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# Measurement of Transport Properties of Liquids with Equilibrium and Nonequilibrium Rayleigh Scattering[1]

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We have developed an experimental arrangement for measuring Rayleigh scattering in liquids and liquid mixtures that are either in thermal equilibrium or in thermal nonequilibrium states. As an illustrative example we report experimental values for the thermal diffusivity, the mass diffusion coefficient, the Rayleigh-factor ratio, and the Soret coefficient of an equimolar mixture of liquid toluene and *n*-hexane.

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**KEY WORDS:** diffusion coefficient; fluctuations; *n*-hexane; nonequilibrium; Rayleigh scattering; Soret coefficient; thermal diffusivity; toluene.

## 1. INTRODUCTION

Dynamic light scattering from fluctuations in liquids and liquid mixtures is a modern technique for measuring various transport properties. Rayleigh scattering from temperature fluctuations yields the thermal diffusivity $D_T$ and, from concentration fluctuations, the mass diffusion coefficient $D$ [1]. Recently, we have also demonstrated the feasibility of measuring Rayleigh scattering from nonequilibrium fluctuations in liquids and liquid mixtures subjected to a stationary temperature gradient [2, 3]. In particular, the strength of the nonequilibrium concentration fluctuations produced by a temperature gradient is proportional to the square of the Soret coefficient $S_T$ [3, 4]. As a consequence, Rayleigh scattering from nonequilibrium

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concentration fluctuations provides, in principle, a sensitive method for determining Soret coefficients [3].

In this paper we describe an experimental apparatus which enabled us to measure Rayleigh scattering of liquids and liquid mixtures in thermal equilibrium and thermal nonequilibrium states. We present new experimental results for the thermal diffusivity $D_T$, the mass diffusion coefficient $D$, the Rayleigh-factor ratio $\mathscr{R}$, and the Soret coefficient of an equimolar mixture of toluene and $n$-hexane. The results presented in this paper supplement results obtained for this mixture in previous experiments [3, 5].

## 2. PRINCIPLE OF THE MEASUREMENTS

### 2.1. Equilibrium Rayleigh Scattering

The relaxation times of the temperature and concentration fluctuations probed at a scattering angle of 90° in typical liquid mixtures are rather small, usually of the order of $10^{-8}$ to $10^{-6}$ s. This makes it necessary to perform the Rayleigh scattering experiments at small scattering angles [6].

In dynamic light-scattering experiments the intensity autocorrelation function $\langle I(0)\, I^*(t)\rangle$ of the scattered light is measured as a function of the delay time $t$. This correlation function can be expressed as the superposition of the contribution from the background light intensity, $I_0$, and the contributions from the coherent scattering intensities, $I_T$ and $I_c$, in a liquid mixture due to temperature and concentration fluctuations. Since the scattered light intensity is small and the static scattering from the sample windows is large, a heterodyne technique is most suitable for accurate measurements. In small-angle scattering experiments one can easily obtain the condition that $I_0 \gg I_T$ and $I_0 \gg I_c$ so that the heterodyne correlation function can be expressed as [1]

$$\langle I(0)\, I^*(t)\rangle = (I_0 + I_T + I_c)^2 + 2I_0 I_T e^{-k^2 D_T t} + 2I_0 I_c e^{-k^2 D t} \tag{1}$$

The scattering wave number $k$ in Eq. (1) is related to the scattering angle $\theta$ by the Bragg condition $k = (4\pi n/\lambda)\sin(\theta/2)$, where $\lambda$ is the wavelength of the laser light and $n$ the refractive index of the sample. The normalized correlation function is then

$$C(t) = \frac{\langle I(0)\, I^*(t)\rangle}{\langle I(0)\, I^*(0)\rangle} = 1 + C_0(e^{-k^2 D_T t} + \mathscr{R} e^{-k^2 D t}) \tag{2}$$

where the coefficient $C_0 = 2I_T I_0/(I_0 + I_T + I_c)^2 \approx 2I_T/I_0$ determines the ratio of signal to background and the Rayleigh-factor ratio $\mathscr{R} = I_c/I_T$ determines the ratio of the scattering intensity from the concentration-mode and the heat-mode fluctuations.

