07±0.05	0.77±0.11	0.64±0.11	0.19±0.03
77.46	4.52±0.40	1.92±0.05	1.17±0.05	1.04±0.05	0.30±0.04
89.44	5.72±0.25		1.79±0.05	1.23±0.05	0.41±0.03
100.00		2.92±0.12	1.90±0.16		0.51±0.05
122.47		4.76±0.17	2.71±0.15		0.83±0.08

The theoretical predictions for these coefficients are given by Eqs. (2.7)–(2.9). As discussed in Sec. II, there are two mechanisms leading to the presence of long-range nonequilibrium fluctuations in a liquid mixture. First, there is a direct coupling between the velocity fluctuations $\delta \mathbf{v}$ and the temperature gradient ∇T, leading to the presence of nonequilibrium thermal and viscous fluctuations identical to those present in a one-component liquid [13,14]. The strength of these nonequilibrium fluctuations is given by Eqs. (2.7)–(2.9) with $S_T=0$, and is represented by the dashed lines in Figs. 3(b), 3(c), 4(b), and 4(c). In addition, there is a coupling between the velocity fluctuations $\delta \mathbf{v}$ and the concentration gradient ∇c induced by the temperature gradient, leading to the presence of nonequilibrium concentration fluctuations, shown in Figs. 3(a) and 4(a), as well as yielding an additional contribution to the nonequilibrium thermal and viscous fluctuations. To predict the strength of these nonequilibrium fluctuations, we need a reliable value of the Soret coefficient S_T. Ecenarro *et al.* have reported some experimental data for the thermal-diffusion factor α for toluene and n-hexane at 37.5 °C, obtained with a conventional

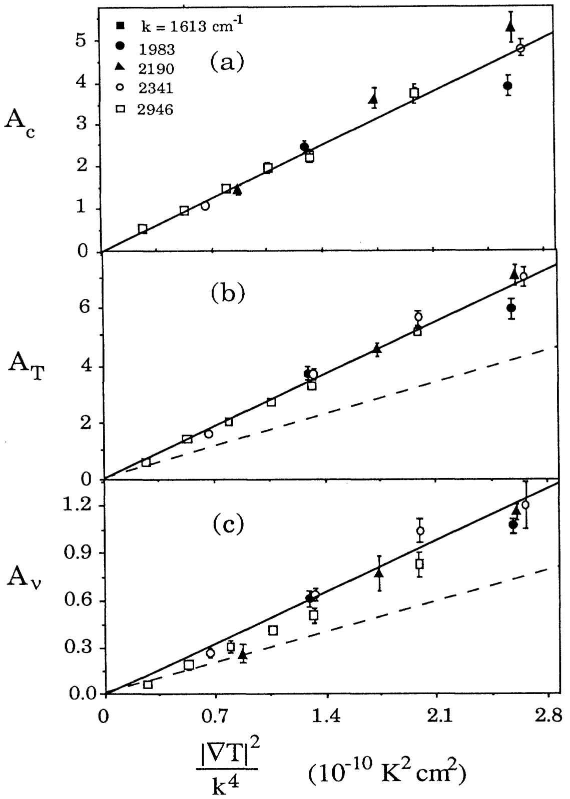

FIG. 3. Amplitudes A_c, A_T, and A_v as a function of $(\nabla T)^2/k^4$. The symbols indicate experimental data. The solid lines represent the linear variation with $(\nabla T)^2/k^4$ in accordance with fluctuating hydrodynamics. The dashed lines represent the contributions to the nonequilibrium temperature and viscous fluctuations when the effect of the induced concentration gradient is neglected ($S_T=0$).

