Non-equilibrium Thermodynamics and Hydrodynamic Fluctuations

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Abstract

The reformulation of nonequilibrium thermodynamics, to include the treatment of thermodynamic fluctuations, is applied to the hydrodynamic fluctuations of a simple fluid. It is shown that the nonequilibrium thermodynamic scheme leads to the explicit form of the Fokker-Planck equation which describes the time behaviour of the probability distribution function of these hydrodynamic fluctuations as well as the irreversible processes which are connected with this behaviour.
1 Introduction

In a recent paper [1] one of the authors (P.M.) showed that the scheme and formalism of nonequilibrium thermodynamics can be reformulated in such a way that the equations describing the dynamics of thermodynamic fluctuations are obtained in a simple manner. In particular one is thus led directly to a theory of fluctuations as Gaussian Markov processes obeying a multivariate Fokker-Planck equation [2,3]. In this reformulation of thermodynamics of irreversible processes fluctuations were considered as internal degrees of freedom of a thermodynamic system. Moreover Gibbs entropy postulate was used to define the system’s entropy as a functional of the probability density in internal coordinate space.

In this paper we apply the formalism developed in [1] to the case of hydrodynamic fluctuations in a simple fluid. It is our aim to show that nonequilibrium thermodynamics yields indeed the multivariate Fokker-Planck equation describing the behaviour in time of hydrodynamic fluctuations and thus implicitly also the Langevin-like equations of fluctuating hydrodynamics [4].

In Section 2 we introduce the hydrodynamic fluctuations as fluctuation of the Fourier transformed (in space) fields of mass, density, temperature and the three components of fluid velocity. We also introduce in this section the probability density function of these fluctuations as well as the system’s entropy as a functional of this distribution function. This functional for the entropy which is an expression for Gibb’s entropy postulate contains also the equilibrium distribution function. We give an explicite calculation in Gaussian approximation of the latter in section 3 (and the appendix). In Section 4 we calculate the entropy production when the system is not in equilibrium. We obtain for this quantity an expression which is, in analogy to its form in macroscopic nonequilibrium thermodynamics [5], a sum of products of dissipative fluxes, which are components of the probability flux, and conjugate thermodynamic forces, which are derivatives of probability densities. As usual in thermodynamics of irreversible processes linear relations containing phenomenological coefficients are established between fluxes and forces. When these are introduced into the continuity equation for the time dependent probability density the differential equation, the Fokker-Planck equation, governing the dynamics of the hydrodynamic fluctuations as Markov processes, is obtained. We then determine in section 5 the phenomenological, or Onsager coefficients, introduced formally in section 4 by deriving mean regression laws from the Fokker-Planck equation which was found, and comparing these with the macroscopic equations for the corresponding irreversible processes.

We conclude with a few remarks, made also previously regarding the applicability of the formalism used.

2 Hydrodynamic fluctuations as internal degrees of freedom of a thermodynamic system

We consider a simple fluid enclosed in a cubic container of volume $V$, and having constant total mass $M$ and total energy $E$. The macroscopic thermodynamic internal state at time $t$
and position \( \vec{r} \), of the system may be characterized by 5 fields \( A_i(\vec{r}, t) \) corresponding to the 5 conserved quantities \( \rho(\vec{r}, t), e(\vec{r}, t), \rho \vec{v}(\vec{r}, t) \) where \( \rho \) is the mass density, \( e \) the energy per unit of volume and \( \vec{v} \) the local velocity.

For our purpose it is more convenient to use an alternative and equivalent set of fields which we choose as follows

\[
\begin{align*}
A_1(\vec{r}, t) & = \rho(\vec{r}, t) \\
A_2(\vec{r}, t) & = T(\vec{r}, t) \\
A_i(\vec{r}, t) & = v_\alpha(\vec{r}, t), (i = 3, 4, 5; \ \alpha = x, y, z),
\end{align*}
\]

where \( T(\vec{r}, t) \) is the temperature field and where the index \( \alpha \) denotes the 3 cartesian components of \( \vec{v} \). In the equilibrium state the fields \( A_i \) have uniform constant values \( A_i^0 \)

\[
A_1^0 = \rho_0 = \frac{M}{V}; \quad A_2^0 = T_0; \quad A_i = 0, \quad i = 3, 4, 5 \tag{2.2}
\]

