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A derivation of the constitutive equations for non-equilibrium stationary states from extended irreversible thermodynamics

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Abstract. A derivation is given of the constitutive equations required for the study of the behaviour of a fluid in a stationary state far from equilibrium using the Navier–Stokes equations of hydrodynamics. The presence of the external gradients producing such stationary states is explicitly accounted for in the hydrodynamic equations. The method used in the derivation is based on the theory of extended irreversible thermodynamics.

1. Introduction

The generalisation of linear irreversible thermodynamics to cope with problems which lie outside its scope, such as the introduction of a finite propagation velocity for elastic and thermal disturbances in solids and fluids, and the introduction of nonlinear constitutive equations supplementing the information required by the macroscopic dynamical model of a given system, has been a subject of recent interest (Cattaneo 1958, Carrasi and Morro 1972, Gyarmati 1977). In this paper we discuss how one can derive the constitutive equations for a binary non-reactive mixture of fluids which is brought to a stationary state far from equilibrium by some external agent, using the methods of extended irreversible thermodynamics (EIT). The study of systems in stationary states far from equilibrium has attracted the attention of many people, mainly because their features, such as the spectra of the light dispersed by a fluid, are considerably different from those characterising the system when it is in a state not far from equilibrium (Kirkpatrick *et al* 1980, Ronis and Putterman 1980, Tremblay *et al* 1980, Van der Zwann and Mazur 1980).

In relation to these questions we have proposed a phenomenological model to explain this behaviour which is based on the fluctuating Navier–Stokes equations of hydrodynamics, but supplemented by constitutive equations which explicitly contain the fact that the external gradient maintaining the stationary state must give rise to a privileged direction in the fluid, insofar as the propagation of the corresponding flow is concerned (García-Colín and Velasco 1981). With such a model we have predicted a change in the Kirchhoff–Stokes formula for the sound absorption in the fluid, a modification of Rayleigh’s peak unpredicted so far and the shift in the Brillouin peaks already obtained by other authors (Kirkpatrick *et al* 1980, Tremblay *et al* 1981, Ronis and Putterman 1980).

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To keep the paper short but self-contained, § 2 is devoted to the study of the non-reactive binary mixture according to EIT, § 3 contains the derivation of the Navier–Stokes equations modified with constitutive equations which have the properties mentioned above, and in § 4 we obtain the correlation functions for the fluctuating parts of the various fluxes appearing in the model.

2. The binary mixture in EIT

Consider a system which is composed of an isotropic fluid containing two chemically distinct and inert chemical species. The states of such a fluid will be described in terms of the local mass density $\rho(\mathbf{r}, t)$, the local concentration of any of the species $c_i(\mathbf{r}, t)$, ($i = 1, 2$), $c_1 + c_2 = 1$, the local specific internal energy density $u(\mathbf{r}, t)$ and the local baricentric velocity $\mathbf{v}(\mathbf{r}, t)$. The time evolution of these local variables is given by the well known conservation equations together with Gibbs' relation as stated by the local equilibrium assumption. Combination of all these equations leads to an entropy balance equation with well defined, though not unique, expressions for the entropy flux and the local entropy production (de Groot and Mazur 1962). To obtain a complete set of equations one must introduce the constitutive equations relating the fluxes to the gradients of the local densities, the thermodynamic forces. The solution to any given physical situation of a chosen system depends only on the knowledge of the initial conditions of the state variables and the boundary conditions.

In EIT one considers as independent variables not only the local densities required by linear irreversible thermodynamics but also the fluxes, namely, the diffusion flux \mathbf{J}_d , the traceless part of the viscous tensor $\hat{\mathcal{J}}$, its trace \mathcal{J} and $\mathbf{J} = \mathbf{J}_q - \mu\mathbf{J}_d$ where \mathbf{J}_q is the heat flux and μ the chemical potential of the mixture. This ansatz leads to the generalisation of the Gibbs relation which now has the following form (Jou *et al* 1979b, Lebon *et al* 1980):