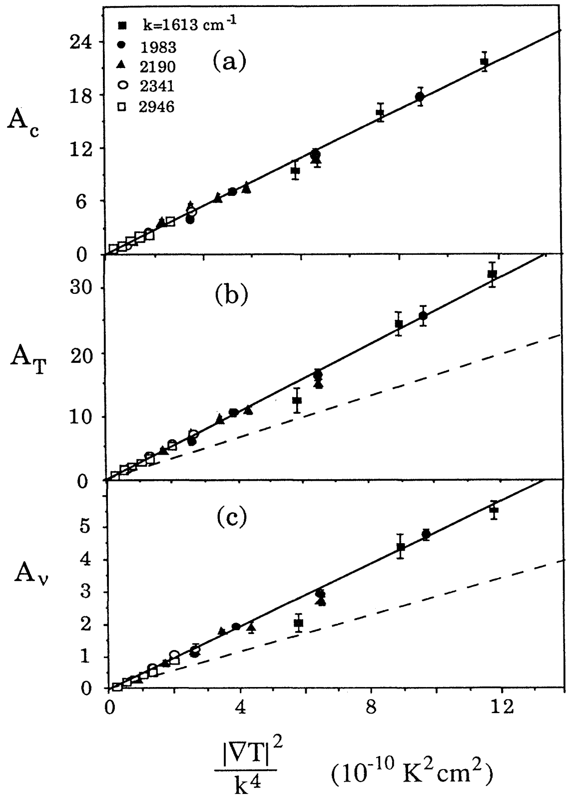

FIG. 4. Amplitudes A_c, A_T, and A_v as a function of $(\nabla T)^2/k^4$. The symbols indicate experimental data. The solid lines represent the linear variation with $(\nabla T)^2/k^4$ in accordance with fluctuating hydrodynamics. The dashed lines represent the contributions to the nonequilibrium temperature and viscous fluctuations when the effect of the induced concentration gradient is neglected ($S_T=0$).

TABLE VI. Reduced amplitudes A_c^*, A_T^*, and A_ν^* of the measured nonequilibrium fluctuations.

k (cm^{-1})	A_c^* ($10^{10}\ \mathrm{K}^{-2}\mathrm{cm}^{-2}$)	A_T^* ($10^{10}\ \mathrm{K}^{-2}\mathrm{cm}^{-2}$)	A_ν^* ($10^{10}\ \mathrm{K}^{-2}\mathrm{cm}^{-2}$)
1613	1.77±0.03	2.57±0.03	0.440±0.018
1983	1.77±0.02	2.60±0.03	0.464±0.010
2190	1.78±0.01	2.65±0.03	0.475±0.015
2341	1.77±0.02	2.65±0.03	0.473±0.020
2946	1.82±0.03	2.53±0.04	0.413±0.026
Average:	1.78±0.02	2.60±0.05	0.453±0.026

thermal-diffusion column [29], from which we deduce $S_T=+3.70\times10^{-3}\ \mathrm{K}^{-1}$. However, we find it difficult to assess the accuracy of this determination [18], nor is it clear how this result, obtained at a single temperature, can be extrapolated to 25 °C. For a definitive check of the theory of fluctuating hydrodynamics for the description of nonequilibrium fluctuations in a fluid mixture, it is desirable to have an accurate independent experimental determination of the Soret coefficient S_T, and we hope to perform such measurements in the future. However, in the mean time we assume the validity of the theory of fluctuating hydrodynamics and use the observed intensity A_c^* of the nonequilibrium concentration fluctuations to deduce the Soret coefficient in accordance with Eq. (2.9). The values thus obtained for the Soret coefficient are included in Table II, and we find

$$S_T=+(6.07\pm0.10)\times10^{-3}\ \mathrm{K}^{-1}\ . \tag{4.4}$$

The values of A_c corresponding to this Soret coefficient are represented by the solid lines in Figs. 3(a) and 4(a). With the values (4.4) of the Soret coefficient, we can now predict from Eqs. (2.7) and (2.8) the additional mixture contributions to the nonequilibrium thermal and viscous fluctuations. The values thus predicted for A_T and A_ν are represented by the solid lines in Figs. 3(b), 3(c), 4(b), and 4(c), which correspond to

$$(A_T^*)_{\mathrm{calc}}=2.63\times10^{10}\ \mathrm{K}^{-2}\mathrm{cm}^{-2}\ , \tag{4.5}$$

$$(A_\nu^*)_{\mathrm{calc}}=0.475\times10^{10}\ \mathrm{K}^{-2}\mathrm{cm}^{-2}\ . \tag{4.6}$$

On comparing the predicted values (4.5) and (4.6) with the experimental values (4.2) and (4.3), as well as from the information provided in Figs. 3 and 4, we conclude that our experimental results are fully consistent with the theoretical predictions for the nature of the nonequilibrium fluctuations in a liquid mixture.