It is around these values that the fields \( A_i(\vec{r}, t) \) will fluctuate due to thermal agitation. To deal with these fluctuations a statistical description is needed, a statistical description which can best be effectuated in term of the Fourier components of the fields (2.1). To introduce these we choose for simplicity’s sake periodic boundary conditions and write

\[
A_i(\vec{r}, t) = V^{-1} \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} A_i(\vec{k}, t) \tag{2.3}
\]

with

\[
A_i(\vec{k}, t) = \int_V d\vec{r} e^{-i\vec{k} \cdot \vec{r}} A_i(\vec{r}, t) \tag{2.4}
\]

The wave vector \( \vec{k} \) in eq. (2.3) and (2.4) will assume a denumerable set of values.

We shall now introduce the probability density \( P(\{A_i(\vec{k})\}, t) \) that the system is at time \( t \) in a state defined by the set of values \( \{A_i(\vec{k})\} = \mathbb{A} \). To normalize this probability density we introduce a cut-off wave number \( k_{max} \) such that no state occurs for which \( |\vec{k}| \geq k_{max} \). The wave number \( k_{max} \) in fact defines a length scale which is much larger than the molecular scale but small enough for a hydrodynamic and thermodynamic description to hold. With the above considerations in mind we now normalize the probability density as follows

\[
\int_{|\vec{k}| \leq k_{max}} P(\mathbb{A}, t)d\mathbb{A} = 1 \tag{2.5}
\]

In the limit as \( t \to \infty \) the distribution function \( P(\mathbb{A}, t) \) becomes the equilibrium distribution function \( P_0(\mathbb{A}) \) for which the state variables have mean values \( \langle A_i(\vec{k}) \rangle \)

\[
\langle A_i(\vec{k}) \rangle = \int \langle A_i(\vec{k}) \rangle P_0(\mathbb{A})d\mathbb{A} \tag{2.6}
\]
Substituting eq. (2.4) into eq. (2.6) we have

\[ \langle A_i(\vec{k}) \rangle = V \langle A_i(\vec{r}) \rangle \delta_{\vec{k},0} \]  

(2.7)

where we have used the fact that \( \langle A_i(\vec{r}) \rangle \) is independent of \( \vec{r} \) and that

\[ \delta_{\vec{k},0} = \frac{1}{V} \int d\vec{r} e^{i\vec{k} \cdot \vec{r}} \]  

(2.8)

Since the equilibrium averages of \( A_i(\vec{r}) \) should be equal to the values of the equilibrium state given in eq. (2.2) it follows that

\[ \langle A_1(\vec{k}) \rangle = M \delta_{\vec{k},0}; \quad \langle A_2(\vec{k}) \rangle = VT_0 \delta_{\vec{k},0}; \quad \langle A_i(\vec{k}) \rangle = 0, \quad i = 3, 4, 5. \]  

(2.9)

We now define fluctuations

\[ \alpha_i(\vec{k}) = A_i(\vec{k}) - \langle A_i(\vec{k}) \rangle \]  

(2.10)

These obey the distribution functions \( P(\alpha, t) \) and \( P_0(\alpha, t) \) introduced above. We also note at this point that the fluctuations \( \alpha_i(\vec{k}) \) vanish for \( \vec{k} = 0 \): while this is true rigorously for \( \alpha_1 \) as a consequence of mass conservation it is also true to linear order in fluctuations (that is to the order relevant for our developments) as a consequence of energy and momentum conservation.

We may now consider the fluctuations \( \alpha_i(\vec{k}) \) as internal degrees of freedom of the fluid in the sense of nonequilibrium thermodynamics [6] as was done in the more formal preceding paper [1]. In this perspective in which the fluid is considered as a many component system with mass densities \( MP(\alpha, t) \), its total entropy \( S \) obeys a Gibb’s equation

\[ \delta S = -M \int d\alpha \frac{\mu(\alpha)}{T_0} \delta P + \frac{1}{T_0} \delta E - \frac{\mu_0}{T_0} \delta M \]  

(2.11)

where \( \mu(\alpha) \) is the chemical potential of the component with mass density \( MP(\alpha, t) \) and \( \mu_0 \) the chemical potential per unit of mass of the fluid system at equilibrium.