## 2.2. Nonequilibrium Rayleigh Scattering

When a binary liquid mixture is subjected to a steady temperature gradient $\nabla T$, it is also subjected to a resulting concentration gradient $\nabla c$ because of the Soret effect [7] that is described by the phenomenological relation $\nabla c = -S_{\mathrm{T}}c(1-c)\,\nabla T$, where $S_{\mathrm{T}}$ is the Soret coefficient and $c$ the mass concentration of the heavier component. It has been found that long-range correlations are present in liquids brought out of homogeneous equilibrium by the imposition of an external dissipative field [8]. Specifically, the presence of a temperature and a concentration gradient in a liquid mixture causes a coupling between the local diffusive fluctuations and the transverse-momentum fluctuations, so that three coupled hydrodynamic viscous–heat–concentration modes appear in the Rayleigh spectrum. Strictly speaking, the three nonequilibrium modes are neither purely diffusive nor purely viscous [4, 9]. However, in typical liquid mixtures with experimentally accessible temperature gradients, these three nonequilibrium modes decouple to a viscous mode, a heat mode, and a concentration mode, with decay rates of $\nu k^2$, $D_{\mathrm{T}}k^2$, and $Dk^2$, respectively, where $\nu$ is the kinematic viscosity [4, 9]. The normalized correlation function $C(t)$ is now given by [4, 9]

$$C(t) = 1 + C_0[(1 + A_{\mathrm{T}})\,e^{-k^2 D_{\mathrm{T}} t} - A_\nu e^{-k^2 \nu t} + \mathscr{R}(1 + A_{\mathrm{c}} e^{-k^2 D t})] \qquad (3)$$

For $\mathbf{k} \perp \nabla T$, which is the configuration adopted in our experiments, the amplitudes $A_{\mathrm{T}}$, $A_\nu$, and $A_{\mathrm{c}}$ of the nonequilibrium fluctuations in Eq. (3) are proportional to $(\nabla T)^2/k^4$. The singular dependence of these amplitudes on $k^{-4}$ confirms the long-range nature of these fluctuations [8]. The explicit expressions for the amplitudes $A_{\mathrm{T}}$, $A_\nu$, and $A_{\mathrm{c}}$ have been presented in earlier papers [3, 5, 9]. Here we are specifically interested in the amplitude $A_{\mathrm{c}}$ of the nonequilibrium concentration fluctuations given by [5]

$$\begin{aligned} A_{\mathrm{c}} = \frac{\Psi_n^2}{\mathscr{R}} \frac{c_{\mathrm{p,c}}}{T(\nu^2 - D^2)} \left(\frac{\nu}{D}\right) \Bigg\{ \left[ 1 + 2\left(\frac{D}{D_{\mathrm{T}}}\right)\left(1 + \frac{1}{\Psi_n}\right) \right] \\ \times \left[ 1 + 2\left(\frac{D}{D_{\mathrm{T}}}\right)\left(\frac{\varepsilon}{\Psi_n} + \Psi_n\right) \right] \Bigg\} \frac{(\nabla T)^2}{k^4} \end{aligned} \qquad (4)$$

where $c_{\mathrm{p,c}}$ is the isobaric specific heat capacity at constant concentration and where $\Psi_n = -[S_{\mathrm{T}}c(1-c)](\partial n/\partial c)_{\mathrm{p,T}}/(\partial n/\partial T)_{\mathrm{p,c}}$, which is the ratio of the refractive index gradients resulting from the concentration gradient and the temperature gradient, and $\varepsilon = T[S_T c(1-c)]^2/c_{p,c}(\partial c/\partial \mu)_{p,T}$, with $\mu = \mu_1 - \mu_2$ being the difference between the chemical potentials per unit mass of the two components of the mixture. For typical liquid mixtures such as toluene + $n$-hexane, the magnitude of terms inside the square brackets in Eq. (4) differ from unity by only 25%. Therefore, the amplitude $A_c$ of the nonequilibrium concentration fluctuations is, to a good approximation, proportional to the square of $\Psi_n$ and, hence, to the square of the Soret coefficient $S_T$.

