

# Light-scattering spectrum of a viscoelastic fluid subjected to an external temperature gradient

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Recibido el 19 de marzo de 2001; aceptado el 30 de abril de 2001

The light-scattering spectrum for a Maxwell fluid in a steady state due to the presence of an external temperature gradient is computed. In such a fluid heat conduction is assumed to be governed by the classical Fourier law. The calculation is carried out through the use of fluctuating hydrodynamics. The effect of the non-Newtonian character of the fluid in the resulting spectrum is discussed.

*Keywords:* Fluctuating hydrodynamics; nonequilibrium steady states; Maxwell fluid; dynamic structure factor

Se calcula el espectro de dispersión de luz para un fluido de Maxwell en un estado estacionario debido a la presencia de un gradiente de temperatura externo. Se supone que en el fluido la conducción de calor está regida por la ley de Fourier clásica. El cálculo se lleva a cabo usando la hidrodinámica fluctuante. Se discute el efecto del carácter no newtoniano del fluido sobre el espectro resultante.

*Descriptores:* Hidrodinámica fluctuante; estados estables fuera de equilibrio; fluido de Maxwell; factor de estructura dinámica.

PACS: 05.70.Ln; 83.60.Bc; 78.35+c

## 1. Introduction

When light passes through a fluid, correlations over space and time in the density fluctuations are responsible for the scattering of light. In fact, the dynamic structure factor  $S(\mathbf{k}, \omega)$ , which is the space-time Fourier transform of the space-time correlations of density fluctuations in the fluid [1], reflects the strength of the exchanges of energy and momentum between a light beam and the fluid as a function of wavevector  $\mathbf{k}$  and frequency  $\omega$ . For a one-component newtonian fluid in equilibrium, the theory for  $S(\mathbf{k}, \omega)$  was first given correctly in 1934 by Landau and Placzek [2] and later rederived using fluctuating hydrodynamics [3] and the approach advocated by Mountain [4–6]. In fluctuating hydrodynamics, random fluxes are added to the hydrodynamic equations (linearized about equilibrium) which then appear as stochastic equations of the Langevin type. The fluctuation-dissipation theorem provides a connection between the spectrum of spontaneous fluctuations in thermal equilibrium and the transport properties of the system. In contrast, the dynamic structure factor in Mountain's work is derived directly from the linearized hydrodynamic equations without resorting to any kind of fluctuating term added to the constitutive equations. It is worthwhile to note here that both routes lead to the same results and that these results have been confirmed many times by light scattering measurements in various systems.

For nonequilibrium fluctuations in newtonian fluids, the theory was developed rather more recently [7–18] and the few

available experiments seem also to confirm its validity at least for situations out of but not too far from equilibrium [19–21]. The extension of fluctuating hydrodynamics to steady states is made on the basis of the simple hypothesis that the fast degrees of freedom behave as “if they were in local equilibrium at the value of the thermodynamic parameters determined from the solution to the steady state problem” [11]. With this statement it is assumed that the statistics of the stochastic forces behaves as if they were within a local equilibrium environment around each point  $\mathbf{r}$  of the system [14]. It is usual under this hypothesis to rewrite the correlation functions of the stochastic fluxes by substituting the equilibrium thermodynamic properties and transport coefficients by their space dependent values. Another way to see this assumption is based on the Markov property: the random fluxes are not affected by the applied gradients since the correlation length is of microscopic order [18].

Studies of fluctuations in non-newtonian fluids are also relatively abundant. Some of these systems have also been described under the scope of linear Langevin approaches, as is the case of viscoelastic fluids near equilibrium states [22], suspensions in viscoelastic fluids under density and velocity gradients [17] and colloidal suspensions including memory effects [18]. On the other hand, there are many treatments *à la Mountain* in this kind of fluids as well [23–26]. Among these, although at the time meant in a different context, we want to mention here explicitly the study of (equilibrium) Rayleigh-Brillouin scattering in polyatomic fluids within an extended

irreversible thermodynamic treatment [24] carried out by López de Haro, Rodríguez and García-Colín a few years ago [25]. There, no explicit emphasis on the non-newtonian character of the fluid was made, although of course the evolution equations for the trace and the symmetric traceless part of the stress tensor clearly imply this character. More recently, Vázquez and López de Haro [27] have shown the equivalence of the computation of the equilibrium dynamic structure factor of a Maxwell fluid both using fluctuating hydrodynamics and Mountain’s approach. It is a major aim of the present paper to profit from the results of these previous works and to generalize them to the case where the fluid is subjected to an external temperature gradient. The idea is to assess to what extent non-newtonian effects, which have been considered negligible in actual experiments, do affect the light-scattering spectrum.

The paper is organized as follows. In Sect. II we compute the equilibrium dynamic structure factor of a Maxwell fluid in which thermal conduction is governed by Fourier’s law. This is done using fluctuating hydrodynamics. Sec. III deals with the same fluid which has now been brought to a steady state by the action of an externally imposed temperature gradient. Here we compute the light-scattering spectrum with the aid of the extension of fluctuating hydrodynamics to nonequilibrium steady states. The paper is closed in Sec. IV with a discussion and some concluding remarks.