The entropy \( S(t) \) can moreover be expressed as a functional of \( P(\alpha, t) \) according to Gibb’s entropy postulate

\[ S = -k_B \int P(\alpha, t) \ln \frac{P(\alpha, t)}{P_0(\alpha)} d\alpha + S_0(E, M) \]  

(2.12)

where \( S_0 \) is the entropy at equilibrium and \( k_B \) Boltzmann’s constant. This expression yields for the differential of \( S \)

\[ \delta S = -k_B \int d\alpha \ln \frac{P(\alpha, t)}{P_0(\alpha)} \delta P + \frac{1}{T_0} \delta E - \frac{\mu_0}{T_0} \delta M \]  

(2.13)

Comparing eq. (2.11) and eq. (2.13) and using eq. (2.5) we find for \( \mu(\alpha) \)

\[ \mu(\alpha, t) = \frac{k_B T_0}{M} \ln \frac{P(\alpha, t)}{P_0(\alpha)} + \mu_0 \]  

(2.14)
The previous formulae in particular eqs. (2.11) and (2.13) on which our further analysis will be based indicate the essential role played by the equilibrium distribution function $P_0(\mathbf{o})$. It is for this reason that we shall now first establish the explicit form of this function for the variables $\alpha_{i}(\mathbf{k})$ introduced above.

3 The equilibrium distribution function of fluctuations

To discuss the equilibrium distribution function $P_0(\mathbf{o})$ we use the connexion between the probability of a given state $\mathbf{o}$ and the value of its entropy $S(\mathbf{o})$

$$P_0(\mathbf{o}) = \text{const} \times e^{S(\mathbf{o})/k_B}$$ (3.1)

or

$$P_0(\mathbf{o}) = P_0(0)e^{\Delta S(\mathbf{o})/k_B}$$ (3.2)

with

$$\Delta S(\mathbf{o}) = S(\mathbf{o}) - S(0)$$ (3.3)

where $S(0)$ refers to the entropy of the equilibrium state.

We will therefore now calculate $\Delta S(\mathbf{o})$ to second order in the fluctuating variables which we have introduced in section 2. We first observe that the entropy of our fluid may be written as the volume integral of an entropy density per unit of volume $s(\mathbf{r})$

$$\Delta S = \int_V \Delta s(\mathbf{r})d\mathbf{r}$$ (3.4)

At each point $\mathbf{r}$ the entropy density $s(\mathbf{r})$ and its fluctuation $\Delta$ will be a function of the internal energy density $u(\mathbf{r})$ and the mass density $\rho(\mathbf{r})$.

If we then calculate $\Delta S$ to second order in $\Delta u$ and $\Delta \rho$ which is sufficient within the context of a linear fluctuation theory we have

$$\Delta S = \int d\mathbf{r} \left \{ \left ( \frac{\partial s}{\partial u} \right )_\rho \Delta u + \left ( \frac{\partial s}{\partial \rho} \right )_u \Delta \rho + \frac{1}{2} \frac{\partial^2 s}{\partial u^2} (\Delta u)^2 + \frac{\partial^2 s}{\partial u \partial \rho} \Delta u \Delta \rho + \frac{1}{2} \frac{\partial^2 s}{\partial \rho^2} (\Delta \rho)^2 \right \}$$ (3.5)