V. CONCLUSIONS

In a liquid mixture in the presence of an externally imposed stationary temperature gradient, new types of nonequilibrium fluctuations, not present in pure liquids, appear as a result of a coupling between the velocity fluctuations and the concentration gradient induced by the temperature gradient. This coupling leads to the presence of nonequilibrium concentration fluctuations and also yields additional contributions to the nonequilibrium heat and viscous fluctuations over those previously observed in a pure liquid. Rayleigh-scattering experiments for an equimolar mixture of toluene and *n*-hexane have confirmed the presence of these types of nonequilibrium fluctuations. We have verified that the intensity of all nonequilibrium fluctuations is proportional to the square of the temperature gradient ∇T and inversely proportional to the fourth power of the wave number k. The strength of the observed nonequilibrium fluctuations appears to be fully consistent with the strength of those fluctuations expected on the basis of the theory of fluctuating hydrodynamics. Assuming the validity of the theory of fluctuating hydrodynamics for nonequilibrium liquid mixtures, we submit that it is possible to deduce the Soret coefficient of liquid mixtures by measuring the strength of the nonequilibrium concentration fluctuations with low-angle Rayleigh-scattering experiments. From the information provided in Table VI, we estimate that this technique can provide Soret coefficients with an accuracy fully competitive with the best available experimental techniques [17,18,30].

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APPENDIX: NONEQUILIBRIUM RAYLEIGH-SCATTERING SPECTRUM OF LIQUID MIXTURES

The complete expression for the Rayleigh-scattering spectrum of a liquid mixture in the presence of a temperature gradient, derived by Law and Nieuwoudt [15,16], contains three diffusive modes with the decay rates given by

$$\lambda_\nu=\nu k^2,\quad \lambda_\pm=\frac{(D_T+\mathcal{D})k^2}{2}\pm\frac{k^2}{2}[(D_T+\mathcal{D})^2-4D_TD]^{1/2}\ , \tag{A1}$$

where

$$\mathcal{D}=D(1+\epsilon)\ , \tag{A2}$$

with

$$\epsilon=\frac{[S_Tc(1-c)]^2}{(c_{p,c}/T)}\left[\frac{\partial\mu}{\partial c}\right]_{p,T}\ . \tag{A3}$$

For an equimolar mixture of toluene and *n*-hexane, $\epsilon\approx0.028$. Expanding the decay rates λ_ν and $\lambda_\pm$ in terms of the parameter ϵ, we obtain

$$\begin{aligned}\lambda_\nu&=\nu k^2\ ,\\ \lambda_+&=D_T(1+\epsilon D/D_T+O((\epsilon D/D_T)^2))k^2\ ,\\ \lambda_-&=D(1+O(\epsilon^2))k^2\ .\end{aligned} \tag{A4}$$

The small differences of the decay rates $\lambda_+ = D_T k^2$ and $\lambda_- = Dk^2$ with the values given in (A4) have been neglected in (2.4). In addition, to obtain the three pure modes represented by (2.4), we have also made use of the large difference in time scales, since $\nu/D \approx 181$ and $D_T/D \approx 31$, which are substantially larger than unity. We estimate that the contributions neglected would contribute no more than a few percent to the calculated amplitudes of the fluctuations. Velasco and García-Colín [31] have suggested that the Rayleigh-scattering spectrum should contain an additional term proportional to $(\partial\mu/\partial T)_{p,c}$. However, this term is a higher-order term that, like many other higher-order terms, is negligibly small in practice.

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