### 2. Dynamic structure factor for a Maxwell fluid in equilibrium

We here first analyze the case of a Maxwell fluid in equilibrium in which heat conduction is governed by the classical Fourier law. For this case, the corresponding full hydrodynamic equations (written in terms of the density, velocity and entropy density of the fluid denoted by  $\rho, \mathbf{v}$  and  $s$ , respectively) are the continuity equation, the momentum balance equation and the energy balance equation, namely

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

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p - \nabla \cdot \overleftrightarrow{\tau}, \tag{2}$$

and

$$\rho T \frac{\partial s}{\partial t} + \rho T \mathbf{v} \cdot \nabla s = -\nabla \cdot \mathbf{q} - \overleftrightarrow{\tau} : \nabla \mathbf{v}, \tag{3}$$

which must be complemented with the constitutive equations for the heat flux vector  $\mathbf{q}$  and the stress tensor  $\overleftrightarrow{\tau}$ . These equations in our case read

$$\mathbf{q} = -\lambda \nabla T \tag{4}$$

and

$$-\tau_r \frac{\partial \overleftrightarrow{\tau}}{\partial t} - \tau_r \mathbf{v} \cdot \nabla \overleftrightarrow{\tau} = \overleftrightarrow{\tau} + 2\eta \overset{\circ}{\nabla} \mathbf{v} + \eta_v (\nabla \cdot \mathbf{v}) \overleftrightarrow{\mathbb{1}}. \tag{5}$$

Here,  $p$  is the hydrostatic pressure,  $T$  is the temperature,  $\eta$  is the shear viscosity,  $\eta_v$  is the bulk viscosity,  $C_\rho$  is the constant density heat capacity,  $\lambda$  is the thermal conductivity,  $\overleftrightarrow{\mathbb{1}}$  is the unit tensor,  $\overset{\circ}{\nabla} \mathbf{v} = [\nabla \mathbf{v} + (\nabla \mathbf{v})^T]/2 - \nabla \cdot \mathbf{v} \overleftrightarrow{\mathbb{1}}/3$  stands for the symmetric and traceless part of the velocity gradient and  $\tau_r$  is the Maxwell relaxation time. In Eq. (2) one can eliminate the hydrostatic pressure in favor of  $\rho$  and  $s$  using the fact that  $\nabla p = -c^2 \nabla \rho + T \alpha \nabla s / C_\rho \kappa_T$  (where  $c$  is the adiabatic speed of sound in the fluid,  $\alpha$  is the thermal expansion coefficient and  $\kappa_T$  is the isothermal compressibility) but the form we have chosen will prove convenient later on. Note also that on the left hand side of Eq. (5) we have considered the usual material time derivative rather than the corrotational time derivative. Although the latter choice would be more satisfactory from the rheological point of view, Eq. (5) represents the simplest form of the Maxwell model. In any case, since later on we will retain only the linear terms, the use of the material time derivative will not imply loss of generality.

We consider for simplicity the case where  $\alpha = 0$  (which implies that  $C_\rho = C_p$ , where  $C_p$  is the constant pressure heat capacity) and take  $\eta, \eta_v, c, \lambda, C_\rho$  and  $\tau_r$  to be constant. Let a subscript zero refer to the equilibrium value and a subscript one denote the (small) deviation from equilibrium, so that  $\rho = \rho_0 + \rho_1, \mathbf{v} = \mathbf{v}_1, s = s_0 + s_1, T = T_0 + T_1$  and  $\overleftrightarrow{\tau} = \overleftrightarrow{\tau}_1$ . Keeping only linear contributions in the deviations, one gets from Eqs. (1), and (2)–(5)

$$\frac{\partial \rho_1}{\partial t} = -\rho_0 \nabla \cdot \mathbf{v}_1, \tag{6}$$

$$\rho_0 \frac{\partial \mathbf{v}_1}{\partial t} = -c^2 \nabla \rho_1 - \nabla \cdot \overleftrightarrow{\tau}_1, \tag{7}$$

$$\rho_0 T_0 \frac{\partial s_1}{\partial t} = \lambda \nabla^2 T_1, \tag{8}$$

and

$$-\tau_r \frac{\partial \overleftrightarrow{\tau}_1}{\partial t} = \overleftrightarrow{\tau}_1 + 2\eta \overset{\circ}{\nabla} \mathbf{v}_1 + \eta_v (\nabla \cdot \mathbf{v}_1) \overleftrightarrow{\mathbb{1}}. \tag{9}$$

Within fluctuating hydrodynamics [3], stochastic contributions  $\overleftrightarrow{\sigma}$  and  $\mathbf{g}$  are added to the momentum and heat fluxes, respectively. At this stage it is convenient to work in Fourier space. Denoting by an upper tilde the space and time Fourier transform of a given quantity, the linearized continuity, momentum and energy equations in  $(\mathbf{k}, \omega)$ -space (with  $\mathbf{k}$  the wavevector and  $\omega$  the frequency) are written as

$$-i\omega \tilde{\rho}_1 = -i\rho_0 \mathbf{k} \cdot \tilde{\mathbf{v}}_1, \tag{10}$$

$$-i\omega \rho_0 \tilde{\mathbf{v}}_1 = -ic^2 \mathbf{k} \tilde{\rho}_1 - \frac{(1 + i\omega \tau_r)}{1 + \omega^2 \tau_r^2} \left( \frac{4}{3} \eta + \eta_v \right) k^2 \tilde{\mathbf{v}}_1 - i\mathbf{k} \cdot \overleftrightarrow{\tilde{\sigma}}, \tag{11}$$

and

$$-i\omega \rho_0 T_0 \tilde{s}_1 = -\lambda k^2 \tilde{T}_1 - i\mathbf{k} \cdot \tilde{\mathbf{g}}. \tag{12}$$