In the appendix, we show that this expression can be reduced to a quadratic form in the fluctuations $\Delta \rho(\mathbf{r})$, $\Delta T(\mathbf{r})$ and $\mathbf{v}(\mathbf{r})$ or alternatively $\Delta \rho(\mathbf{k})$, $\Delta T(\mathbf{k})$ and $\mathbf{v}(\mathbf{k})$

$$\Delta S = -\frac{1}{2T_0} \int d\mathbf{r} \left \{ \frac{1}{\rho_0} (\frac{\partial p}{\partial \rho}) \tau_0 (\Delta \rho)^2 + \frac{\rho_0 c_v}{T_0} (\Delta T)^2 + \rho_0 v^2 \right \}$$
\[ -\frac{1}{2TV_0} \sum_k \{ \rho_0^{-1} \beta \Delta \rho(k) \Delta \rho(-k) + \frac{\rho_0}{T_0} \Delta T(k) \Delta T(-k) + \rho_0 \bar{v}(k) \cdot \bar{v}(-k) \} \]

where \( p \) is the pressure and \( c_v = \rho_0^{-1} \partial u/\partial T \) the specific heat per unit of mass; \( \beta = (\partial P/\partial \rho)_T \) denotes the isothermal compressibility. The fluctuating variables in the sum over \( \vec{k} \) correspond to the five variables \( \alpha_i(k), i = 1, 2, \ldots, 5 \) introduced in section 2.

We shall redefine in a minor way three of these variables, namely those for \( i = 3, 4, 5 \) and rewrite the scalar product \( \bar{v}(k) \cdot \bar{v}(-k) \) as follows

\[ \bar{v}(k) \cdot \bar{v}(-k) = v(k) v(-k) + \bar{v}^T(k) \cdot \bar{v}^T(-k) \]

where the scalar function \( v(k) \) and the transverse vector \( \bar{v}^T(k) \) are given by

\[ v(k) = \hat{k} \cdot \bar{v}(k) \]
\[ \bar{v}^T(k) = (1 - \hat{k} \hat{k}) \cdot \bar{v}(k) \]

with \( \hat{k} \) the unit vector in the direction of \( k, \hat{k} = k/k \). Defining now the modified variables

\[ \alpha_3(k) = v(k) \]
\[ \alpha_i(k) = v_i^T(k), \quad (i = 4, 5; \gamma = 1, 2), \]

with \( \gamma \) denoting the transverse orthogonal components of \( \bar{v}^T(k) \), \( \Delta S \) can be written as

\[ \Delta S = -\frac{1}{2} \sum_{k,ij} g_{ij}(k) \alpha_i(k) \alpha_j(-k) \]

The real matrix \( g_{ij}(k) \) in this quadratic form is diagonal, \( g_{ij} = g_{ii} \delta_{ij} \) and has elements

\[ g_{11} = (VT_0 \rho_0)^{-1} \beta; \quad g_{22} = (VT_0^2)^{-1} \rho_0 c_v \]
\[ g_{ii} = (VT_0)^{-1} \rho_0; \quad i = 3, 4, 5 \]

Formulae (3.2), (3.12) and (3.13) completely determine the equilibrium distribution function \( P_0(\vec{\alpha}) \) and yield for variables \( X_i(k) \), conjugate to \( \alpha_i(k) \) according to

\[ X_i(k) \equiv -k_B \frac{\partial \ln P_0}{\partial \alpha_i(k)} = \sum_j g_{ij} \alpha_j(k), \]
the relations

\[
\begin{align*}
X_1(\vec{k}) &= (T_0 V \rho_0)^{-1} \beta \Delta \rho(\vec{k}), \\
X_2 &= (VT_0^2)^{-1} \rho_0 c_v \Delta T(\vec{k}) \\
X_i(\vec{k}) &= (T_0 V)^{-1} \rho_0 \vec{v}(\vec{k}), \quad i = 3, 4, 5
\end{align*}
\]

(3.15)

We shall now evaluate in the next section the entropy produced in the system when the hydrodynamic fluctuations do not have their equilibrium distribution and derive, following the rules of non-equilibrium thermodynamics, the Fokker-Planck equation describing the dynamics of these fluctuations.

