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## Viscoheat coupling in a binary mixture

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**Abstract.** This work is concerned with the behaviour of fluctuations in a binary mixture which is in a non-equilibrium steady state (NESS), produced by a temperature gradient. Fluctuating hydrodynamics lead us to a resonant coupling between the viscous and the heat modes in the system. The Rayleigh peak shows an anomalous behaviour arising from this coupling. A shift in the Brillouin peaks also appears but its magnitude is too small to be observable.

### 1. Introduction

The behaviour of fluctuations in thermodynamic systems which are in a non-equilibrium steady state (NESS) has been the subject of several theoretical and experimental studies [1, 2]. It is known that a system in a NESS presents long-range correlations produced by the effects of extra couplings between the hydrodynamic modes, which are absent in an equilibrium state. One of the most striking features of the light-scattering spectra in these systems is the asymmetry of the Brillouin peaks, which has been confirmed experimentally. The Rayleigh peak [3–5] also has an interesting behaviour produced by a coupling between the shear and the heat mode in a simple system in an external temperature gradient. In fact, there is an enhancement proportional to  $k^{-4}(\nabla T)_0^2$ , which has also been measured recently [6, 7]. Here we are interested in the study of a binary mixture in an external temperature gradient in order to see if a similar behaviour exists [8].

The starting point of our study will be the usual fluctuating hydrodynamics for the mixture [9, 10]. The ensuing equations will be linearized around the steady state to calculate the dynamic structure factor [11, 12]. This procedure gives us several important features concerning the behaviour of the system. First of all a concentration gradient appears which is proportional to the temperature gradient and the thermal diffusion coefficient. Secondly the Rayleigh peak presents an enhancement of the same structure as in the simple fluid. This effect appears because there exists a coupling between transverse viscous modes and the temperature gradient, but there is also an extra term which comes from the coupling between the fluctuating diffusion flux and the temperature gradient, which is proportional to  $k^{-2}(\nabla T)_0^2$  and represents a new effect in the mixture. Because of its dependence on the wavevector, the transport coefficients and some thermodynamic quantities, this term is negligible. The fluctuation calculations in this paper are based on the fluctuations of density, and the simplification of constant pressure, as occurs in the literature [8], was not needed.

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The paper is organized as follows. In section 2 we discuss the basic equations of fluctuating hydrodynamics for a binary mixture. In section 3 this set of equations is linearized around the steady state, a procedure resulting in an equation for the density in the wavelength-frequency representation, which clearly exhibits the different contributions to the density fluctuations. In section 4 we compute the dynamic structure factor and study its main features under conditions which are easily comparable with experimental results. Lastly we compare our calculation with the constant pressure approximation. Care is taken in pointing out the salient aspects of our work not taken into account in other treatments as well as comparison with other well-established results.

## 2. Basic equations

Our starting point to study the fluctuations in NESS will be the usual fluctuating hydrodynamics for a binary mixture. This means that we write the balance equations for the total density of the mixture  $\rho$ , the concentration  $c$ , the hydrodynamic velocity  $\mathbf{v}$  and the local entropy  $s$ , namely,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0 \quad (2.1)$$

$$\rho \left( \frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c \right) = -\nabla \cdot \mathbf{J} \quad (2.2)$$

$$\frac{\partial}{\partial t} \rho \mathbf{v} + \nabla \cdot \rho \mathbf{v} \mathbf{v} = -\nabla p - \nabla \cdot \boldsymbol{\sigma} \quad (2.3)$$

$$\rho \left( \frac{\partial s}{\partial t} + \mathbf{v} \cdot \nabla s \right) = -\nabla \cdot \left( \frac{1}{T} (\mathbf{J}_q - \mu \mathbf{J}) \right) + \frac{1}{T} \boldsymbol{\sigma} : (\nabla \mathbf{v})^\circ - \frac{1}{T^2} (\mathbf{J}_q - \mu \mathbf{J}) \cdot \nabla T - \frac{1}{T} \mathbf{J} \cdot \nabla \mu \quad (2.4)$$

where  $p$  is the hydrostatic pressure,  $\boldsymbol{\sigma}$  is the viscous tensor,  $T$  is the local temperature,  $\mathbf{J}_q$  is the heat flux,  $\mu = \mu_1/m_1 - \mu_2/m_2$  is the chemical potential for the mixture,  $\mathbf{J}$  is the diffusion flux and  $(\ )^\circ$  denotes a symmetric traceless tensor.

