

# Non-equilibrium fluctuations in liquids and liquid mixtures subjected to a stationary temperature gradient

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Received 24 September 1993, in final form 26 October 1993

**Abstract.** We have investigated non-equilibrium fluctuations in liquids subjected to a stationary temperature gradient by performing small-angle Rayleigh scattering experiments. Experimental results have been obtained for liquid toluene, liquid *n*-hexane and for three mixtures of these liquids. The experiments confirm that the strength of the non-equilibrium fluctuations is proportional to the square of the temperature gradient and inversely proportional to the fourth power of the wave number of the fluctuations. In the case of the pure liquids excellent agreement is obtained with theoretical predictions based on the linearized equations of fluctuating hydrodynamics. In the case of the mixtures some questions remain about the magnitude of the Soret effect.

## 1. Introduction

During the past decade there has been an increased interest in the nature of fluctuations in fluids in steady non-equilibrium states. In this paper we consider fluctuations in liquid systems that are brought out of thermal equilibrium by the application of a stationary temperature gradient, but that still remain in a non-convecting stationary state. One may distinguish between propagating sound modes that can be probed experimentally by Brillouin scattering and diffusive fluctuations that can be probed by Rayleigh scattering. Here we consider the effect of a temperature gradient on the local diffusive fluctuations. These local diffusive fluctuations cannot feel the direction of the temperature gradient  $\nabla T$ , but will depend on  $(\nabla T)^2$  [1]. Moreover, it has been found that these diffusive fluctuations in the presence of a temperature gradient become long range and will vary as  $k^{-4}$  with the wave number  $k$  of the fluctuations [1]. This singular dependence on the wave number  $k$  is now considered to be a generic property of non-equilibrium steady states [2, 3].

We have performed a set of Rayleigh-scattering experiments in liquid systems subjected to a stationary temperature gradient. Experimental results have been obtained for liquid toluene [4, 5], for liquid *n*-hexane [6] and for three mixtures of liquid *n*-hexane with toluene [6, 7]. In this paper we discuss the major conclusions that can be drawn from these experiments.

## 2. Theoretical predictions

Light-scattering experiments probe fluctuations in the local refractive index  $n$  of the fluid, which in turn are proportional to a time-dependent structure factor  $S(k, t)$ .

### 2.1. One-component liquids

For a one-component fluid in thermal equilibrium the Rayleigh component of the dynamic structure factor is given by  $S_E(k, t) = S_0 \exp(-D_T k^2 t)$ , where  $D_T$  is the thermal diffusivity and where  $S_0$  is a measure of the amplitude of the equilibrium fluctuations. The expression for the Rayleigh component of the dynamic structure factor of a one-component fluid subjected to a stationary temperature gradient was first derived by Kirkpatrick *et al* [1]. The temperature gradient  $\nabla T$  causes a coupling between the temperature fluctuations and the transverse-momentum fluctuations, also referred to as viscous fluctuations. The latter relax with a decay rate  $\nu k^2$ , where  $\nu$  is the kinematic viscosity, and the non-equilibrium dynamic structure factor becomes [1]

$$S_N(k, t) = S_0[(1 + A_T)e^{-D_T k^2 t} - A_\nu e^{-\nu k^2 t}]. \quad (1)$$

Equation (1) can be recovered by describing the fluctuations in terms of the linearized equations of fluctuating hydrodynamics under the assumption that the correlation functions of the random noise terms retain their local equilibrium values [8–10].

The amplitudes  $A_T$  and  $A_\nu$  of the non-equilibrium fluctuations in (1) reach their maximum values when the scattering wave vector  $\mathbf{k}$  is perpendicular to the temperature gradient  $\nabla T$ , which is the configuration adopted in our experiments. They are then given by [1]

$$A_T = A_T^* (\nabla T)^2 / k^4 \quad A_\nu = A_\nu^* (\nabla T)^2 / k^4 \quad (2)$$

$$A_T^* = [c_p / T (\nu^2 - D_T^2)] \nu / D_T \quad A_\nu^* = c_p / T (\nu^2 - D_T^2) \quad (3)$$

where  $T$  is the local temperature and  $c_p$  the local isobaric specific heat capacity [1, 8–10].