## 3. RAYLEIGH SCATTERING IN THERMAL EQUILIBRIUM

The optical arrangement is shown schematically in Fig. 1. The light-scattering cell itself is the same as that used in our most recent nonequilibrium Rayleigh-scattering experiments [5]. The cell has optical windows in top and bottom copper plates whose temperatures can be controlled to within 5 mK. The liquid sample is confined within a 2.5-mm glass ring spacer which is sealed against the top and the bottom plates by indium. The two copper plates are held together by Teflon bolts whose tension is adjusted to produce a uniform cell height $d = 0.27$ cm. A helium-neon laser beam ($\lambda = 633$ nm, 6 mW) passes through the cell at an angle of about 1.5° to the normal of the entrance window and is focused at the transparent liquid to be investigated. The scattered light, which is observed at typical scattering angles of 2-3°, is collected by pinhole $P_1$ (400 $\mu$m), which is attached on a Vernier scale place 22 cm away from the center of the liquid

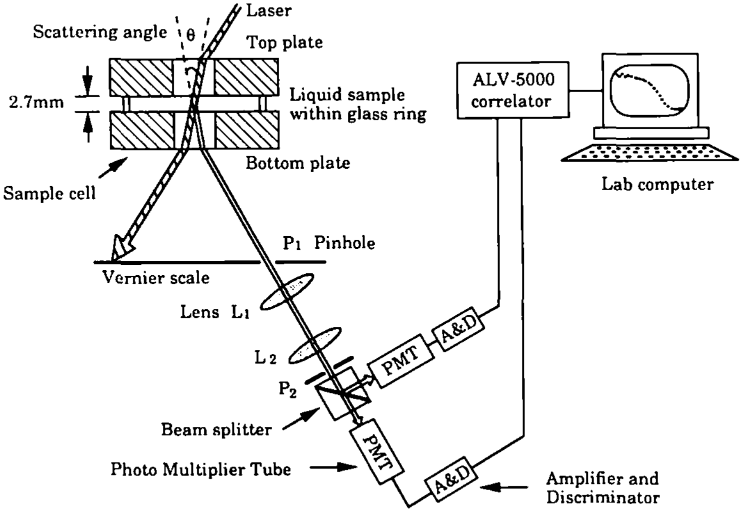

Fig. 1. Schematic representation of the experimental arrangement.

volume. One can determine the scattering angle $\theta$ with an accuracy of ±1% by measuring the distance between the collection pinhole $P_1$ and the straight light spot on the Vernier scale. Since the scattering angle $\theta$ inside the liquid is related to the angle measured outside the sample cell by Snell's law of deflection, a systematic error may arise from the nonparallelism of the optical surfaces of the exit window. We have used an interference method [10] to measure the angle between the optical surfaces of the top and the bottom windows and found that the degrees of parallelism are within 1 min in both cases. This implies that any systematic error associated with the nonparallelism of the optical windows for the determination of the scattering angle $\theta$ is less than 0.001%.

The correlation function $C(t)$ of the scattered light is measured by heterodyning the scattered light with residual stray light [2, 3]. To avoid any problems from afterpulse and dead-time effects of the photomultiplier tubes (PMTs), we actually cross-correlate the output signal with two photomultipliers as we did in earlier light-scattering experiments in pure toluene [2]. Each run lasted about 6 to 10 h, with typical count rates of 30 to 130 kHz in the PMT channels. A new feature in the present experiments is the use of an ALV-5000 multiple-tau digital correlator, which is especially suited for resolving multiple relaxation times in the correlation function [11].