The balance equations are completed with the usual constitutive equations for the fluxes in the system [13], namely,

$$\mathbf{J} = -\rho D \left( \frac{k_p}{p} \nabla p + \frac{k_T}{T} \nabla T + \nabla c \right) \quad (2.5)$$

$$\mathbf{J}_q - \mu \mathbf{J} = -\lambda \nabla T - \rho D (k_T \mu_c - T \mu_T) \left( \frac{k_p}{p} \nabla p + \frac{k_T}{T} \nabla T + \nabla c \right) \quad (2.6)$$

$$\boldsymbol{\sigma} = -2\eta (\nabla \mathbf{v})^\circ - \zeta (\nabla \cdot \mathbf{v}) \mathbf{I} \quad (2.7)$$

where the transport coefficients are the shear viscosity  $\eta$ , the bulk viscosity  $\zeta$ , the thermal conductivity  $\lambda$ , the diffusion coefficient  $D$ , the thermodiffusion ratio  $k_T$  and the barodiffusion  $k_p = p(\partial \mu / \partial p)_{T,c} (\partial \mu / \partial c)_{p,T}^{-1}$ .

As a second step, the set of equations are solved for the steady state given by a fixed temperature gradient. The solution has the following characteristics:

- (i) the steady state temperature is  $T_{ss} = T_0 + \mathbf{r} \cdot (\nabla T)_0$ ;
- (ii) the pressure turns out to be constant in the steady state and the hydrodynamic velocity is zero;

(iii) the diffusion flux in the steady state  $J_{ss} = 0$ , implying that there is a concentration gradient in the system, coupled with the temperature gradient and given by

$$(\nabla c)_0 = -\frac{k_T}{T}(\nabla T)_0 \tag{2.8}$$

(iv) the density, chemical potential and entropy gradients are related to the temperature gradient by means of the corresponding equations of state and the condition (2.8), namely,

$$\begin{aligned} (\nabla \rho)_0 &= -\rho_0 \left( \gamma_T + \frac{k_T \gamma_c}{T} \right) (\nabla T)_0 \\ (\nabla \mu)_0 &= \left( \mu_T - \frac{k_T \mu_c}{T} \right) (\nabla T)_0 \\ (\nabla s)_0 &= \frac{1}{T} (c_p + \mu_T k_T) (\nabla T)_0. \end{aligned} \tag{2.9}$$

Here we have defined the following quantities:

$$\rho_0 \gamma_T = -\left( \frac{\partial \rho}{\partial T} \right)_{p,c} \quad \rho_0 \gamma_c = -\left( \frac{\partial \rho}{\partial c} \right)_{p,T} \quad \mu_T = \left( \frac{\partial \mu}{\partial T} \right)_{p,c} \quad \mu_c = \left( \frac{\partial \mu}{\partial c} \right)_{p,T}.$$

Let us now denote by  $j$ ,  $q_1$  and  $\tau$  the fluctuating parts of the fluxes in equations (2.5)-(2.7). In the third step we assume that their direct and cross-correlation functions are Gaussian delta-correlated noises, with their correlation functions given by [9, 10]

$$\begin{aligned} \langle \tau_{ij}(\mathbf{r}, t) \tau_{lm}(\mathbf{r}', t') \rangle \\ = 2K_B T [\eta (\delta_{il} \delta_{jm} + \delta_{im} \delta_{jl}) + (\zeta - \frac{2}{3} \eta) \delta_{ij} \delta_{lm}] \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \end{aligned} \tag{2.10}$$

$$\langle j_l(\mathbf{r}, t) j_m(\mathbf{r}', t') \rangle = 2K_B T \frac{\rho_0 D}{\mu_c} \delta_{lm} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \tag{2.11}$$

$$\begin{aligned} \langle q_{1i}(\mathbf{r}, t) q_{1j}(\mathbf{r}', t') \rangle \\ = 2K_B T \left( T\lambda + \frac{\rho_0 D}{\mu_c} (k_T \mu_c - T\mu_T)^2 \right) \delta_{ij} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \end{aligned} \tag{2.12}$$