### 2.2. Liquid mixtures

The Rayleigh component of the dynamic structure factor of liquid mixtures is related to both temperature and concentration fluctuations. For a liquid mixture in thermal equilibrium it is given by [11]  $S_E(k, t) = S_0[\exp(-D_T k^2 t) + \tilde{R} \exp(-D k^2 t)]$ , where  $D$  is the binary mass diffusion coefficient and where  $\tilde{R}$  is a Rayleigh-factor ratio that measures the strength of the concentration fluctuations relative to that of the temperature fluctuations in thermal equilibrium.

When a liquid mixture is subjected to a temperature gradient  $\nabla T$  a concentration gradient  $\nabla c$  is induced such that  $\nabla c = -S_T c(1 - c) \nabla T$ , where  $S_T$  is the Soret coefficient and where  $c$  is the mass concentration of the heavier component (toluene). The presence of the concentration gradient causes an additional coupling between the transverse-momentum fluctuations and the concentration fluctuations. The complete expression for the non-equilibrium dynamic structure factor, first derived by Law and Nieuwoudt [12, 13], is rather complicated [14, 15]. Fortunately, the expression can be simplified by neglecting terms that contribute less than 1% in a mixture of normal liquids such as toluene and *n*-hexane and one obtains [6, 7]

$$S_N(k, t) = S_0[(1 + A_T) \exp(-D_T k^2 t) - A_\nu \exp(-\nu k^2 t) + \tilde{R}(1 + A_c) \exp(-D k^2 t)]. \quad (4)$$

The amplitudes

$$A_T = A_T^* (\nabla T)^2 / k^4 \quad A_\nu = A_\nu^* (\nabla T)^2 / k^4 \quad A_c = A_c^* (\nabla T)^2 / k^4 \quad (5)$$

of the non-equilibrium fluctuations are again proportional to  $(\nabla T)^2/k^4$  with coefficients

$$A_T^* = [c_{p,c}/T(v^2 - D_T^2)](v/D_T)(1 + 2\Psi_n) \quad (6)$$

$$A_v^* = [c_{p,c}/T(v^2 - D_T^2)]\{(1 + \Psi_n)^2[1 + 2(D/D_T)\Psi_n]\} \quad (7)$$

$$A_c^* = (\Psi_n^2/\bar{R})[c_{p,c}/T(v^2 - D^2)](v/D)[1 + 2(D/D_T)(1 + 1/\Psi_n)][1 + 2(D/D_T)(\epsilon/\Psi_n + \Psi_n)] \quad (8)$$

where  $c_{p,c}$  is the isobaric specific heat capacity at constant concentration and where  $\Psi_n = -c(1 - c)S_T(\partial n/\partial c)_{p,T}/(\partial n/\partial T)_{p,c}$  and  $\epsilon = T[S_T c(1 - c)]^2/c_{p,c}(\partial c/\partial \mu)_{p,T}$  with  $\mu = \mu_1 - \mu_2$  being the difference between the chemical potentials per unit mass of the two components of the mixture [6].

### 3. Experimental results

Experimental results have been obtained for liquid toluene [4, 5], liquid *n*-hexane [6] and for three mixtures of these liquids [6, 7]. The liquids were confined between two horizontal plates. Convection was avoided by heating the liquid layer from above. An incident light beam entered the fluid layer vertically opposite to the direction of the temperature gradient  $\nabla T$ . The scattering vector was located in the horizontal plane perpendicular to  $\nabla T$ . The dynamic structure factor was measured by heterodyning the scattered light. In the case of liquid toluene the measurements were obtained at temperature gradients up to  $220 \text{ K cm}^{-1}$  [5]. In the case of liquid *n*-hexane and of the mixtures the maximum temperature gradient was  $155 \text{ K cm}^{-1}$  [6]. Because of the singular dependence of the non-equilibrium fluctuations on the wave number for small  $k$ , it is necessary to perform the Rayleigh-scattering experiments at very small values of the scattering angle. Detailed descriptions of the experimental arrangement can be found elsewhere [4–6].