We performed the light-scattering experiments with an equimolar mixture of toluene and *n*-hexane at 25°C after it had been cleaned with micropore (0.22-μm porosity) filtration. A typical experimental correlogram is shown in Fig. 2.

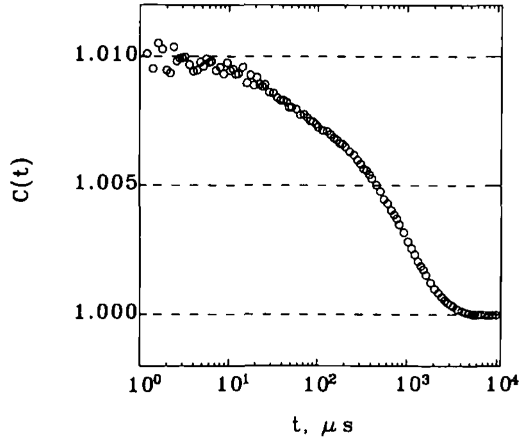

**Fig. 2.** Experimental correlogram recorded by the ALV-5000 multiple-tau correlator.

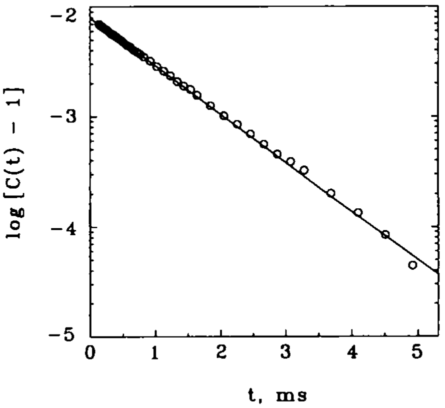

**Fig. 3.** Plot of $\log[C(t) - 1]$ as a function of time for $5\tau_T \leqslant t \leqslant 5\tau_c$.

We can analyze the heat-mode and concentration-mode contributions separately, because the correlation times $\tau_T$ and $\tau_c$ of these modes differ by a factor of 30. At longer delay times the temperature fluctuations are fully relaxed and the correlation function is determined by the concentration fluctuations. This is illustrated in Fig. 3, which shows that $\log[C(t) - 1]$ for $5\tau_T \leqslant t \leqslant 5\tau_c$ is well described by a single exponential. The slope and amplitude of this quantity yield the mass diffusion coefficient $D$ and the strength $C_0\mathscr{R}$ of the concentration fluctuations. The thermal diffusivity $D_T$ and the strength $C_0$ of the contribution from the temperature fluctuations

**Table I.** Experimental Results for the Mutual Diffusion Coefficient $D$, Thermal Diffusivity $D_T$, and Rayleigh-Factor Ratio $\mathscr{R}$ of an Equimolar Mixture of Toluene and $n$-Hexane at 25°C

| $k$ ($\mathrm{cm}^{-1}$) | $D$ ($10^{-5}\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$) | $D_T$ ($10^{-3}\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$) | $\mathscr{R}$ |
|---|---|---|---|
| 5998 | 2.79 | 0.83 | 3.6 |
| 6182 | 2.77 | 0.73 | 4.0 |
| 6459 | 2.77 | 0.90 | 4.1 |
| 6643 | 2.76 | 0.81 | 3.2 |
| 6828 | 2.72 | 0.86 | 3.7 |
| 7013 | 2.74 | 0.93 | 3.8 |
| 7197 | 2.79 | 0.80 | 3.2 |
| 7382 | 2.78 | 0.80 | 4.1 |
| Average | 2.77 ± 0.03 | 0.83 ± 0.06 | 3.7 ± 0.3 |
| Literature | 2.76[a] | 0.84[b] | 3.8[b] |

[a] From Ref. 12.