Note that in writing Eq. (11) we have made use of the  $(\mathbf{k}, \omega)$ -space version of Eq. (9), namely

$$\overleftrightarrow{\tau}_1 = -\frac{(1 + i\omega\tau_r)}{1 + \omega^2\tau_r^2} \left[ 2i\eta \overset{\circ}{\mathbf{k}} \tilde{\mathbf{v}}_1 + i\eta_v \mathbf{k} \cdot \tilde{\mathbf{v}}_1 \overset{\circ}{\mathbf{1}} \right]. \tag{13}$$

In order to close the fluctuating hydrodynamics approach, we now require the corresponding fluctuation-dissipation relations. Since in the  $(\mathbf{r}, \omega)$ -space it follows from Eq. (9) that

$$\overleftrightarrow{\tau}_1(\mathbf{r}, \omega) = -\frac{(1 + i\omega\tau_r)}{1 + \omega^2\tau_r^2} \left\{ 2\eta \overset{\circ}{\nabla} \mathbf{v}_1(\mathbf{r}, \omega) + \eta_v [\nabla \cdot \mathbf{v}_1(\mathbf{r}, \omega)] \overset{\circ}{\mathbf{1}} \right\} \equiv 2\eta^D(\omega) \overset{\circ}{\nabla} \mathbf{v}_1(\mathbf{r}, \omega) + \eta_v^D(\omega) [\nabla \cdot \mathbf{v}_1(\mathbf{r}, \omega)] \overset{\circ}{\mathbf{1}}, \tag{14}$$

*i.e.* in the frequency domain the Maxwell model implies a *linear* relationship between the stress tensor and the thermodynamic forces but with dispersive transport coefficients,  $\eta^D(\omega)$  and  $\eta_v^D(\omega)$  being the dispersive (complex and frequency-dependent) transport coefficients, then following Landau and Lifshitz [3] the fluctuation-dissipation relations read

$$\langle \tilde{g}_i(\mathbf{k}, \omega) \tilde{g}_j^*(\mathbf{k}', \omega') \rangle = 2k_B T_0^2 (2\pi)^4 \lambda \delta_{ij} \delta^3(\mathbf{k} - \mathbf{k}') \delta(\omega - \omega'), \tag{15}$$

$$\langle \tilde{\sigma}_{ij}(\mathbf{k}, \omega) \tilde{\sigma}_{lm}^*(\mathbf{k}', \omega') \rangle = \frac{2k_B T_0}{1 + \omega^2\tau_r^2} (2\pi)^4 \left[ 2\eta \Delta_{ijklm} + \left( \eta_v - \frac{2}{3}\eta \right) \delta_{ij} \delta_{lm} \right] \delta^3(\mathbf{k} - \mathbf{k}') \delta(\omega - \omega'), \tag{16}$$

and

$$\langle \tilde{\sigma}_{ij}(\mathbf{k}, \omega) \tilde{g}_l^*(\mathbf{k}', \omega') \rangle = \langle \tilde{\sigma}_{ij}(\mathbf{k}, \omega) \rangle = \langle \tilde{g}_l(\mathbf{k}, \omega) \rangle = 0, \tag{17}$$

the angular brackets denoting an (equilibrium) ensemble average over the initial states of the system, the asterisk meaning complex conjugation and  $\Delta_{ijklm} = (\delta_{il}\delta_{jm} + \delta_{im}\delta_{jl})/2$ ,  $\delta_{rs}$  being the Kronecker delta.

Note that the energy equation within the present approximation is decoupled from both the continuity equation and the momentum balance equation. Since the dynamic structure factor  $S(\mathbf{k}, \omega)$  is related to the density-density correlation function through

$$\langle \tilde{\rho}_1(\mathbf{k}, \omega) \tilde{\rho}_1^*(\mathbf{k}', \omega') \rangle \equiv (2\pi)^4 \delta^3(\mathbf{k} - \mathbf{k}') \delta(\omega - \omega') S_B^{\text{eq}}(\mathbf{k}, \omega), \tag{18}$$

the subscript  $B$  having been introduced to stress the fact that, within the present approximation, it will give the Brillouin spectrum, and since from Eqs. (10), (11) and (16) it follows that

$$\langle \tilde{\rho}_1(\mathbf{k}, \omega) \tilde{\rho}_1^*(\mathbf{k}', \omega') \rangle = (2\pi)^4 \delta^3(\mathbf{k} - \mathbf{k}') \delta(\omega - \omega') \times \frac{2k_B T_0 (1 + \omega^2\tau_r^2) \left( \frac{4}{3}\eta + \eta_v \right) k^4}{\left[ (\omega^2 - c^2 k^2)(1 + \omega^2\tau_r^2) - \omega^2 \frac{\tau_r}{\rho_0} \left( \frac{4}{3}\eta + \eta_v \right) k^2 \right]^2 + \frac{\omega^2}{\rho_0^2} \left( \frac{4}{3}\eta + \eta_v \right)^2 k^4}, \tag{19}$$