#### 3.1. One-component liquids

Our measurements with toluene and *n*-hexane have confirmed that the Rayleigh component of the non-equilibrium dynamic structure factor  $S_N$  indeed consists of two exponentials with decay rates  $D_T k^2$  and  $\nu k^2$  in accordance with (1) [4, 5]. With the known values of the decay rates  $D_T k^2$  and  $\nu k^2$  for toluene and *n*-hexane, we deduce from the measured correlation functions the amplitudes  $A_T$  and  $A_v$  of the non-equilibrium fluctuations. The values observed for these amplitudes for liquid toluene [5] and for liquid *n*-hexane [6] are plotted as a function of  $(\nabla T)^2/k^4$  in figure 1. The experimental results for toluene correspond to an average temperature of  $40^\circ\text{C}$  [4, 5] and those for *n*-hexane to an average temperature of  $25^\circ\text{C}$  [6, 7]. It has been verified that any effects associated with the spatial variations of the thermodynamic and transport properties due to their dependence on temperature are negligibly small [5]. It is seen that the amplitudes  $A_T$  and  $A_v$  of the non-equilibrium fluctuations indeed vary linearly with  $(\nabla T)^2/k^4$ . The solid lines in figure 1 do not represent lines fitted to the experimental amplitudes of the non-equilibrium fluctuations. Instead they represent the theoretical behaviour implied by (2) with the known values  $\nu$ ,  $D_T$  and  $c_p$  of toluene and of *n*-hexane at the average temperature [5, 6]. We conclude that for the pure liquids the experimentally observed non-equilibrium fluctuations are in excellent quantitative agreement with the theoretical predictions.