$$T \frac{ds}{dt} = \frac{du}{dt} - \frac{p}{\rho^2} - \mu \frac{dc}{dt} + \frac{\alpha_1}{\rho} \cdot \frac{d\mathbf{J}}{dt} + \frac{\alpha_0}{\rho} \frac{d\mathcal{J}}{dt} + \frac{\hat{\alpha}_2}{\rho} \cdot \frac{d\hat{\mathcal{J}}}{dt} + \frac{\alpha_3}{\rho} \cdot \frac{d\mathbf{J}_d}{dt} \quad (1)$$

where p and T are the local equilibrium analogues of pressure and temperature, respectively, c is the independent concentration and α_0 , α_1 , $\hat{\alpha}_2$ and α_3 are functions of the algebraic invariants which can be constructed from the independent variables, of the independent variables themselves and have the indicated tensorial nature.

Thus

$$\begin{aligned} \alpha_1 &= \alpha_{10}\mathbf{J} + \alpha_{13}\mathbf{J}_d, & \alpha_0 &= \alpha_{01}\mathcal{J}, \\ \hat{\alpha}_2 &= \alpha_{21}\hat{\mathcal{J}}, & \alpha_3 &= \alpha_{30}\mathbf{J} + \alpha_{31}\mathbf{J}_d, \end{aligned} \quad (2)$$

where the α_{ij} are scalar functions of p , u and c and are evaluated at equilibrium.

Following the prescription of EIT, one can now use equations (1) and (2) together with the conservation equations for ρ , u and c to derive formally an entropy balance equation with specific equations for \mathbf{J}_s and σ . However, in these quantities the unknown time rates of change for the fluxes will appear. The main task of the theory is to find a prescription that allows the computation of such quantities. This is done by recalling that \mathbf{J}_s and σ must be a vector and a scalar in the new space of variables in which the Pfaffian for ds , namely equation (1) is defined. By restricting ourselves to terms

which are at most of second order in the fluxes, the vector \mathbf{J}_s is of the form

$$\mathbf{J}_s = (\beta_{00} + \beta_{01}\mathcal{F})\mathbf{J} + \beta_{10}\overset{\circ}{\mathcal{F}} \cdot \mathbf{J} + (\beta_{30} + \beta_{31}\mathcal{F})\mathbf{J}_d + \beta_{40}\overset{\circ}{\mathcal{F}} \cdot \mathbf{J}_d + \dots \quad (3)$$

where the scalar coefficients $\beta_{ij} = \beta_{ij}(\rho, u, c)$ are equilibrium quantities. In order that \mathbf{J}_s defined in equation (3) reduce to the well known expression for the linear case, namely that $\mathbf{J}_s = T^{-1}\mathbf{J}_q$, we choose $\beta_{00} = T^{-1}$ and $\beta_{30} = 0$.

On the other hand, the most general form for the scalar σ is

$$\sigma = \mathbf{X} \cdot \mathbf{J} + X_0\mathcal{F} + \overset{\circ}{\mathbf{X}}_2 : \overset{\circ}{\mathcal{F}} + \mathbf{X}_d \cdot \mathbf{J}_d \quad (4)$$

where \mathbf{X} , X_0 , $\overset{\circ}{\mathbf{X}}_2$ and \mathbf{X}_d play the role of the generalised thermodynamic forces which are obtained when one substitutes the conservation equations into equation (1) and adds to the resulting expression the term $\text{div } \mathbf{J}_s$ obtained from equation (3). Factorising the result as suggested by equation (4) leads immediately to the result that

$$\mathbf{X} = \nabla\left(\frac{1}{T}\right) + \frac{\alpha_{10}}{T} \frac{d\mathbf{J}}{dt} + \frac{\alpha_{30}}{T} \frac{d\mathbf{J}_d}{dt} + \frac{1}{2}\mathcal{F}\nabla\beta_{01} + \beta_{01}\nabla\mathcal{F} + \beta_{10}\nabla \cdot \overset{\circ}{\mathcal{F}} + \frac{1}{2}\overset{\circ}{\mathcal{F}} \cdot \nabla\beta_{10}, \quad (5)$$