[b] From Ref. 3.

can then be obtained from a fit of the experimental correlation-function data at shorter times ($t \leqslant 5_T$) to Eq. (2). The experimental results thus obtained for $D$, $D_T$, and $\mathscr{M}$ of the mixture at 25°C are presented in Table I. The estimated experimental accuracy is 2% for $D$ and 8% for $D_T$ and $\mathscr{M}$. Our experimental values agree with the values reported in the literature [3, 12], and quoted in Table I, to well within the experimental accuracy.

## 4. RAYLEIGH SCATTERING IN THERMAL NONEQUILIBRIUM STATES

The optical arrangement for the nonequilibrium Rayleigh-scattering experiments differs from that described in Section 3 in three aspects. First, the layer between the plates has to be leveled carefully horizontally to avoid convection when a temperature gradient $\nabla T$ is applied. Furthermore, the incident laser beam now propagates along the vertical axis so that beam bending as a result of the refractive-index gradient induced by the temperature gradient is avoided. Finally, because of the $k^{-4}$ wavenumber dependence of the strength of the nonequilibrium fluctuations, the measurements need to be made at very small wavenumbers, i.e., at very small scattering angles ($\theta < 1°$).

We have performed nonequilibrium Rayleigh-scattering experiments with an equimolar mixture of toluene and $n$-hexane at 25°C, originally with

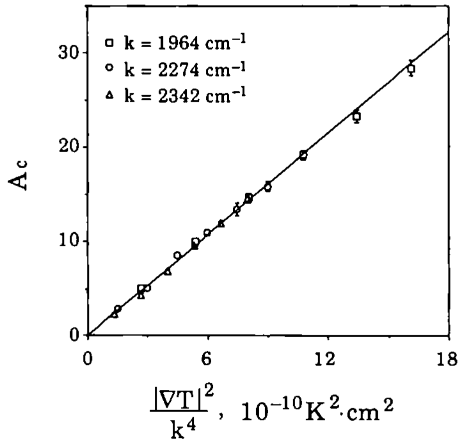

**Fig. 4.** Amplitude $A_c$ of the nonequilibrium correlation fluctuations in an equimolar mixture of toluene and $n$-hexane at 25°C as a function of $(\nabla T)^2/k^4$.

an argon-ion laser as the light source and cross-correlation [3] and subsequently with a helium–neon laser as the light source but without cross-correlation [5]. In Fig. 4 we show the amplitude $A_c$ of the nonequilibrium correlation fluctuations as a function of $(\nabla T)^2/k^4$, deduced from our most recent experiments [5]. This amplitude indeed varies linearly with $(\nabla T)^2/k^4$. Because of the small scattering angles, which are difficult to measure accurately, we determined the experimental wave number $k$ from the exponential decay of the concentration fluctuations in thermal equilibrium adopting the literature value of $2.76 \times 10^{-5}\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$ [12] for the diffusion coefficient. Our new experiments presented in Section 3 have now confirmed the validity of this procedure.

In principle it is possible to determined the Soret coefficient $S_T$ by fitting the experimental values of $A_c$ to Eq. (4) provided that all other properties of the mixture in Eq. (4) are known. The kinematic viscosity $\nu$ and the density $\rho$ appear to be known for this mixture [12]. We have measured the refractive-index derivatives in our laboratory [13]. The only parameter for which no direct experimental information is available is the specific heat capacity $c_{p,c}$ of the mixture. We can estimate this specific heat capacity in two ways. First, we can calculate it from the known specific heat capacities of the pure components [14, 15], neglecting any heat of mixing, yielding $c_{p,c} = 1.98\ \mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$ [5]. Alternatively, we can estimate the thermal conductivity $\kappa$ of the mixture from the know thermal conductivities of the pure components [16] using an interpolation formula proposed by Tsederberg [17], yielding $\kappa = 0.1247\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$ [5]. The specific heat capacity is related to $D_T$ as $c_{p,c} = \kappa/\rho D_T$, and with $\rho = 747.8\ \mathrm{kg \cdot m^{-3}}$ we obtain $c_{p,c} = 2.01\ \mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$, in good agreement with the estimate given above. Fitting Eq. (4) to the experimental data for $A_c$ then yields [5]