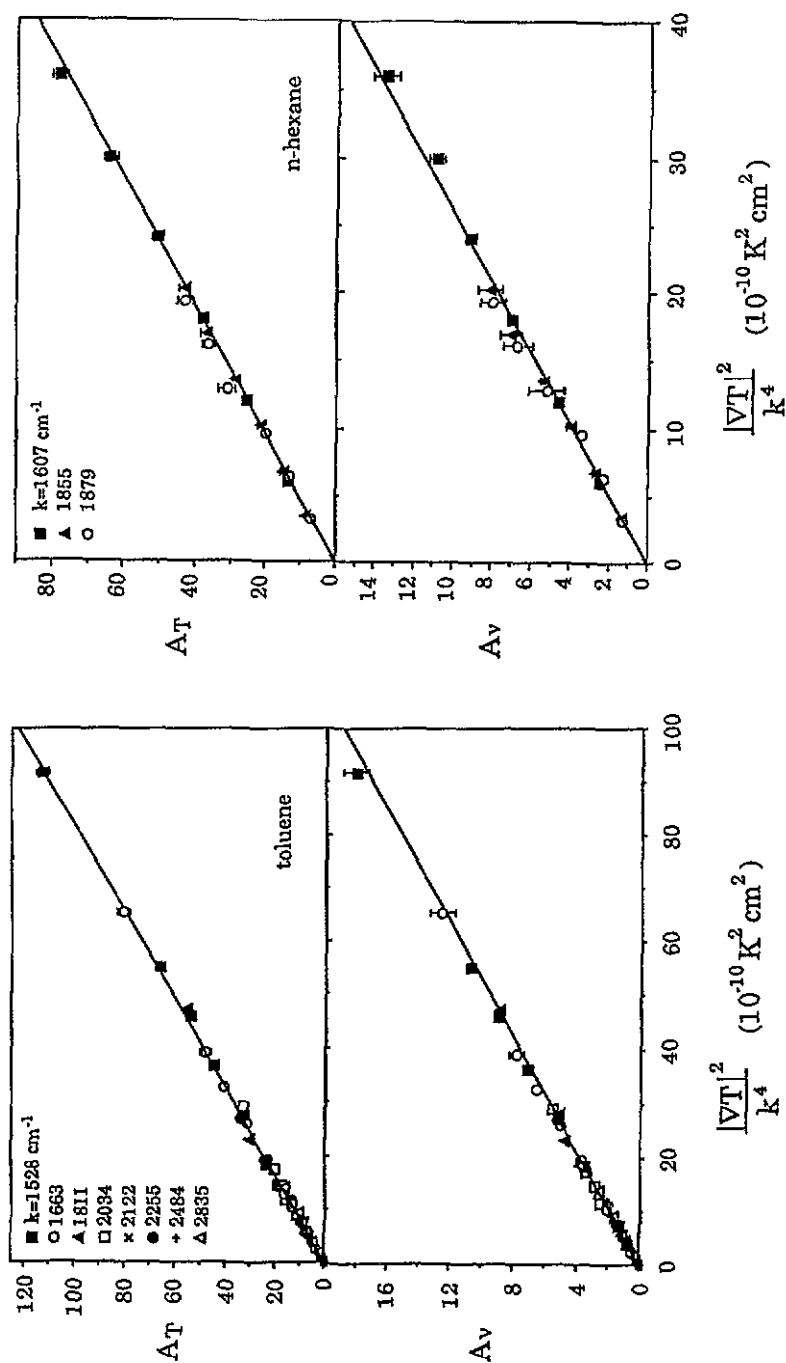


Figure 1. Amplitudes  $A_T$  and  $A_v$  of the non-equilibrium fluctuations in liquid toluene [5] and in liquid *n*-hexane [6] as a function of  $(VT)^2/k^4$ . The symbols indicate the experimental values. The solid lines represent the values calculated from (3).