$$\langle j_l(\mathbf{r}, t) q_{1m}(\mathbf{r}', t') \rangle = 2K_B T \frac{\rho_0 D}{\mu_c} (k_T \mu_c - T\mu_T) \delta_{lm} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \tag{2.13}$$

$$\langle \tau_{il}(\mathbf{r}, t) j_m(\mathbf{r}', t') \rangle = \langle \tau_{il}(\mathbf{r}, t) q_{1m}(\mathbf{r}', t') \rangle = 0. \tag{2.14}$$

The correlation functions written above are the same as in equilibrium. This is a hypothesis commonly made [1] and it is based on the fact that the correlation length of the fluxes is very small, so they do not feel the influence of the fixed external gradient. The above correlation functions are needed in the wavevector space, thus implying that the temperature to be taken in the fluctuation dissipation theorem will be an average temperature, as is usually done [3, 8].

### 3. Linearized equations

The set of equations established in the last section are now ready to be linearized around the steady state. In this process the temperature gradient and the quantities proportional to it are considered to be of zeroth order in the fluctuations. Following standard procedures and straightforward steps to take the Fourier transforms of the

ensuing linearized equations and separating the transverse  $v^i(\mathbf{k}, \omega)$  and the longitudinal  $\tilde{v}^i(\mathbf{k}, \omega)$  parts of the velocity, we obtain a set of equations given as follows,

$$i\omega\tilde{\rho} - ik\rho_0\tilde{v}^i + (\nabla\rho)_0 \circ v^i = 0 \quad (3.1)$$

$$\frac{Dk_p}{p} k^2 \tilde{p} + \frac{Dk_T}{T} k^2 \tilde{T} + (i\omega + Dk^2) \tilde{c} + (\nabla c)_0 \circ v^i = \frac{1}{\rho_0} i\hat{\mathbf{k}} \circ \tilde{\mathbf{j}} \quad (3.2)$$

$$-\frac{ik}{\rho_0} \tilde{p} + (i\omega + \nu_1 k^2) \tilde{v}^i = \frac{ik}{\rho_0} \hat{\mathbf{k}} \hat{\mathbf{k}} : \tilde{\boldsymbol{\tau}} \quad (3.3)$$

$$\rho_0(i\omega + \nu_1 k^2) v^i = (i\mathbf{k} \circ \tilde{\boldsymbol{\tau}}) \circ (1 - \hat{\mathbf{k}} \hat{\mathbf{k}}) \quad (3.4)$$

$$\begin{aligned} & \left( -\frac{T\gamma_T}{\rho_0 c_p} i\omega + \frac{Dk_p}{c_p \rho_0} (k_T \mu_c - T\mu_T) k^2 \right) \tilde{p} + \left( i\omega + \chi k^2 + \frac{Dk_T}{c_p T} (k_T \mu_c - T\mu_T) k^2 \right) \tilde{T} \\ & + \left( -\frac{T\mu_T}{c_p} i\omega + \frac{D}{c_p} (k_T \mu_c - T\mu_T) k^2 \right) \tilde{c} + \frac{T}{c_p} (\nabla s)_0 \circ v^i \\ & = \frac{i\hat{\mathbf{k}} \circ \mathbf{q}_1}{\rho_0 c_p} - \frac{1}{\rho_0 c_p} \tilde{\mathbf{j}} \circ (\nabla \mu)_0 \end{aligned} \quad (3.5)$$

where  $\nu_1 = \eta/\rho_0$ ,  $\nu_1 = 1/\rho_0(\frac{4}{3}\eta + \zeta)$ ,  $\hat{\mathbf{k}}$  is the unitary wavevector, and  $k = |\mathbf{k}|$ , the wavevector magnitude.

To simplify the calculations we have taken the case in which the temperature gradient and the wavevector are perpendicular to each other, so  $\hat{\mathbf{k}} \circ (\nabla T)_0 = 0$ .