one readily identifies

$$S_B^{\text{eq}}(\mathbf{k}, \omega) = \frac{2k_B T_0 (1 + \omega^2\tau_r^2) \left( \frac{4}{3}\eta + \eta_v \right) k^4}{\left[ (\omega^2 - c^2 k^2)(1 + \omega^2\tau_r^2) - \omega^2 \frac{\tau_r}{\rho_0} \left( \frac{4}{3}\eta + \eta_v \right) k^2 \right]^2 + \frac{\omega^2}{\rho_0^2} \left( \frac{4}{3}\eta + \eta_v \right)^2 k^4}. \tag{20}$$

The spectrum given in Eq. (20) consists of two (symmetric) Brillouin peaks slightly displaced from  $\omega_{\pm} = \pm ck$  and a peak centered at  $\omega_c = 0$ , known as the Mountain peak, whose origin can be ascribed to the viscoelastic character of the fluid [28].

Although in the approximation we have taken of  $\alpha = 0$ , there is no Rayleigh line, if this restriction were avoided, the Rayleigh line, also centered around  $\omega_c = 0$ , would follow from the entropy-entropy correlation function. In any case, since to a first approximation the Rayleigh line is determined by the coupling of the temperature fluctuations to the transverse velocity fluctuations [20], the missing terms (proportional to  $\alpha$ ) in Eqs. (11) and (12) will play no role in the final result. So we compute the entropy-entropy correlation function by manipulating Eqs. (12) and (15). The result is

$$\langle \tilde{s}_1(\mathbf{k}, \omega) \tilde{s}_1^*(\mathbf{k}, \omega) \rangle = S_R^{\text{eq}}(\mathbf{k}, \omega) = \frac{2(2\pi)^4 k_B T_0^2 C_p D_T k^2}{\rho_0 (\omega^2 + D_T^2 k^4)}, \tag{21}$$

where  $D_T = \lambda/\rho_0 C_p$  is the thermal diffusivity and the subscript  $R$  serves to make reference to the connection with the Rayleigh line.

### 3. Fluctuating hydrodynamics and the light-scattering spectrum of a Maxwell fluid under an external temperature gradient

We now examine the same Maxwell fluid in which heat conduction is governed by Fourier's law but in a layer confined between two parallel plates at  $z = +L/2$  and  $z = -L/2$  and of infinite extension in the  $xy$ -plane. In the fluid layer a steady temperature gradient is maintained by fixing the temperatures of the upper and lower planes at different values, namely  $T_1$  at  $z = -L/2$  and  $T_2$  at  $z = +L/2$ . We assume that neither the gravitational force nor any other external forces act on the system. A time-independent solution to Eqs. (1) to (5) leading to a stationary state (denoted by a subscript  $s$ ) for the system satisfies the relations

$$\mathbf{v}_s = \mathbf{0}, \tag{22}$$

$$\nabla p_s = 0, \tag{23}$$

$$\nabla \cdot \mathbf{q}_s = 0. \tag{24}$$

Due to the symmetry of the problem, Eq. (24) together with Eq. (4) leads to

$$\frac{d}{dz} \left( \lambda_s \frac{dT_s}{dz} \right) = \left( \frac{\partial \lambda}{\partial T} \right)_s \left( \frac{dT_s}{dz} \right)^2 + \lambda_s \frac{d^2 T}{dz^2} = 0. \tag{25}$$

For simplicity, let us look at the case where  $\alpha_s = 0$  and take  $\eta_s, \eta_{vs}, c_s, \lambda_s, C_{ps}$  and  $\tau_{rs}$  to be constant. Since  $\lambda_s$  has been assumed to be a constant, it follows from Eq. (25) and the boundary conditions that

$$T_s = T_0 - Az,$$

where

$$T_0 = \frac{T_1 + T_2}{2} = T_s(0),$$

and

$$A = \frac{T_1 - T_2}{L}.$$

Further, the condition implied by Eq. (23) leads to  $\nabla \rho_s = 0$  or  $\rho_s = \rho_0$ , while Eq. (22) implies that  $\vec{\tau}_s = \vec{0}$ . Let a subscript  $1s$  now denote the (small) deviation from the steady state, so that  $\rho = \rho_s + \rho_{1s}$ ,  $\mathbf{v} = \mathbf{v}_s + \mathbf{v}_{1s} = \mathbf{v}_{1s}$ ,  $s = s_s + s_{1s}$ ,  $T = T_s + T_{1s}$ ,  $\mathbf{q} = \mathbf{q}_s + \mathbf{q}_{1s} = -\lambda_s \nabla T_s + \mathbf{q}_{1s}$  and  $\vec{\tau} = \vec{\tau}_s + \vec{\tau}_{1s} = \vec{\tau}_{1s}$ . Keeping only linear contributions

in the deviations, one gets from Eqs. (1)–(5)

$$\frac{\partial \rho_{1s}}{\partial t} = -\rho_s \nabla \cdot \mathbf{v}_{1s}, \tag{26}$$