$$\mathbf{X}_d = -\frac{\nabla\mu}{T} + \frac{\alpha_{13}}{T} \frac{d\mathbf{J}}{dt} + \frac{\alpha_{33}}{T} \frac{d\mathbf{J}_d}{dt} + \frac{1}{2}\mathcal{F}\nabla\beta_{31} + \beta_{31}\nabla\mathcal{F} + \beta_{40}\nabla \cdot \overset{\circ}{\mathcal{F}} + \frac{1}{2}\overset{\circ}{\mathcal{F}} \cdot \nabla\beta_{40}, \quad (6)$$

$$X_0 = -\frac{1}{T}\nabla \cdot v + \frac{\alpha_{01}}{T} \frac{d\mathcal{F}}{dt} + \frac{1}{2}\mathbf{J} \cdot \nabla\beta_{01} + \beta_{01}\nabla \cdot \mathbf{J} + \frac{1}{2}\mathbf{J}_d \cdot \nabla\beta_{31} + \beta_{31}\nabla \cdot \mathbf{J}_d, \quad (7)$$

$$\overset{\circ}{\mathbf{X}}_2 = -\frac{1}{T}(\overset{\circ}{\nabla}v)^s + \frac{\alpha_{21}}{T} \frac{d\overset{\circ}{\mathcal{F}}}{dt} + \beta_{10}(\overset{\circ}{\nabla}\mathbf{J})^s + \beta_{40}(\overset{\circ}{\nabla}\mathbf{J}_d)^s + \frac{1}{2}(\mathbf{J}_d\overset{\circ}{\nabla}\beta_{40})^s + \frac{1}{2}(\mathbf{J}\overset{\circ}{\nabla}\beta_{10})^s. \quad (8)$$

On the other hand, these same quantities may also be constructed using the same symmetry arguments as before, taking for each one of them the most general form which is consistent with their tensorial character. Then,

$$\mathbf{X} = \gamma_{10}\mathbf{J} + \gamma_{11}\mathcal{F}\mathbf{J} + \gamma_{12}\overset{\circ}{\mathcal{F}} \cdot \mathbf{J} + \gamma_{13}\mathbf{J}_d + \gamma_{14}\mathcal{F}\mathbf{J}_d + \gamma_{15}\overset{\circ}{\mathcal{F}} \cdot \mathbf{J}_d, \quad (9)$$

$$X_0 = \gamma_{01}\mathcal{F} + \gamma_{02}\mathcal{F}^2 + \gamma_{03}\mathbf{J} \cdot \mathbf{J} + \gamma_{04}\overset{\circ}{\mathcal{F}} : \overset{\circ}{\mathcal{F}} + \gamma_{05}\mathbf{J}_d \cdot \mathbf{J}_d + \gamma_{06}\mathbf{J} \cdot \mathbf{J}_d, \quad (10)$$

$$\overset{\circ}{\mathbf{X}}_2 = \gamma_{21}\overset{\circ}{\mathcal{F}} + \gamma_{22}(\overset{\circ}{\mathcal{F}} \cdot \overset{\circ}{\mathcal{F}})^s + \gamma_{23}(\overset{\circ}{\mathbf{J}\mathbf{J}})^s + \gamma_{24}(\mathbf{J}_d\overset{\circ}{\mathbf{J}_d})^s + \gamma_{25}(\overset{\circ}{\mathbf{J}\mathbf{J}_d})^s + \gamma_{26}\mathcal{F}\overset{\circ}{\mathcal{F}}, \quad (11)$$

$$\mathbf{X}_d = \gamma_{30}\mathbf{J}_d - \gamma_{31}\mathcal{F}\mathbf{J}_d + \gamma_{32}\overset{\circ}{\mathcal{F}} \cdot \mathbf{J}_d + \gamma_{33}\mathbf{J} + \gamma_{34}\mathcal{F}\mathbf{J} + \gamma_{35}\overset{\circ}{\mathcal{F}} \cdot \mathbf{J}, \quad (12)$$

and the γ_{ij} are scalar functions of ρ, u and c evaluated at equilibrium.