The transverse part of the velocity is decoupled as shown in equation (3.4), and it is easily eliminated from the set of equations. Notice further that the terms in which the transverse mode appears are coupled with the gradients in the steady state, and they will carry the contribution of the temperature and concentration gradients to the structure factor.

The linearized equations are then written in matrix form,

$$\mathbf{M}(\mathbf{k}, \omega) \mathbf{A}(\mathbf{k}, \omega) = \mathbf{F}(\mathbf{k}, \omega) \quad (3.6)$$

where  $\mathbf{A}(\mathbf{k}, \omega)$  represents a column matrix containing the fluctuations of hydrodynamic variables,

$$\mathbf{A}_1 = \tilde{p}(\mathbf{k}, \omega) \quad \mathbf{A}_2 = \tilde{T}(\mathbf{k}, \omega) \quad \mathbf{A}_3 = \tilde{c}(\mathbf{k}, \omega) \quad (\mathbf{A}_4 = \tilde{v}^i(\mathbf{k}, \omega)) \quad (3.7)$$

and  $\mathbf{F}(\mathbf{k}, \omega)$  contains the fluctuating fluxes

$$\mathbf{F}_1(\mathbf{k}, \omega) = -\frac{(i\mathbf{k} \circ \boldsymbol{\tau}(\mathbf{k}, \omega)) \circ (1 - \hat{\mathbf{k}} \hat{\mathbf{k}}) \circ (\nabla \rho)_0}{\rho_0^2 \gamma_T (i\omega + \nu_1 k^2)} \quad (3.8)$$

$$\mathbf{F}_2(\mathbf{k}, \omega) = \frac{1}{\rho_0} i\mathbf{k} \circ \tilde{\mathbf{j}}(\mathbf{k}, \omega) - \frac{(i\mathbf{k} \circ \boldsymbol{\tau}(\mathbf{k}, \omega)) \circ (1 - \hat{\mathbf{k}} \hat{\mathbf{k}}) \circ (\nabla c)_0}{\rho_0 (i\omega + \nu_1 k^2)} \quad (3.9)$$

$$\mathbf{F}_3(\mathbf{k}, \omega) = \frac{ik}{\rho_0} \hat{\mathbf{k}} \hat{\mathbf{k}} : \boldsymbol{\tau}(\mathbf{k}, \omega) \quad (3.10)$$

$$\mathbf{F}_4(\mathbf{k}, \omega) = \frac{i\hat{\mathbf{k}} \circ \mathbf{q}_1(\mathbf{k}, \omega)}{\rho_0 c_p} - \frac{1}{\rho_0 c_p} \mathbf{j}(\mathbf{k}, \omega) \circ (\nabla \mu)_0 - \left( \frac{\gamma_c}{\gamma_T} - \frac{T\mu_T}{c_p} \right) \frac{(i\mathbf{k} \circ \boldsymbol{\tau}) \circ (1 - \hat{\mathbf{k}} \hat{\mathbf{k}}) \circ (\nabla c)}{\rho_0 (i\omega + \nu_1 k^2)} \quad (3.11)$$

where  $\mathbf{M}(\mathbf{k}, \omega)$  is the hydrodynamic matrix, given by

$$\begin{aligned}
 \mathbf{M}_{11} &= \frac{\gamma_p}{\gamma_T} i\omega & \mathbf{M}_{12} &= -i\omega & \mathbf{M}_{13} &= \frac{\gamma_c}{\gamma_T} i\omega & \mathbf{M}_{14} &= -\frac{ik}{\gamma_T} \\
 \mathbf{M}_{21} &= \frac{Dk_p}{\rho} k^2 & \mathbf{M}_{22} &= \frac{Dk_T}{T} k^2 & \mathbf{M}_{23} &= (i\omega + Dk^2) & \mathbf{M}_{24} &= 0 \\
 \mathbf{M}_{31} &= -\frac{ik}{\rho_0} & \mathbf{M}_{32} &= 0 & \mathbf{M}_{33} &= 0 & \mathbf{M}_4 &= (i\omega + \nu_1 k^2) \\
 \mathbf{M}_{41} &= \left( \frac{\gamma_p}{\gamma_T} - \frac{T\gamma_T}{\rho_0 c_p} \right) i\omega + \frac{Dk_p}{\rho c_p} (k_T \mu_c - T\mu_T) k^2 \\
 \mathbf{M}_{42} &= \left( \chi + \frac{Dk_T}{T c_p} (k_T \mu_c - T\mu_T) \right) k^2 \\
 \mathbf{M}_{43} &= \left( \frac{\gamma_c}{\gamma_T} - \frac{T\mu_T}{c_p} \right) i\omega + \frac{D}{c_p} (k_T \mu_c - T\mu_T) k^2 \\
 \mathbf{M}_{44} &= -\frac{ik}{\gamma_T}.
 \end{aligned} \tag{3.12}$$