$$\rho_s \frac{\partial \mathbf{v}_{1s}}{\partial t} = -c_s^2 \nabla \rho_{1s} - \nabla \cdot \vec{\tau}_{1s}, \tag{27}$$

$$\rho_0 T_0 \frac{\partial s_{1s}}{\partial t} + \rho_0 T_0 \mathbf{v}_{1s} \cdot \nabla T_s = -\nabla \cdot \mathbf{q}_{1s}, \tag{28}$$

$$\mathbf{q}_{1s} = -\lambda_s \nabla T_{1s}, \tag{29}$$

and

$$-\tau_{rs} \frac{\partial \vec{\tau}_{1s}}{\partial t} = \vec{\tau}_{1s} + 2\eta_s \nabla \circ \mathbf{v}_{1s} + \eta_{vs} (\nabla \cdot \mathbf{v}_{1s}) \vec{1}. \tag{30}$$

The balance equations in the  $(\mathbf{r}, \omega)$ -domain read

$$-i\omega \rho_{1s} = -\rho_s \nabla \cdot \mathbf{v}_{1s}, \tag{31}$$

$$-i\omega \rho_s \mathbf{v}_{1s} = -c_s^2 \nabla \rho_{1s} - \nabla \cdot \vec{\tau}_{1s}, \tag{32}$$

and

$$-i\omega \rho_0 T_0 s_{1s} + A \rho_0 C_{ps} \mathbf{v}_{1s} \cdot \hat{\mathbf{z}} = -\nabla \cdot \mathbf{q}_{1s}. \tag{33}$$

where  $\hat{\mathbf{z}}$  is a unit vector in the  $z$  direction. We now add fluctuating contributions to the heat flux and stress tensor denoted by  $\mathbf{g}_s$  and  $\vec{\sigma}_s$ , respectively, take the spatial Fourier transform and make use of the stationary state analog of Eq. (14) to arrive at

$$-i\omega \tilde{\rho}_{1s} = -i\rho_s \mathbf{k} \cdot \tilde{\mathbf{v}}_{1s}, \tag{34}$$

$$-i\omega \rho_s \tilde{\mathbf{v}}_{1s} = -ic_s^2 \mathbf{k} \tilde{\rho}_{1s} - \frac{\left( \frac{4}{3} \eta_s + \eta_{vs} \right) (1 + i\omega \tau_{rs}) k^2}{(1 + \omega^2 \tau_{rs}^2)} \tilde{\mathbf{v}}_{1s} - i\mathbf{k} \cdot \tilde{\vec{\sigma}}_s, \tag{35}$$

and

$$-i\omega \rho_0 T_0 \tilde{s}_{1s} = -\rho_0 T_0 D_{Ts} k^2 \tilde{s}_{1s} - i\mathbf{k} \cdot \tilde{\mathbf{g}}_s - A \rho_0 C_{ps} \mathbf{v}_{1s} \cdot \hat{\mathbf{z}}. \tag{36}$$

In order to proceed any further, we require the fluctuation-dissipation relations obeyed by  $\tilde{\mathbf{g}}_s$  and  $\tilde{\vec{\sigma}}_s$ . Under the hypothesis mentioned in the introduction, we follow previous authors in assuming that the fluctuation-dissipation relations have the same form as that for thermal equilibrium, but with the equilibrium temperature replaced by the stationary temperature and the average taken over an stationary ensemble. Thus, restricting to small gradients (linear order in  $A$ ) in our case one gets

$$\langle \tilde{g}_{is}(\mathbf{k}, \omega) \tilde{g}_{js}^*(\mathbf{k}', \omega') \rangle = 2k_B T_0^2 (2\pi)^4 \lambda_s \delta_{ij} \delta(\omega - \omega') \left\{ \delta^3(\mathbf{k} - \mathbf{k}') + \frac{iAL}{T_0} \left[ \delta^3 \left( \mathbf{k} - \mathbf{k}' + \frac{\hat{\mathbf{z}}}{L} \right) - \delta^3 \left( \mathbf{k} - \mathbf{k}' - \frac{\hat{\mathbf{z}}}{L} \right) \right] \right\}, \tag{37}$$

and

$$\langle \tilde{\sigma}_{sij}(\mathbf{k}, \omega) \tilde{\sigma}_{slm}^*(\mathbf{k}', \omega') \rangle = \frac{2k_B T_0}{1 + \omega^2 \tau_r^2} (2\pi)^4 \left[ 2\eta_s \Delta_{ijlm} + \left( \eta_{vs} - \frac{2}{3}\eta_s \right) \delta_{ij} \delta_{lm} \right] \delta(\omega - \omega') \times \left\{ \delta^3(\mathbf{k} - \mathbf{k}') + \frac{iAL}{2T_0} \left[ \delta^3\left(\mathbf{k} - \mathbf{k}' + \frac{\hat{\mathbf{z}}}{L}\right) - \delta^3\left(\mathbf{k} - \mathbf{k}' - \frac{\hat{\mathbf{z}}}{L}\right) \right] \right\}, \quad (38)$$

while

$$\langle \tilde{\sigma}_{sij}(\mathbf{k}, \omega) \tilde{g}_{sl}^*(\mathbf{k}', \omega') \rangle = \langle \tilde{\sigma}_{sij}(\mathbf{k}, \omega) \rangle = \langle \tilde{g}_{sl}(\mathbf{k}, \omega) \rangle = 0. \quad (39)$$