Since the set of equations (5)–(8) and (9)–(12) gives two alternative expressions for each of the quantities \mathbf{X} , X_0 , $\overset{\circ}{\mathbf{X}}_2$ and \mathbf{X}_d respectively, equating them leads us to the sought equations describing the time rate of change of the various fluxes.

These expressions are

$$\begin{aligned} \frac{d\mathbf{J}}{dt} - \frac{\alpha_{30}}{\alpha_{10}} \frac{d\mathbf{J}_d}{dt} &= \frac{T}{\alpha_{10}}(-\nabla T^{-1} + \gamma_{10}\mathbf{J} + \gamma_{13}\mathbf{J}_d - \beta_{01}\nabla\mathcal{F} \\ &\quad - \beta_{10}\nabla \cdot \overset{\circ}{\mathcal{F}} + \gamma_{11}\mathcal{F}\mathbf{J} + \gamma_{12}\overset{\circ}{\mathcal{F}} \cdot \mathbf{J} + \gamma_{14}\mathcal{F}\mathbf{J}_d + \gamma_{15}\overset{\circ}{\mathcal{F}} \cdot \mathbf{J}_d), \end{aligned} \quad (13)$$

$$\begin{aligned} \frac{d\mathbf{J}_d}{dt} + \frac{\alpha_{13}}{\alpha_{33}} \frac{d\mathbf{J}}{dt} &= \frac{T}{\alpha_{33}}(T^{-1}\nabla\mu + \gamma_{30}\mathbf{J}_d + \gamma_{33}\mathbf{J} - \beta_{31}\nabla\mathcal{F} \\ &\quad - \beta_{40}\nabla \cdot \overset{\circ}{\mathcal{F}} + \gamma_{31}\mathcal{F}\mathbf{J}_d + \gamma_{32}\overset{\circ}{\mathcal{F}} \cdot \mathbf{J}_d + \gamma_{34}\mathcal{F}\mathbf{J} + \gamma_{35}\overset{\circ}{\mathcal{F}} \cdot \mathbf{J}), \end{aligned} \quad (14)$$

$$\frac{d\mathcal{F}}{dt} = \frac{T}{\alpha_{01}}(T^{-1}\nabla \cdot \mathbf{v} + \gamma_{01}\mathcal{F} - \beta_{01}\nabla \cdot \mathbf{J} - \beta_{31}\nabla \cdot \mathbf{J}_d + \gamma_{02}\mathcal{F}^2 + \gamma_{03}\mathbf{J} \cdot \mathbf{J} + \gamma_{04}\mathcal{F} : \mathcal{F} + \gamma_{05}\mathbf{J}_d \cdot \mathbf{J}_d + \gamma_{06}\mathbf{J}_d \cdot \mathbf{J}), \tag{15}$$

$$\frac{d\mathcal{F}}{dt} = \frac{T}{\alpha_{21}}(T^{-1}(\nabla \mathbf{v})^s + \gamma_{21}\mathcal{F} - \beta_{10}(\nabla \mathbf{J})^s - \beta_{40}(\nabla \mathbf{J}_d)^s + \gamma_{22}(\mathcal{F} \cdot \mathcal{F})^s + \gamma_{23}(\mathbf{J}\mathbf{J})^s + \gamma_{24}(\mathbf{J}_d\mathbf{J}_d)^s + \gamma_{25}(\mathbf{J}\mathbf{J}_d)^s + \gamma_{26}\mathcal{F}\mathcal{F}), \tag{16}$$

where we have omitted all the terms $\nabla\beta_{ij}$ which are irrelevant. This requirement in fact is equivalent to the assumption that the transport coefficients of the mixture are independent of the position coordinates.