### 4 Entropy production and the Fokker-Planck equation for hydrodynamic fluctuations

Since the system considered is a closed one with constant total mass and energy, its rate of change of entropy with respect to time is according to equations (2.11) and (2.13), or equivalently (2.12)

\[
\frac{dS}{dt} = -k_B \int d\alpha \ln \frac{P(\alpha, t)}{P_0(\alpha)} \frac{\partial P(\alpha, t)}{\partial t}
\]

(4.1)

We shall now make use of the continuity equation obeyed by the probability density \( P(\alpha, t) \)

\[
\frac{\partial P(\alpha, t)}{\partial t} = -\sum_{\vec{k}, i} \frac{\partial}{\partial \alpha_i(\vec{k})} J_{\vec{k}, i} P(\alpha, t)
\]

(4.2)

where \( J_{\vec{k}, i} \) can be interpreted as a current per unit of phase space density along the \( \vec{k}, i \) axis of the phase space spanned by the complex state variables \( \alpha_{\vec{k}, i} \). Equation (4.2) represents as it were, the local form in \( \alpha \)-space of probability conservation. Notice that, since \( A_i(\vec{r}) \) is a real quantity, the state variables \( \alpha_i(\vec{k}) \) obey the relation \( \alpha_i^*(\vec{k}) = \alpha_i(-\vec{k}) \). Consequently, volume elements in the phase-space will be real and positive and since probabilities are real and positive by definition so will be the probability density \( P(\alpha) \) as it should. Equation (4.1) then implies that the currents \( J_{\vec{k}, i} \) have the property

\[
J_{\vec{k}, i}^* = J_{-\vec{k}, i}.
\]

We now substitute eq. (4.2) into (4.1) and obtain, integrating by parts and using the fact that \( P(\alpha, t) \) tends to zero sufficiently rapidly for \( \alpha_i(\vec{k}) \) tending to infinity, for the irreversible rate of change of entropy

\[
\frac{dS}{dt} = \int P(\alpha, t) \sigma(\alpha, t) d\alpha \geq 0
\]

(4.3)

with

\[
\sigma(\alpha) = -k_B \sum_{\vec{k}, i} J_{\vec{k}, i}^* \frac{\partial}{\partial \alpha_i(\vec{k})} \ln \frac{P(\alpha, t)}{P_0(\alpha)}
\]

(4.4)
the local entropy production in $\alpha$-space. As usual in non-equilibrium thermodynamics the entropy production is a sum of products of currents and thermodynamic forces. In the present case the latter are the gradients in $\alpha$-space of the chemical potential (2.14).

The total entropy production for the system is according to eq. (4.3) an average over possible fluctuating states of $\sigma(\alpha)$, the entropy production accompanying the evolution of a particular state. Since moreover the inequality (4.3) is valid for an arbitrary choice of the probability density $P(\alpha)$, it follows that the second law of thermodynamics holds not only for the average of $\sigma(\alpha)$ but also for $\sigma(\alpha)$ itself

$$\sigma(\alpha) \geq 0 \quad (4.5)$$

In equilibrium when $\sigma(\alpha)$ vanishes, both the currents and thermodynamics forces occurring in expression (4.4) vanish. In non-equilibrium and within a sufficiently wide range of physical conditions we may then suppose that these quantities are connected by linear relations. In a strictly linear theory of hydrodynamic fluctuations to which we will restrict ourselves, the coefficients in these laws, linear in the thermodynamic forces, must be constant with respect to the variables $\alpha_i(\vec{k})$, while the various modes do not couple. The linear laws will then be of the form

$$J_{k,i} = -k_B \sum_{j=1}^{5} L_{ij}(\vec{k}) \frac{\partial}{\partial \alpha_j(\vec{k})} \ln \frac{P(\alpha, t)}{P_0(\alpha)} \quad (4.6)$$

If we furthermore introduce the variables $X_j(\vec{k})$ conjugate to $\alpha_j(\vec{k})$ according to eq. (3.14) relations (4.6) can alternatively be written as

$$J_{k,i} = -\sum_j L_{ij} \left( X_j + k_B \frac{\partial}{\partial \alpha_j(\vec{k})} \ln P(\alpha) \right) \quad (4.7)$$

Substituting equation (4.7) into the conservation law (4.2) the following differential equation is obtained

$$\frac{\partial P}{\partial t} = \sum_{\vec{k}} \sum_{i,j} L_{ij}(\vec{k}) \frac{\partial}{\partial \alpha_i(\vec{k})} \left\{ P X_j(\vec{k}) + k_B \frac{\partial P}{\partial \alpha_j(\vec{k})} \right\} \quad (4.8)$$

which describes the time evolution of the probability density $P(\alpha, t)$.