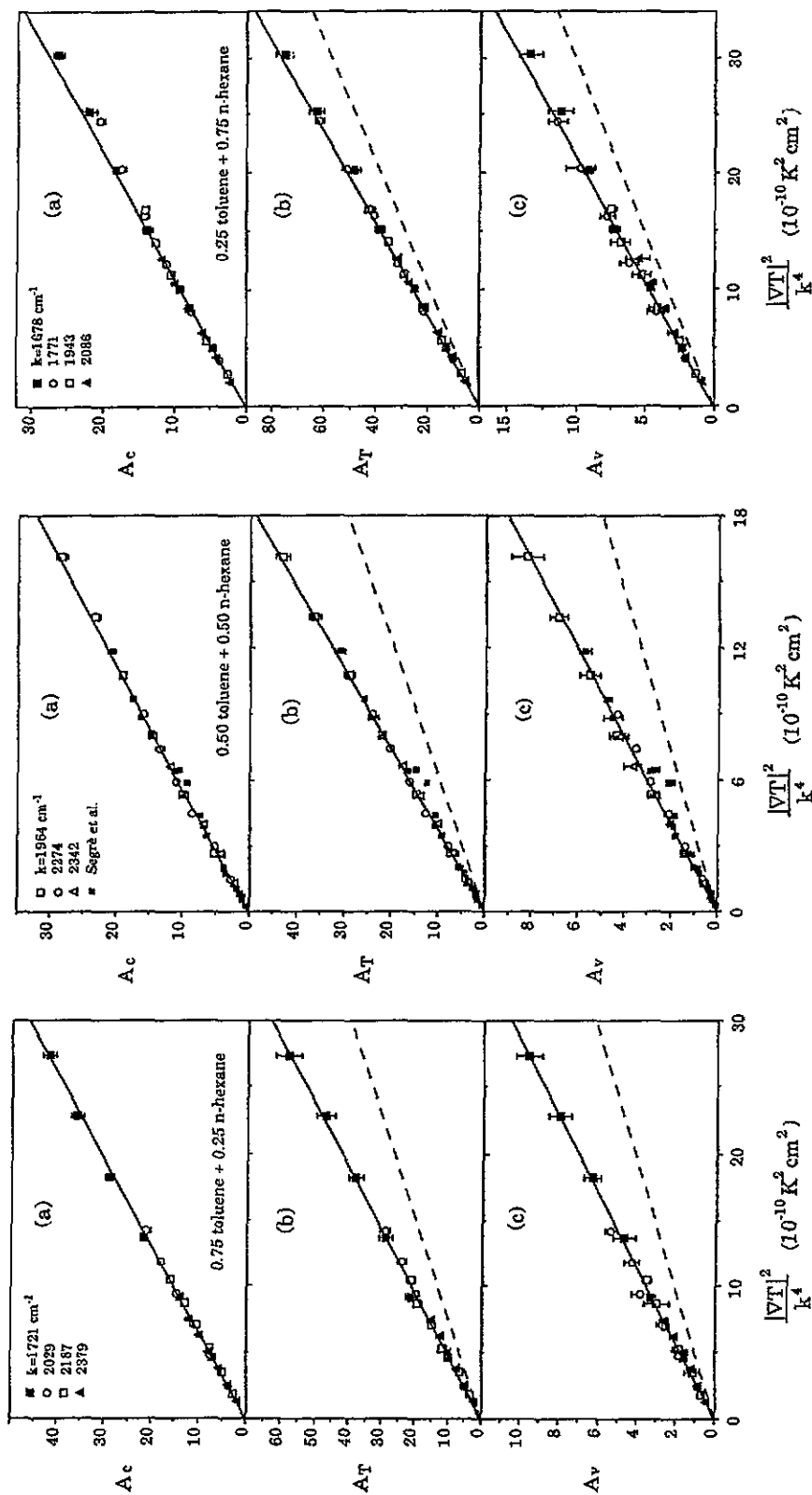


Figure 2. Amplitudes  $A_c$ ,  $A_T$  and  $A_v$  of the non-equilibrium fluctuations in liquid  $x$  toluene +  $(1 - x)$ -n-hexane mixtures, with toluene mole fractions  $x = 0.75$ ,  $0.50$  and  $0.25$ , as a function of  $(\Delta T)^2/k^4$ . The symbols indicate experimental values. The dashed lines represent the values calculated from (6) and (7) with  $S_T = 0$ . The solid lines represent the values calculated from (6)-(8) with effective values for  $S_T$ .

### 3.2. Liquid mixtures

We have also measured the non-equilibrium fluctuations in three mixtures of liquid toluene and *n*-hexane subjected to a stationary temperature gradient. We have verified that in this case the non-equilibrium dynamic structure factor  $S_N(k, t)$  indeed consists of three exponents with decay rates  $D_T k^2$ ,  $\nu k^2$  and  $Dk^2$  in accordance with (4) [7]. The values observed for the amplitudes  $A_c$ ,  $A_T$  and  $A_\nu$  of the non-equilibrium fluctuations for the three mixtures at an average temperature of 25°C [6, 7] are plotted as a function of  $(\nabla T)^2/k^4$  in figure 2. The three mixtures correspond to toluene mole fractions  $x$  of 0.75, 0.50 and 0.25. The experiments confirm that all non-equilibrium fluctuations again vary linearly with  $(\nabla T)^2/k^4$ .

A quantitative analysis of the observed strength of the non-equilibrium fluctuations is hampered by the lack of a reliable data base for the Soret coefficient  $S_T$  of the mixtures, which determines the magnitude of the concentration gradient. The dashed lines in figure 2 represents the behaviour of  $A_T$  and  $A_\nu$  from (6) and (7) with  $S_T = 0$ . For the non-equilibrium fluctuations  $S_T = 0$  implies  $A_c = 0$ . Hence, the observed amplitudes of the non-equilibrium concentration fluctuations yield an effective value of the Soret coefficient  $S_T$ , if we assume the validity of (8). The values calculated for the amplitudes  $A_c$ ,  $A_T$  and  $A_\nu$  with effective Soret coefficients thus obtained at each concentration are represented by the solid lines in figure 2. Hence, it appears that the experimental results are consistent with the predictions from the linearized fluctuating hydrodynamic equations.

The effective values  $S_T = 0.00659 \text{ K}^{-1}$ ,  $0.00616 \text{ K}^{-1}$  and  $0.00469 \text{ K}^{-1}$  needed to produce the solid lines for  $x = 0.75, 0.50$  and  $0.25$  at 25°C in figure 2 appear to be about 60% larger than the values for the Soret coefficients implied by measurements of the thermal diffusion factors  $\alpha = TS_T$  at 38°C measured by Ecenarro *et al* with a thermogravitational column method [16]. The origin of this discrepancy has not yet been resolved [6].

The authors acknowledge valuable discussions with E G D Cohen, J R Dorfman, T R Kirkpatrick, B M Law and R Schmitz. The research is supported by National Science Foundation Grant DMR-9215128.

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