It is pertinent to indicate here that if in equations (13)–(16) one neglects all terms which are of second order, one obtains in the stationary state the well known constitutive equations of linear irreversible thermodynamics. This allows the identification of the well known transport coefficients so that $\lambda = 1/\gamma_{10}T^2$ is the thermal conductivity, $\zeta = 1/\gamma_{01}T$ is the bulk viscosity, $2\eta = 1/\gamma_{20}T$ is the shear viscosity,

$$D = \frac{\gamma_{10}}{\rho T}(\gamma_{30}\gamma_{10} - \gamma_{33}^2)^{-1}\left(\frac{\partial\mu}{\partial c}\right)_{P,T}$$

the diffusion coefficient and

$$k_T = \frac{T}{\gamma_{10}(\partial\mu/\partial c)_{P,T}}\left[\gamma_{10}\left(\frac{\partial\mu}{\partial T}\right)_{P,C} - \frac{\gamma_{33}}{T}\right]$$

the thermodiffusion ratio. Since at this order in the approximation Onsager’s relations are valid, we see that $\gamma_{33} = \gamma_{13}$.

3. The constitutive equations for a stationary state

Let us now consider that the binary fluid mixture is in a stationary state far from equilibrium to which it has been driven by the action of an external agent. For instance, one could think of a state produced by the action of a thermal gradient $(\nabla T)_0$, a constant shear rate $\dot{\Sigma}$ or a concentration gradient $(\nabla c)_0$. In such a state the following conditions have to be obeyed, namely that

$$\left.\frac{d\mathcal{F}}{dt}\right|_{ss} = 0, \quad \left.\frac{d\mathcal{F}}{dt}\right|_{ss} = 0, \quad \left.\frac{d\mathbf{J}}{dt}\right|_{ss} = 0, \quad \left.\frac{d\mathbf{J}_d}{dt}\right|_{ss} = 0. \tag{17}$$

These equations will lead us to new constitutive equations which are no longer linear ones since they will contain terms which are second-order derivatives of the independent variables. That this is the case can be seen through the following argument. In the presence of the external gradient the fluxes may be separated into two parts, one containing the fluxes present in the system due to the external gradient, which we shall denote by a superscript ⁽⁰⁾, and which keep the system in the stationary state, and the ordinary contributions which will be denoted by the superscript ⁽¹⁾. Thus

$$\begin{aligned} \mathcal{F} &= \mathcal{F}^{(0)} + \mathcal{F}^{(1)}, & \mathcal{F} &= \mathcal{F}^{(0)} + \mathcal{F}^{(1)}, \\ \mathbf{J} &= \mathbf{J}^{(0)} + \mathbf{J}^{(1)}, & \mathbf{J}_d &= \mathbf{J}_d^{(0)} + \mathbf{J}_d^{(1)}. \end{aligned} \tag{18}$$

The fluxes with the superscript ⁽⁰⁾ define the reference state of the system and are therefore regarded as quantities of order zero, whereas the other contributions are first-order quantities. Substituting equation (18) back into equations (13)–(16) and keeping only linear terms with respect to the stationary state, we obtain that

$$\begin{aligned} \frac{d\mathcal{J}^{(1)}}{dt} = \frac{T}{\alpha_{01}} & [T^{-1}\nabla \cdot \mathbf{v}^{(1)} + \gamma_{01}\mathcal{J}^{(1)} - \beta_{01}\nabla \cdot \mathbf{J}^{(1)} - \beta_{31}\nabla \cdot \mathbf{J}_d^{(1)} + 2\gamma_{02}\mathcal{J}^{(0)}\mathcal{J}^{(1)} \\ & + 2\gamma_{03}\mathbf{J}^{(0)} \cdot \mathbf{J}^{(1)} + 2\gamma_{04}\mathcal{J}^{(0)} : \mathcal{J}^{(1)} + 2\gamma_{05}\mathbf{J}_d^{(0)} \cdot \mathbf{J}_d^{(1)} \\ & + \gamma_{06}(\mathbf{J}_d^{(0)} \cdot \mathbf{J}^{(1)} + \mathbf{J}_d^{(1)} \cdot \mathbf{J}^{(1)})] \end{aligned} \tag{19}$$