With the linear relation between $X_j(\vec{k})$ and $\alpha_j(\vec{k})$ (c.f. eq.(3.14)), the differential equation (4.8) can also be written in the form

$$\frac{\partial P}{\partial t} = \sum_{\vec{k}} \sum_{i,j} \left\{ M_{ij}(\vec{k}) \frac{\partial}{\partial \alpha_i(\vec{k})} \alpha_j(\vec{k}) P + k_B L_{ij}^S(\vec{k}) \frac{\partial^2 P}{\partial \alpha_i(\vec{k}) \partial \alpha_j(\vec{k})} \right\} \quad (4.9)$$

where

$$M_{ij} = \sum_l L_{il} g_{lj}, \quad L_{ij} = \sum_l M_{il} g_{lj}^{-1} \quad (4.10)$$
and
\[ L_{ij}^S = \frac{1}{2}(L_{ij} + L_{ji}) \]  
(4.11)

This equation has the standard form of a linear Fokker-Planck equation and describes therefore the dynamics of the hydrodynamic fluctuations as Gaussian-Markov processes. As stated previously this result has been obtained here within the framework of non-equilibrium thermodynamics and its extension to system with internal degrees of freedom.

5 Identification of the Onsager coefficients in the Fokker-Planck equation

Note that the Fokker-Planck equation (4.9) contains the scheme of coefficients \( M_{ij} \) or equivalently \( L_{ij} \) (the matrix \( g_{ij} \) connecting these has already been specified above) which must still be determined to make the description of the dynamics of the fluctuations complete. The determination can be achieved by observing that fluctuations regress in the mean according to the macroscopic laws for irreversible processes. This experimentally verified behaviour is known as Onsager’s regression hypothesis [7] and enables one to identify, in the case of linear laws the coefficients \( L_{ij} \) in terms of macroscopic quantities.

We establish the mean regression laws from the Fokker-Planck equation (4.9) by multiplying both of its members by \( \alpha_i(\vec{k}) \) and integrating over all variables \( \alpha \). We then find for the first moments of the variables \( \alpha_i \) after partial integration the ordinary differential equations

\[
\frac{d\overline{\alpha_i\alpha_i^0}(\vec{k}, t)}{dt} = -\sum_j L_{ij}(\vec{k})\overline{X_j\alpha_i^0}(\vec{k}, t) = -\sum_l M_{il}(\vec{k})\overline{\alpha_l\alpha_i^0}(\vec{k}, t),
\]  
(5.1)

where the conditional mean \( \overline{\alpha_i\alpha_i^0} \) is given by
\[
\overline{\alpha_i\alpha_i^0} = \int \alpha_i(\vec{k}, t)P(\alpha, t)d\alpha
\]  
(5.2)

with
\[
P(\alpha, 0) = \prod_{\vec{k}, i} \delta \left( \alpha_i(\vec{k}) - \alpha_{i0}(\vec{k}) \right)
\]  
(5.3)

The mean regression equations constitute one of the fundaments of Onsager’s derivation [7] of reciprocal relations for the coefficients \( L_{ij} \), which follow by applying microscopic reversibility. For the equations (5.1) containing complex variables \( \alpha_i(\vec{k}) \), defined through equations (2.1) these reciprocal relation are [8] for complex Onsager coefficients \( L_{ij} \),
\[
L_{ij} = L_{ji}^* \varepsilon_i \varepsilon_j
\]  
(5.4)
with

\[ \varepsilon_i = \begin{cases} 
1 & \text{for } i = 1, 2 \\
-1 & \text{for } i = 3, 4, 5 
\end{cases} \quad (5.5) \]