$$S_T = (6.16 \pm 0.11) \times 10^{-3}\ \mathrm{K}^{-1} \tag{5}$$

A classical method for measuring Soret coefficients of liquid mixtures is based on the observation of concentration differences in a thermogravitational column [18]. Very recently, Ecenarro and co-workers used this method to determine the $S_T$ of an equimolar mixture of toluene and $n$-hexane at 25°C and obtained $S_T = 4.60 \times 10^{-3}\ \mathrm{K}^{-1}$ [19]. The origin of the sizable discrepancy with the Soret-coefficient value deduced from our Rayleigh-scattering measurements is unresolved.

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## REFERENCES

1. J. N. Shaumeyer, R. W. Gammon, J. V. Sengers, and Y. Nagasaka, in *Experimental Thermodynamics III: The Measurement of Transport Properties of Fluids*, W. A. Wakeham, A. Nagashima, and J. V. Sengers, eds. (Blackwell Scientific, Oxford, 1991), p. 195.
2. P. N. Segrè, R. W. Gammon, J. V. Sengers, and B. W. Law, *Phys. Rev. A* **45**:714 (1992).
3. P. N. Segrè, R. W. Gammon, and J. V. Sengers, *Phys. Rev. E* **47**:1026 (1993).
4. B. M. Law and J. C. Nieuwoudt, *Phys. Rev. A* **40**:3880 (1989).
5. W. B. Li, P. N. Segrè, J. V. Sengers, and R. W. Gammon, *Physica A* **204**:399 (1994).
6. A. Leipertz, *Int. J. Thermophys.* **9**:897 (1988).
7. H. J. V. Tyrell, *Diffusion and Heat Flow in Liquids* (Butterworths, London, 1961), Chap. 9.
8. J. R. Dorfman, T. R. Kirkpatrick, and J. V. Sengers, *Annu. Rev. Phys. Chem.* **45**:213 (1994).
9. P. N. Segrè and J. V. Sengers, *Physica A* **198**:46 (1993).
10. M. Born and E. Wolf, *Principle of Optics* (Pergamon, Oxford, 1965), Chap. 7.
11. K. Schätzel, in *Optical Measurements in Fluid Mechanics 1985, Inst. Phys. Conf. Ser. No. 77*, P. H. Richards, ed. (Adam Hilger, Bristol, 1985), p. 175.
12. R. K. Ghai and F. A. L. Dullien, *J. Phys. Chem.* **78**:2283 (1974).
13. W. B. Li, P. N. Segrè, R. W. Gammon, J. V. Sengers, and M. Lamvik, *J. Chem. Phys.* **101**:5058 (1994).
14. D. W. Scott, G. B. Guthrie, J. F. Messerly, S. S. Todd, W. T. Berg, I. A. Hossenlopp, and J. P. McCullough, *J. Phys. Chem.* **66**:911 (1962).
15. R. Thaw, *J. Chem. Eng. Data* **14**:461 (1969).
16. H. Kashiwagi, M. Oishi, Y. Tanaka, H. Kubota, and T. Makita, *Int. J. Thermophys.* **3**:101 (1982).
17. N. V. Tsederberg, *Thermal Conductivity of Gases and Liquids* (MIT Press, Cambridge, MA, 1965), p. 212.
18. O. Ecenarro, J. A. Madariaga, J. Navarro, C. M. Santamaría, J. A. Carrió, and J. M. Saviró, *J. Phys. Condens. Matter* **2**:2289 (1990).
19. O. Ecenarro, personal communication (1994).