$$\begin{aligned} \frac{d\mathcal{J}^{(1)}}{dt} = \frac{T}{\alpha_{21}} & [T^{-1}(\nabla \mathbf{v}^{(1)})^s + \gamma_{21}\mathcal{J}^{(1)} - \beta_{10}(\nabla \mathbf{J}^{(1)})^s - \beta_{40}(\nabla \mathbf{J}_d^{(1)})^s + 2\gamma_{22}(\mathcal{J}^{(0)} \cdot \mathcal{J}^{(1)})^s \\ & + 2\gamma_{23}(\mathbf{J}^{(0)} \mathbf{J}^{(1)})^s + 2\gamma_{24}(\mathbf{J}_d^{(0)} \mathbf{J}_d^{(1)})^s - \gamma_{25}(\mathbf{J}_d^{(1)} \mathbf{J}^{(0)} + \mathbf{J}_d^{(0)} \mathbf{J}^{(1)})^s \\ & + \gamma_{26}(\mathcal{J}^{(0)} \mathcal{J}^{(1)} + \mathcal{J}^{(1)} \mathcal{J}^{(0)})], \end{aligned} \tag{20}$$

$$\begin{aligned} \frac{d\mathbf{J}^{(1)}}{dt} + \frac{\alpha_{30}}{\alpha_{10}} \frac{d\mathbf{J}_d^{(1)}}{dt} = \frac{T}{\alpha_{10}} & [-\nabla(1/T)^{(1)} + \gamma_{10}\mathbf{J}^{(1)} + \gamma_{13}\mathbf{J}_d^{(1)} - \beta_{01}\nabla\mathcal{J}^{(1)} - \beta_{10}\nabla \cdot \mathcal{J}^{(1)} \\ & + \gamma_{11}(\mathcal{J}^{(0)}\mathbf{J}^{(1)} + \mathcal{J}^{(1)}\mathbf{J}^{(0)}) + \gamma_{12}(\mathcal{J}^{(0)} \cdot \mathbf{J}^{(1)} + \mathcal{J}^{(1)} \cdot \mathbf{J}^{(0)}) \\ & + \gamma_{14}(\mathcal{J}^{(0)}\mathbf{J}_d^{(1)} + \mathcal{J}^{(1)}\mathbf{J}_d^{(0)}) + \gamma_{15}(\mathcal{J}^{(0)} \cdot \mathbf{J}_d^{(1)} + \mathcal{J}^{(1)} \cdot \mathbf{J}_d^{(0)})] \end{aligned} \tag{21}$$

and,

$$\begin{aligned} \frac{d\mathbf{J}_d^{(1)}}{dt} + \frac{\alpha_{13}}{\alpha_{33}} \frac{d\mathbf{J}^{(1)}}{dt} = \frac{T}{\alpha_{33}} & [T^{-1}\nabla\mu^{(1)} + \gamma_{30}\mathbf{J}_d^{(1)} + \gamma_{33}\mathbf{J}^{(1)} - \beta_{31}\nabla\mathcal{J}^{(1)} - \beta_{40}\nabla \cdot \mathcal{J}^{(1)} \\ & + \gamma_{31}(\mathcal{J}^{(1)}\mathbf{J}_d^{(0)} + \mathcal{J}^{(0)}\mathbf{J}_d^{(1)}) + \gamma_{32}(\mathcal{J}^{(0)} \cdot \mathbf{J}_d^{(1)} + \mathcal{J}^{(1)} \cdot \mathbf{J}_d^{(0)}) \\ & + \gamma_{34}(\mathcal{J}^{(0)}\mathbf{J}^{(1)} + \mathcal{J}^{(1)}\mathbf{J}^{(0)}) + \gamma_{35}(\mathcal{J}^{(0)} \cdot \mathbf{J}^{(1)} + \mathcal{J}^{(1)} \cdot \mathbf{J}^{(0)})]. \end{aligned} \tag{22}$$