The coefficients \( L_{ij} \) satisfy, in addition to the reciprocal relations, certain conditions imposed by the spatial symmetry of the system. For the isotropic fluid considered this implies that scalar and vectorial phenomena do not couple so that

\[ L_{ij} = L_{ji} = 0 \quad \text{for} \quad \{ i = 1, 2, 3 \} \quad (5.6) \]

and also that the matrix \( L_{ij}, i, j = 4, 5 \) is diagonal

\[ L_{ij} = L \delta_{ij}, \quad i, j = 4, 5 \quad (5.7) \]

To identify finally the coefficients \( L_{ij} \) we list below the familiar [9] fully linear macroscopic hydrodynamic equations for the density, temperature and velocity fields, \( \rho(\vec{k}, t), T(\vec{k}, t) \) and \( v(\vec{k}, t) \). These equations are

\[ \frac{\partial \rho(\vec{k}, t)}{\partial t} = -i \rho_0 k \hat{k} \cdot \vec{v}(\vec{k}, t) \quad (5.8) \]

\[ \frac{\partial T(\vec{k}, t)}{\partial t} = -T_0 \left( \frac{\partial T}{\partial T} \right) \rho_0 \frac{k^2 \lambda}{\rho_0 c_v} \rho_0 \rho_0 \cdot \vec{v}(\vec{k}, t) - \frac{k^2 \lambda}{\rho_0 c_v} T(\vec{k}, t) \quad (5.9) \]

\[ \frac{\partial \vec{v}(\vec{k}, t)}{\partial t} = -i \beta \rho_0 \rho_0 \rho_0 \rho_0 \left( \frac{\partial p}{\partial T} \right) \rho_0 \rho_0 \rho_0 \rho_0 \cdot \vec{v}(\vec{k}, t) - \frac{1}{\rho_0} \left\{ k^2 \eta + \left( \frac{1}{3} \eta + \eta_v \right) \vec{k} \cdot \vec{k} \right\} \vec{v}(\vec{k}, t) \quad (5.10) \]

In equation (5.9) \( \lambda \) is the heat conductivity; \( \eta \) and \( \eta_v \) in equation (5.10) are the viscosity and volume viscosity respectively.

By multiplying moreover eq. (5.10) successively with the unit vector \( \hat{k} \), and the projection operator \( 1 - \hat{k} \hat{k} \) one obtains the macroscopic equations for the variables \( v(\vec{k}) \) and \( \vec{v}(\vec{k}) \) introduced in section 3, cf. eqs. (3.8) and (3.9).

Comparing then the mean regression equation (5.1) with the macroscopic hydrodynamic
equations one finds for the matrix of phenomenological coefficients $M_{ij}$

$$
M = \begin{pmatrix}
0 & 0 & ik\rho_0 & 0 & 0 \\
0 & k^2\frac{\lambda}{\rho_0 c_v} & ikT_0(\frac{\partial P}{\partial T})_{\rho_0} & 0 & 0 \\
\frac{ik\beta}{\rho_0} & \frac{ik}{\rho_0} & k^2(\frac{4}{3}\eta + \eta_v) & 0 & 0 \\
0 & 0 & 0 & k^2\frac{\eta}{\rho_0} & 0 \\
0 & 0 & 0 & 0 & k^2\frac{\eta}{\rho_0}
\end{pmatrix}
$$

and for the matrix of Onsager coefficients $L_{ij}$, using also eqs. (3.13) and (4.10),

$$
L = \begin{pmatrix}
0 & 0 & ikVT_0 & 0 & 0 \\
0 & VT_0^2k^2\frac{\lambda}{\rho_0^2 c_v} & ik(\frac{\partial P}{\partial T})_{\rho_0}VT_0^2/\rho_0^2 c_v & 0 & 0 \\
0 & VT_0 & k^2(\frac{4}{3}\eta + \eta_v)/\rho_0^2 & 0 & 0 \\
0 & 0 & 0 & VT_0k^2\eta/\rho_0^2 & 0 \\
0 & 0 & 0 & 0 & VT_0k^2\eta/\rho_0^2
\end{pmatrix}
$$

This then concludes the specification within the context of nonequilibrium thermodynamics of the Onsager coefficients $L_{ij}$ for the linear fluctuating fluid considered and completely determines the Gaussian solution of the linear Fokker-Planck equation. Observe that the reciprocal relations (5.4) as well as the spatial symmetry requirements (Curie’s principle) (5.6) and (5.7) are automatically satisfied by the coefficients found above.