In order to calculate the structure factor, we solve the last set of equations for the longitudinal part of the velocity and substitute it in the equation for the density given in (3.1), to obtain

$$\begin{aligned}
 \left( \frac{\rho(\mathbf{k}, \omega)}{\rho_0} \right)_\perp &= \left( \frac{\rho(\mathbf{k}, \omega)}{\rho_0} \right)_{\text{eq}} + \left( \frac{kA}{\gamma_T \omega \Delta} - \frac{1}{i\omega} \right) \frac{(i\mathbf{k} \circ \boldsymbol{\tau}) \circ (1 - \hat{\mathbf{k}}\hat{\mathbf{k}}) \circ (\nabla \rho)_0}{\rho_0^2 \gamma_T (i\omega + \nu_1 k^2)} \\
 &\quad - \frac{k}{\omega \Delta} \left[ B + \left( \frac{\gamma_c}{\gamma_T} - \frac{T\mu_T}{c_p} \right) E \right] \frac{(i\mathbf{k} \circ \boldsymbol{\tau}) \circ (1 - \hat{\mathbf{k}}\hat{\mathbf{k}}) \circ (\nabla c)_0}{\rho_0 (i\omega + \nu_1 k^2)} \\
 &\quad - \frac{kE}{\rho_0 c_p \omega \Delta} \mathbf{j} \circ (\nabla \mu)_0
 \end{aligned} \tag{3.13}$$

where  $(\rho/\rho_0)_{\text{eq}}$  are the fluctuations around the equilibrium state. Here  $A, B, E$  and  $\Delta$  are some functions of the wavevector and the frequency which we avoid writing here. Their full form is given in the appendix.

Equation (3.13) shows in a clear way that the density fluctuations have three different contributions, one coming from the equilibrium fluctuations, the second one coming from the coupling with the transverse part of the velocity and the last one coming from the coupling of the fluctuating diffusion flux and the gradient of the chemical potential in the steady state, which can be expressed in terms of the temperature gradient. This last term has been systematically ignored in previous studies of this problem [8].

#### 4. Structure factor

The calculation of the structure factor is now straightforward. We call  $S_{\text{eq}}$  and  $S_\perp$  the

equilibrium and the steady-state structure factors, respectively, so that

$$S_{\perp} - S_{\text{eq}} = \frac{2KT\eta k^2}{\rho_0^2(\omega^2 + \nu_t^2 k^4)} \left| A_1 \frac{(\nabla \rho)_0}{\rho_0} - \frac{k}{\omega} \frac{B_1}{\Delta} (\nabla c)_0 \right|^2 + \left( \frac{2KT}{\rho_0^2 c_p^2} \right) \left| \frac{kE}{\omega \Delta} \right|^2 \frac{\rho_0 D}{\mu_c} (\nabla \mu)_0 \circ (\nabla \mu)_0. \quad (4.1)$$

We notice that the anomalous part of the structure factor has two main contributions, one of them coming from the coupling between the transverse mode and the temperature gradient, and the last one arises from the coupling between the fluctuating part of the diffusion flux and the temperature gradient.

To better understand this result, we calculate the Rayleigh peak taking the leading terms of equation (4.1) in the poles [12]  $-D_T k^2$  and  $-D'_T k^2$ , where

$$2D_T = \chi + \mathbb{D} - [(\chi + \mathbb{D})^2 - 4\chi D]^{1/2} \\ 2D'_T = \chi + \mathbb{D} + [(\chi + \mathbb{D})^2 - 4\chi D]^{1/2} \quad (4.2)$$

where  $\mathbb{D} = D(1 + (k_T^2 \mu_c / T c_p))$ .