Tremblay, Arai and Siggia [11] have shown that, in a light scattering experiment in which a fluid in a stationary state due to an external temperature gradient is involved,

$$S_B(\mathbf{k}, \omega) \equiv \langle \tilde{\rho}_1(\mathbf{k}, \omega) \tilde{\rho}_1^*(\mathbf{k}, \omega) \rangle + \left\langle \tilde{\rho}_1\left(\mathbf{k} + \frac{\hat{\mathbf{z}}}{2L}, \omega\right) \tilde{\rho}_1^*\left(\mathbf{k} - \frac{\hat{\mathbf{z}}}{2L}, \omega\right) \right\rangle + \left\langle \tilde{\rho}_1\left(\mathbf{k} - \frac{\hat{\mathbf{z}}}{2L}, \omega\right) \tilde{\rho}_1^*\left(\mathbf{k} + \frac{\hat{\mathbf{z}}}{2L}, \omega\right) \right\rangle,$$

is the correlation function of interest for the Brillouin spectrum. By a simple manipulation of Eqs. (34), (35) and (38) it is easy to arrive at

$$S_B(\mathbf{k}, \omega) = S_B^{\text{eq}}(\mathbf{k}, \omega) \left[ 1 - \frac{2\omega^3 D_{ls}(\omega) A(\mathbf{k} \cdot \hat{\mathbf{z}})}{T_0 \{ [\omega^2 - C_s^2(\omega) k^2]^2 + [\omega D_{ls}(\omega) k^2]^2 \}} \right] \simeq \frac{k_B T_0 \rho_0}{C_s^2(\omega)} \frac{D_{ls}(\omega) k^2}{2} \left\{ \frac{1 - \varepsilon(\mathbf{k}, \omega)}{[\omega - C_s(\omega) k]^2 + \frac{1}{4} [D_{ls}(\omega) k^2]^2} + \frac{1 + \varepsilon(\mathbf{k}, \omega)}{[\omega + C_s(\omega) k]^2 + \frac{1}{4} (D_{ls}(\omega) k^2)^2} \right\}, \quad (40)$$

where  $S_B^{\text{eq}}(\mathbf{k}, \omega)$  is given by Eq. (20) and we have identified  $\rho_s = \rho_0, \eta_s = \eta, \eta_{vs} = \eta_v, c_s = c$ , and  $\tau_{rs} = \tau_r$  and introduced the following quantities

$$D_{ls}(\omega) = \frac{4}{3} \frac{\eta + \eta_v}{\rho_0 (1 + \omega^2 \tau_r^2)}, \quad (41)$$

$$C_s(\omega) = [c^2 + \omega^2 \tau_r D_{ls}(\omega)]^{1/2}, \quad (42)$$

and

$$\varepsilon(\mathbf{k}, \omega) = \frac{C_s(\omega) AL(\mathbf{k} \cdot \hat{\mathbf{z}})}{T_0 D_{ls}(\omega) k^2} \times \left\{ \frac{2[\omega D_{ls}(\omega) k^2]^2}{[\omega^2 - C_s^2(\omega) k^2]^2 + [\omega D_{ls}(\omega) k^2]^2} \right\}. \quad (43)$$

It should be pointed out that in order to perform the expansion leading to the approximation appearing in the second line of Eq. (40), apart from the weak gradient assumption (*i.e.*  $|AL|/T_0 \ll 1$ ) it has also been assumed that  $|C_s(\omega)(\mathbf{k} \cdot \hat{\mathbf{z}})/D_{ls}(\omega) k^2| \ll 1$ .

Now we turn to the Rayleigh line. Again the restriction  $\alpha_s = 0$  implies that the spectrum in Eq. (40) contains no Rayleigh line. If such restriction is removed, in order to compute the Rayleigh line one again requires the entropy-entropy correlation function. By the same line of reasoning used in connection with Eq. (21), the missing terms (proportional to  $\alpha_s$ ) in Eqs. (35) and (36) will play no role in the final result. So we proceed with the calculation. From Eq. (36) and

making the identification  $D_{Ts} = D_T$  it follows that

$$\tilde{s}_{1s}(\mathbf{k}, \omega) = \frac{-i\mathbf{k} \cdot \tilde{\mathbf{g}}_s - \frac{AC_p \tilde{\mathbf{v}}_{1s} \cdot \hat{\mathbf{z}}}{T_0}}{-i\omega + D_T k^2}. \quad (44)$$

We only need the transverse velocity fluctuations  $\tilde{v}_{ts}$  which are obtained from  $\tilde{\mathbf{v}}_{1s}$  as

$$\tilde{v}_{ts} = \tilde{\mathbf{v}}_{1s} \cdot \left( \overset{\leftrightarrow}{1} - \widehat{\mathbf{k}}\widehat{\mathbf{k}} \right) \cdot \hat{\mathbf{z}}. \quad (45)$$