The above application to hydrodynamic fluctuations of the recently developed extension to fluctuation phenomena [1] of the scheme of macroscopic nonequilibrium thermodynamics, illustrates once more previously stated characteristics of this generalized formalism which goes beyond the traditional macroscopic domain. It introduces indeed, while keeping the framework and rules of the macroscopic theory, statistical notions such as:

1. The distribution function of hydrodynamic fluctuations.
2. The definition of entropy as a functional of this distribution function.
3. The calculation of the probability distribution function in equilibrium.

We also stressed before that the extension of the thermodynamic formalism is legitimate because it is limited to events taking place on a time scale which is slow compared to the time
scale of microscopic phenomena. For the case at hand the phenomena dealt with occur at characteristic times which are essentially hydrodynamic relaxation times.

Appendix

In this appendix we show for completeness sake that expression (3.5) for $\Delta S$, the variation of entropy with respect to its equilibrium value up to second order, reduces to the diagonal quadratic form in $\Delta T(\vec{r})$ and $\Delta \rho(\vec{r})$ given in formula (3.6).

We first observe that in the integral (3.5) the linear terms give rise, due to mass and energy conservation to the integral of the quadratic term $1/2 \rho_0 v^2(\vec{r})$:

$$\int \left\{ \frac{\partial s}{\partial u} \Delta u + \frac{\partial s}{\partial \rho} \Delta \rho \right\} d\vec{r} = \frac{1}{2T_0} \rho_0 \int v^2 d\vec{v}, \quad (A.1)$$

since all thermodynamic derivatives in (A.1) are uniform equilibrium quantities and since $\partial s/\partial u = 1/T_0$. Next we observe that the second order terms in the integral (3.5) may be written in the following form

$$\frac{1}{2} \frac{\partial^2 s}{\partial u^2} (\Delta u)^2 + \frac{\partial^2 s}{\partial u \partial \rho} \Delta u \Delta \rho + \frac{\partial^2 s}{\partial \rho^2} (\Delta \rho)^2 = \Delta \frac{1}{T} \Delta u - \Delta \frac{\mu}{T} \Delta \rho \quad (A.2)$$

as

$$\Delta \frac{1}{T} = \Delta \frac{\partial s}{\partial u} = \frac{\partial^2 s}{\partial u^2} \Delta u + \frac{\partial^2 s}{\partial u \partial \rho} \Delta \rho \quad (A.3)$$

and

$$-\Delta \frac{\mu}{T} = \Delta \frac{\partial s}{\partial \rho} = \frac{\partial^2 s}{\partial \rho \partial u} \Delta u + \frac{\partial^2 s}{\partial \rho^2} \Delta \rho. \quad (A.4)$$

Expand now in expression (A.2) $\Delta u$ and $\Delta \mu/T$ to linear order in $\Delta T$ and $\Delta \rho$

$$\Delta u = \frac{\partial u}{\partial T} \Delta T + \frac{\partial u}{\partial \rho} \Delta \rho \quad (A.5)$$

$$\Delta \frac{\mu}{T} = \frac{\partial \mu}{\partial T} \Delta T + \frac{1}{T} \frac{\partial \mu}{\partial \rho} \Delta \rho \quad (A.6)$$

Here again the thermodynamic derivatives are uniform equilibrium quantities.

Finally observe that the total differential of the thermodynamic potential $f/T$, with $f = u - Ts$ the free energy density,

$$\frac{df}{T} = -\frac{u}{T^2} dT + \frac{\mu}{T} d\rho \quad (A.7)$$

leads to the Maxwell relation

$$-\frac{\partial \mu/T}{\partial T} = \frac{1}{T^2} \frac{\partial u}{\partial \rho} \quad (A.8)$$

Substituting then (A.1) and (A.2) with (A.5) and (A.6) into expression (3.5) and taking into account the Maxwell relation (A.8) one obtains the desired result (3.6).
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