The result for the structure factor in its full form is given in the appendix, where we have included the Brillouin peak contribution.

The analysis of some special cases is particularly illuminating. First of all we consider the case where the binary mixture is a diluted one, the thermodiffusion coefficient is negligible,  $k_T \rightarrow 0$ , but the diffusion and the diffusivity  $\chi = \lambda / \rho_0 C_p$  remain finite.

The Lorentzian widths simplify, so  $D_T$  becomes the diffusion coefficient  $D$ ,  $D'_T$  reduces to the thermal diffusivity  $\chi$ , the concentration gradient disappears and the density and chemical potential gradients simplify to  $(\nabla \rho)_0 = -\rho_0 \gamma_T (\nabla T)_0$  and  $(\nabla \mu)_0 = \mu_T (\nabla T)_0$ , respectively, so that the Rayleigh peak is given by

$$(S_{\perp} - S_{\text{eq}})_{\text{Ra}} = \frac{2KT\gamma_T^2}{\omega^2 + \chi^2 k^4} \left[ \frac{\nu_t k^2}{\rho_0(\omega^2 + \nu_t^2 k^4)} + \frac{\rho_0 D}{\mu_c} \left( \frac{\mu_T}{\rho_0 c_p} \right)^2 \right] (\nabla T)_0 \circ (\nabla T)_0. \quad (4.3)$$

The first term in equation (4.3) coincides with the results of Ronis [3] for a simple fluid, but the second one is present only because our system is a binary mixture. It can be traced back to the coupling between the gradient of the chemical potential in the steady state with the fluctuating part of the diffusion vector. The new term which corrects the  $1/k^4$ -dependent coupling between the transverse viscous mode and the external gradient depends on the diffusion in the mixture and has a  $1/k^2$  dependence but, for a mixture of benzene and carbon tetrachloride, is several orders of magnitude smaller than the first one, so we neglect it.

Lastly, we calculate the integrated intensity of the anomalous Rayleigh part of the spectra, which is given by

$$(\Delta I(k))_{\text{Ra}} = \frac{KT\gamma_T^2}{\rho_0 \chi} \left( \frac{1}{k^4(\nu_t + \chi)} \right) (\nabla T)_0 \circ (\partial T)_0. \quad (4.4)$$

Equation (4.4) also shows the characteristics we mentioned about the structure factor, i.e. the square gradient and the  $1/k^4$  dependence on the wavevector.

The calculation of the Rayleigh peak carried out here can be simplified if we do it at constant pressure. This simplification comes from the fact that the pressure fluctuations do not affect the temperature and concentration fluctuations, but do have

an influence on the Brillouin peaks. The calculation we have done using the density fluctuations seems to be more difficult, but in fact it is not, due to the particular way in which the temperature gradient is coupled. The calculation shows that the main contribution to the Rayleigh peak is indeed produced by temperature fluctuations.

This fact can be shown explicitly by calculating the temperature and concentration fluctuations at constant pressure. The leading terms in the Rayleigh peak are then given by

$$\begin{aligned} & \langle \tilde{T}\tilde{T}^* \rangle_{\perp} - \langle \tilde{T}\tilde{T}^* \rangle_{\text{eq}} \\ &= \frac{2KT}{\rho_0(\omega^2 + D_T^2 k^4)(D_T - D_T^t)^2} \left\{ \frac{D}{\mu_c c_p^2} (D - D_T)^2 (\nabla \mu)_0 \circ (\nabla \mu)_0 + \frac{\nu_t k^2}{\omega^2 + \nu_t^2 k^4} \right. \\ & \quad \times \left[ \left( \frac{T\mu_T}{c_p} (D_T - D) + \frac{Dk_T \mu_c}{c_p} \right) (\nabla c)_0 + \frac{T}{c_p} (D - D_T) (\nabla s)_0 \right]^2 \left. \right\} \end{aligned} \quad (4.5)$$

which in the limiting case of negligible thermal diffusion,  $k_T \rightarrow 0$ , simplifies to equation (4.3) as was expected.