We now reduce the set of equations (19)–(22) to the Navier–Stokes regime but for the stationary state. Physically, this means that we shall only consider all those quantities which are of first order with respect to the local equilibrium state which has been established around the stationary state. Therefore the last four terms in equation (1) are set equal to zero and in equations (19)–(22) the left-hand members are zero. Also all those terms in these equations which are of second order, namely those that involve spatial derivatives of the first-order fluxes, are neglected. For the specific case in which the stationary state is produced by a fixed temperature gradient and the system has only a single component so that $\mu = 0$, we readily obtain that

$$\begin{aligned} \mathcal{J}^{(1)} &= -\zeta\nabla \cdot \mathbf{v}^{(1)} + \zeta_1(\nabla T)_0 \cdot \nabla(1/T)^{(1)}, \\ \mathcal{J}^{(1)} &= -2\eta(\nabla \mathbf{v}^{(1)})^s + 2\eta_1[(\nabla T)_0 \nabla(1/T)^{(1)}]^s, \\ \mathbf{J}_q^{(1)} &= -\lambda(\nabla T)^{(1)} - \lambda_1(\nabla \ln T)_0 \nabla \cdot \mathbf{v}^{(1)} - \lambda_2(\nabla \ln T)_0 \cdot (\nabla \mathbf{v}^{(1)})^s, \end{aligned} \tag{23}$$

where ζ_1 , η_1 , λ_1 , and λ_2 are the new transport coefficients. In arriving at equations (23) use has been made of the fact that to lowest order in the gradients $\mathbf{J} = \lambda \nabla T^{-1}$ and that $\nabla T = (\nabla T)_0 + (\nabla T)^{(1)}$. Also, in this case $\mathcal{J}^{(0)} = -2\eta \mathbf{A} = 0$.

For the case in which the stationary state is produced by a constant external shear \mathring{A} rate, one obtains that

$$\begin{aligned} \mathcal{J}^{(1)} &= -\zeta \nabla \cdot \mathbf{v}^{(1)} - L_3 \mathring{A} : (\nabla \mathbf{v})^s, \\ \mathcal{J} &= -2\eta (\nabla \mathbf{v}^{(1)})^s - 2L_5 (\mathring{A} \cdot \nabla \mathbf{v}^{(1)})^s - L_1 \mathring{A} \nabla \cdot \mathbf{v}^{(1)}, \\ \mathbf{J}_q^{(1)} &= -\lambda \nabla T^{(1)} - L_2 \mathring{A} \cdot \nabla T^{(1)}. \end{aligned} \tag{24}$$

Once more, the fact that to lowest order $\mathbf{J} = \lambda \nabla T^{-1}$ and $\mathcal{J} = -2\eta (\nabla \mathbf{v})^s$ has been used in the derivation of equation (24), and L_1, L_2, L_3 and L_5 are the new transport coefficients which couple the different effects arising from the presence of the external gradient. As in any phenomenological theory, the new transport coefficients are to be determined either through experiment or using a microscopic theory. The sets of equations (23) and (24) constitute the basis of the treatment for fluids in stationary states far from equilibrium presented by García-Colín and Velasco (1982).

Although in this section we have considered the specific example of a single component fluid, it is straightforward to see that the method is readily applicable to different types of stationary states far from equilibrium.

4. Fluctuating hydrodynamics

In this section we shall apply the theory of hydrodynamic fluctuations as presented by Landau and Lifshitz (1959) (Jou and Casas-Vázquez 1980) to the modified Navier–Stokes model described in § 3. In particular, we shall consider the stationary states arising from the presence of an external temperature gradient $(\nabla T)_0$ and an external rate of shear \mathring{A} .

In Landau’s theory one begins with an equation relating the thermodynamic forces to the corresponding fluxes in which the fluctuating part of the latter ones is explicitly accounted for. Thus, if \dot{x}_a is a flux and X_b the corresponding force,

$$\dot{x}_a = \sum_b \gamma_{ab} X_b + y_a \tag{25}$$

where y_a is the fluctuating part of \dot{x}_a and γ_{ab} are the constant elements of the transport matrix. Clearly, if an average of (25) is performed over a non-equilibrium ensemble, then it is assumed that

$$\langle y_a \rangle = 0, \quad \langle y_a(t') y_b(t) \rangle = (\gamma_{ab} + \gamma_{ba}) \delta(t - t'). \tag{26}$$