It is clear from this last equation that if the scattering vector  $\mathbf{k}$  is taken parallel to the temperature gradient, then  $\tilde{v}_{ts} = 0$ , so there will be no effect on the entropy-entropy correlation function. Therefore we choose  $\mathbf{k} \perp \hat{\mathbf{z}}$ . From Eqs. (35) and (14) it follows that

$$\tilde{v}_{ts} = - \frac{i\mathbf{k} \cdot \tilde{\sigma}_s \cdot \left( \overset{\leftrightarrow}{1} - \widehat{\mathbf{k}}\widehat{\mathbf{k}} \right) \cdot \hat{\mathbf{z}}}{-i\omega \rho_0 + \frac{\eta(1 + i\omega \tau_r) k^2}{(1 + \omega^2 \tau_r^2)}}. \quad (46)$$

Using this expression in Eq. (44) yields

$$\tilde{s}_{1s}(\mathbf{k}, \omega) = \frac{-i\mathbf{k} \cdot \tilde{\mathbf{g}}_s}{\rho_0 T_0 (-i\omega + D_T k^2)} + \frac{iAC_p \mathbf{k} \cdot \tilde{\sigma}_s \cdot \left( \overset{\leftrightarrow}{1} - \widehat{\mathbf{k}}\widehat{\mathbf{k}} \right) \cdot \hat{\mathbf{z}}}{\rho_0 T_0 (-i\omega + D_T k^2) \left[ -i\omega + \frac{\eta(1 + i\omega \tau_r) k^2}{\rho_0 (1 + \omega^2 \tau_r^2)} \right]}. \quad (47)$$

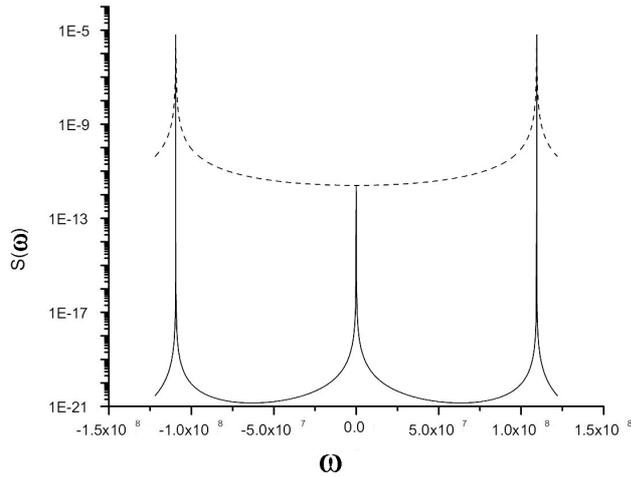


FIGURE 1. Equilibrium light-scattering spectrum as a function of frequency  $\omega$  for a fluid whose thermophysical data correspond to those of toluene at  $T_0 = 277$  K. The scattering wave-number is  $k = 85200 \text{ m}^{-1}$ . (---) represents the results for the newtonian fluid and (—) those of the Maxwell fluid.

Since any asymmetries occur in the  $\hat{z}$  direction, in the scattering plane (which is orthogonal to the temperature

TABLE I. Thermophysical data of toluene as given in Ref. 29.

$\eta = 0.000553 \text{ Pa s}$
$\eta_w = 0.00747 \text{ Pa s}$
$\rho_0 = 861.5 \text{ Kg/m}^3$
$c = 1285 \text{ m/s}$

gradient) spatial and temporal invariance holds. This in turn implies that from the fluctuation-dissipation relations one finds (for  $\mathbf{k}, \mathbf{k}' \perp \hat{z}$ )

$$\langle \mathbf{k} \cdot \tilde{\mathbf{g}}_s(\mathbf{k}, \omega) \mathbf{k}' \cdot \tilde{\mathbf{g}}_s^*(\mathbf{k}', \omega') \rangle = 2k_B T_0^2 (2\pi)^4 \rho_0 C_p D_T k^2 \delta^3(\mathbf{k} - \mathbf{k}') \delta(\omega - \omega'), \quad (48)$$

and

$$\langle \mathbf{k} \cdot \tilde{\tilde{\sigma}}_s \cdot (\hat{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \cdot \hat{z} \cdot \mathbf{k}' \cdot \tilde{\tilde{\sigma}}_s^* \cdot (\hat{1} - \hat{\mathbf{k}}'\hat{\mathbf{k}}') \cdot \hat{z} \sigma \rangle = \frac{2k_B T_0}{1 + \omega^2 \tau_r^2} (2\pi)^4 \eta k^2 \delta^3(\mathbf{k} - \mathbf{k}') \delta(\omega - \omega'). \quad (49)$$

Use of Eqs. (47)–(49) leads finally to

$$\langle \tilde{s}_{1s}(\mathbf{k}, \omega) \tilde{s}_{1s}^*(\mathbf{k}, \omega) \rangle \equiv S_R(\mathbf{k}, \omega) = S_R^{\text{eq}}(\mathbf{k}, \omega) \left\{ 1 + \frac{C_p \frac{\eta}{\rho_0 (1 + \omega^2 \tau_r^2)} A^2}{T_0 D_T \left[ \omega^2 \left( 1 + \frac{\tau_r \eta k^2}{\rho_0 (1 + \omega^2 \tau_r^2)} \right)^2 + \frac{\eta^2 k^4}{\rho_0^2 (1 + \omega^2 \tau_r^2)^2} \right]} \right\}, \quad (50)$$

for ( $\mathbf{k} \perp \hat{z}$ ), with  $S_R^{\text{eq}}(\mathbf{k}, \omega)$  given by Eq. (21). Equations (40) and (50) are the main results of this paper. A brief assessment of their potential use will be carried out in the following Section.