The concentration correlations are given by

$$\begin{aligned} & \langle \tilde{c}\tilde{c}^* \rangle_{\perp} - \langle \tilde{c}\tilde{c}^* \rangle_{\text{eq}} \\ &= \frac{2KT}{\rho_0^2 (D_T^t - D_T)^2 (\omega^2 + D_T^2 k^4)} \left\{ \frac{\rho_0 D}{\mu_c} \left( \frac{Dk_T}{\rho_0 c_p T} \right)^2 (\nabla \mu)_0 \circ (\nabla \mu)_0 + \frac{\eta k^2}{\omega^2 + \nu_t^2 k^4} \right. \\ & \quad \times \left[ \left( -D_T + \chi + \frac{Dk_T}{Tc_p} (k_T \mu_c - T\mu_T) \right) (\nabla c)_0 - \frac{Dk_T}{c_p} (\nabla s)_0 \right]^2 \left. \right\} \end{aligned} \quad (4.6)$$

and the cross-correlations are

$$\begin{aligned} & \langle \tilde{T}\tilde{c}^* \rangle_{\perp} - \langle \tilde{T}\tilde{c}^* \rangle_{\text{eq}} \\ &= \frac{2KT}{(D_T^t - D_T)^2 (\omega^2 + D_T^2 k^4)} \left\{ \frac{\rho_0 D^2 k_T (D - D_T)}{\mu_c (\rho_0 c_p)^2} (\nabla \mu)_0 \circ (\nabla \mu)_0 + \frac{\nu_t k^2}{\omega^2 + \nu_t^2 k^4} \right. \\ & \quad \times \left[ \left( \frac{T\mu_T}{c_p} (D_T - D) + \frac{Dk_T \mu_c}{c_p} \right) (\nabla c)_0 + \frac{T}{c_p} (D - D_T) (\nabla s)_0 \right] \\ & \quad \times \left[ \left( -D_T + \chi + \frac{Dk_T}{Tc_p} (k_T \mu_c - T\mu_T) \right) (\nabla c)_0 - \frac{Dk_T}{c_p} (\nabla s)_0 \right] \left. \right\}. \end{aligned} \quad (4.7)$$

The correlations involving the concentration reduce to zero when the thermal diffusion vanishes.

On the other hand, according to equation (3.13), where we have the density fluctuations we can also calculate the contribution of the Brillouin peaks. This is readily done by taking the leading terms in the poles  $\pm i c_0 k - \Gamma k^2$ , where  $c_0$  is the Laplace sound speed and  $\Gamma$  the sound absorption coefficient in the binary mixture. In fact, the Brillouin peaks have an anomalous contribution due to the coupling of the fluctuating part of the diffusion flux with the chemical potential in the stationary state. It can be written as

$$\left( \frac{S_{\perp} - S_{\text{eq}}}{S_{\text{eq}}} \right)_{\text{Brillouin}} = 2 \left[ \frac{c_0 \gamma_T}{c_p} \left( \mu_T - \frac{k_T}{T} \mu_c \right) \right]^2 \frac{D}{\mu_c \Gamma} \frac{(\nabla T)_0 \circ (\nabla T)_0}{k^2}. \quad (4.8)$$



It should be noticed that we are considering the case where the temperature gradient and the wavevector are perpendicular. This means that we cannot obtain the asymmetry of Brillouin peaks, but instead we have a resonant coupling between diffusion fluctuations and the external gradient. This contribution is not present for a simple fluid, and for the mixture it is in fact very small.

To compare with some papers in the literature, we must say that a similar calculation was done by the Maryland group [8]. They also started with the fluctuating hydrodynamics equations, but their set is somewhat different to ours producing a slightly modified result. Let us try to explain the difference. The construction of fluctuating hydrodynamics equations begins with the balance equations completed with the usual constitutive relationships. Thereafter those equations become stochastic by adding the fluctuating parts of the fluxes, characterized as Gaussian white noises. The next step is the linearization of the set around the steady state. It seems that we agree in all steps so far, except in the entropy balance equation, in which we have an extra term coming from the product of the fluctuating diffusion flux and the external gradient of the chemical potential. Clearly, this term must be considered because it is linear in the fluctuations and of zeroth order in the steady-state quantities. It is precisely this contribution which makes the difference in the equations and accounts for the additional terms in the structure factor.