Let us now apply these results to equations (23). Adding to each one of the corresponding equations their fluctuating components, π , $\hat{\sigma}$ and \mathbf{g} respectively, and using equations (25) and (26), we find that

$$\begin{aligned} \langle \hat{\sigma}_{ij}(\mathbf{r}, t) \hat{\sigma}_{lm}(\mathbf{r}', t') \rangle &= 2\eta T(\mathbf{r}) (\delta_{ij} \delta_{lm} + \delta_{jl} \delta_{im} - \frac{2}{3} \delta_{ij} \delta_{lm}) \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \\ \langle \pi(\mathbf{r}, t) \pi(\mathbf{r}', t') \rangle &= 2\zeta T(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \\ \langle g_i(\mathbf{r}, t) g_j(\mathbf{r}', t') \rangle &= 2\lambda [T(\mathbf{r})]^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \delta_{ij}, \\ \langle \pi(\mathbf{r}, t) g_j(\mathbf{r}', t') \rangle &= (\zeta_1 + \lambda_1) (\nabla T)_{0i} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \\ \langle \pi(\mathbf{r}, t) \hat{\sigma}_{ij}(\mathbf{r}', t') \rangle &= 0, \\ \langle \hat{\sigma}_{ij}(\mathbf{r}, t) g_k(\mathbf{r}', t') \rangle &= \{ \eta_1 [(\nabla T)_{0i} \delta_{jk} + (\nabla T)_{0j} \delta_{ik} - \frac{2}{3} \delta_{ij} (\nabla T)_{0k}] + \frac{1}{3} \lambda_2 [(\nabla T)_{0j} \delta_{ik} + (\nabla T)_{0i} \delta_{jk}] \} \\ &\quad \times \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \end{aligned} \tag{27}$$

Proceeding in a similar fashion with equations (24) we find, after the fluctuating parts have been added, that

$$\begin{aligned}
 \langle \hat{\sigma}_{ij}(\mathbf{r}, t) \hat{\sigma}_{lm}(\mathbf{r}', t') \rangle &= [2\eta T_0(\delta_{il}\delta_{jm} + \delta_{im}\delta_{jl} - \frac{2}{3}\delta_{ij}\delta_{lm}) \\
 &\quad + L_5 T_0(\hat{A}_{im}\delta_{jl} + \hat{A}_{jm}\delta_{il} - \frac{1}{3}\hat{A}_{lm}\delta_{ij})] \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \\
 \langle \pi(\mathbf{r}, t) \pi(\mathbf{r}', t') \rangle &= 2\zeta T_0 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \\
 \langle g_i(\mathbf{r}, t) g_j(\mathbf{r}', t') \rangle &= 2T_0^2 (\lambda \delta_{ij} + L_2 \hat{A}_{ij}) \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \\
 \langle \pi(\mathbf{r}, t) g_i(\mathbf{r}', t') \rangle &= 0, \\
 \langle \hat{\sigma}_{ij}(\mathbf{r}, t) \pi(\mathbf{r}', t') \rangle &= T_0(L_1 + L_3) \hat{A}_{ij} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \\
 \langle \hat{\sigma}_{ij}(\mathbf{r}, t) g_k(\mathbf{r}', t') \rangle &= 0.
 \end{aligned} \tag{28}$$

It is worthwhile pointing out that the new transport coefficients which appear in the constitutive equations (23) and (24) are explicitly contained in these results as well as the external gradient. This is precisely the reason why the intensity of the Brillouin-Rayleigh spectra for the dispersed light by the fluid is modified.

To conclude this paper we would like to emphasise that EIT provides a systematic way of constructing constitutive equations which are useful in the study of stationary states in systems far from equilibrium. These constitutive equations modify substantially the behaviour of the system, since they include all the pertinent transport coefficients coupling the external gradients, which also appear explicitly, with the other isotropically homogeneous thermodynamic forces. Furthermore, these new transport coefficients can be measured by studying the sound dispersion and the light scattering by the fluid.

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