#### 4. Discussion

As a first observation, we note that if the limit  $\tau_r \rightarrow 0$  is taken, then Eqs. (20), (21), (40), and (50) reduce to the well known results for the newtonian fluid (*c.f.* for instance Refs. 5, 11, and 20, as they should). Also, the equilibrium light-scattering spectrum in this paper, Eq. (20), arises as a particular case of the one computed in Ref. 25 provided in the latter the relaxation times of the trace and traceless symmetric part of the stress tensor are both set equal to  $\tau_r$ , the internal degrees of freedom are eliminated and the approximation  $\alpha = 0$  is made. In order to get a picture of the importance of the viscoelastic effects in equilibrium, in Fig. 1 we display the equilibrium spectrum (with  $\alpha = 0$ ) of both the Maxwell fluid and the newtonian fluid. The thermophysical properties, given in Table I, are those of toluene [29], the temperature has been set to  $T_0 = 277$  K, we have taken as wavenumber  $k = 85200 \text{ m}^{-1}$  (which is the value corresponding to a scattering angle of 10 mrad and a wavelength

of 4880 Å) and we have included a very crude estimate of the relaxation time  $\tau_r \sim 10^{-5}$  s of this liquid obtained from Grad's kinetic theory expression.

Concerning the nonequilibrium spectrum again with  $\alpha = 0$ , the presence of the external temperature gradient has a similar effect to the one observed in the newtonian fluids for the Brillouin peaks, as illustrated in Fig. 2. Here we have again used the data corresponding to toluene and taken the gradient to point upwards with  $A = 100 \text{ K/m}$ ,  $L = 0.01 \text{ m}$  and  $T_0 = 277 \text{ K}$ , these latter numbers fulfilling the restrictions involved in our derivation. A noteworthy feature is that the asymmetry in the Brillouin peaks, related to the fact that there are more sound waves absorbed with wavevector  $-\mathbf{k}$  than those emitted with wavevector  $\mathbf{k}$  due to the temperature gradient and its corresponding heat flux, is much more pronounced and the peaks become narrower for the viscoelastic fluid. On the other hand, the Mountain peak is not affected by the temperature gradient. This is a trivial consequence of the fact that the nonequilibrium correction vanishes for  $\omega_c = 0$ .

In conclusion, we want to point out that we have derived (to our knowledge for the first time) the light-scattering spectrum for a Maxwell fluid in a steady state under the action of an external temperature gradient. Although many (reason-

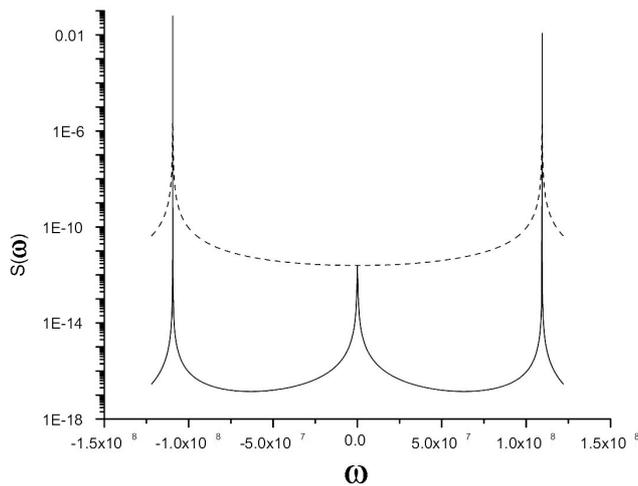


FIGURE 2. Light-scattering spectrum as a function of frequency  $\omega$  for a fluid whose thermophysical data correspond to those of toluene at  $T_0 = 277$  K under the action of an external temperature gradient ( $A = 100$  K/m and  $L = 0.01$  m). The scattering wave-number is  $k = 85200$  m $^{-1}$ . The code is the same as that of Fig. 1.

able) approximations, some of which might be easily disposed of, were made along the way in order to get analytical results, and in spite of the fact that the Maxwell fluid is a very simple model of a viscoelastic fluid, we are persuaded that the present calculation captures the essential (qualitative) features to be observed in light-scattering experiments in connection with the elasticity of fluids. Whether this expectation is real awaits the necessary confrontation with experiment.

## Acknowledgments

This paper is dedicated to Prof. L.S. García-Colín on the occasion of his 70th birthday. We want to stress here our indebtedness to him for his many generous contributions to our academic careers. The work of two of us (M.L.H. and J.A.R.P.) has been partially supported by DGAPA-UNAM under project IN-107798. F.V. acknowledges the partial financial support by PROMEP-UAEM. Thanks are also due to Prof. Jan V. Sengers whose work and a very fruitful conversation a few years ago served as a motivation to carry out the present research.

\*. Also Consultant at Programa de Ingeniería Molecular del Instituto Mexicano del Petróleo.

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