In the literature [8] mention has been made of the fact that the enhancement produced by the resonant viscoheat coupling is found to increase the Rayleigh peak about 60 times for a 0.5 fraction mixture of benzene and carbon tetrachloride with a scattering vector of  $2000 \text{ cm}^{-1}$  and  $100 \text{ K cm}^{-1}$  for the temperature gradient. The additional term derived here, namely the second term within brackets in equation (4.3), was evaluated using the available experimental values for the transport coefficients involved there, assuming that the mixture is ideal. Although we have used crude approximations, one finds that its value is several orders of magnitude smaller than the  $\nu_i k^2$  contribution so that it may be completely neglected.

In spite of this outcome, our calculation allowed us to obtain an expression for the density fluctuations and study the contribution of temperature fluctuations, when we take the constant pressure approximation to understand the difference in the two approaches mentioned above. Also, the density fluctuations show that the behaviour of the Brillouin peaks confirms that they are not affected by the viscoheat resonant coupling, a result that, although expected, had not been clearly pointed out in previous treatments of the problem.

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### Appendix

In this appendix we give the definitions of the functions we used in the calculation of density fluctuations:

$$A(\mathbf{k}, \omega) = \frac{ik^3}{\rho_0} \left[ i\omega \frac{Dk_T}{T} \left( \frac{\gamma_c}{\gamma_T} - \frac{k_T \mu_c}{c_p} \right) - \chi(i\omega + Dk^2) \right]$$

$$B(\mathbf{k}, \omega) + \left( \frac{\gamma_c}{\gamma_T} - \frac{T\mu_T}{c_p} \right) E(\mathbf{k}, \omega) = -\frac{k^3 \omega}{\rho_0} \left[ -\frac{\gamma_c}{\gamma_T} \chi + D \left( 1 + \frac{\gamma_c k_T}{\gamma_T T} \right) \left( \frac{\gamma_c}{\gamma_T} - \frac{k_T \mu_c}{c_p} \right) \right]$$

$$E(\mathbf{k}, \omega) = -\frac{k\omega}{\rho_0} \left[ i\omega + Dk^2 \left( 1 + \frac{\gamma_c k_T}{\gamma_T T} \right) \right]$$

$$A_1(\mathbf{k}, \omega) = \frac{kA(\mathbf{k}, \omega)}{\gamma_T \omega \Delta} - \frac{1}{i\omega}$$

$$B_1(\mathbf{k}, \omega) = B(\mathbf{k}, \omega) + \left( \frac{\gamma_c}{\gamma_T} - \frac{T\mu_T}{c_p} \right) E(\mathbf{k}, \omega).$$

The full form for the structure factor is given by

$$\begin{aligned} (S_{\perp} - S_{eq})_{Ra} &= \frac{2KTv_1 k^2}{\rho_0(\omega^2 + v_1^2 k^4)(D'_T - D_T)^2} \left\{ \alpha_1 \frac{(\nabla\rho)_0}{\rho_0} - \alpha_2 \gamma_T (\nabla c)_0 \right\}^2 \\ &\times \frac{1}{(\omega^2 + D_T^2 k^4)} + 2KT \left( \frac{\gamma_T}{\rho_0 c_p} \right)^2 \frac{\rho_0 D}{\mu_c} \alpha_1^2 \frac{(\nabla\mu)_0 \circ (\nabla\mu)_0}{(D'_T - D_T)^2 (\omega^2 + D_T^2 k^4)} \\ &+ (\text{two similar terms which are obtained changing } D_T \text{ by } D'_T) \\ \alpha_1 &= -D_T + D \left( 1 + \frac{\gamma_c k_T}{\gamma_T T} \right) \\ \alpha_2 &= \left[ -\frac{\gamma_c}{\gamma_T} \chi + D \left( 1 + \frac{\gamma_c k_T}{\gamma_T T} \right) \left( \frac{\gamma_c}{\gamma_T} - \frac{k_T \mu_c}{c_p} \right) \right]. \end{aligned}$$

$\Delta(\mathbf{k}, \omega)$  is the determinant of the hydrodynamic matrix given in equation (3.12).

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