THE EINSTEIN-BOLTZMANN RELATION FOR THERMODYNAMIC AND HYDRODYNAMIC FLUCTUATIONS

A. J. McKane\textsuperscript{a}, F. Vázquez\textsuperscript{b} and M. A. Olivares-Robles\textsuperscript{b, c}

\textsuperscript{a}Theory Group, School of Physics and Astronomy, University of Manchester, Manchester M13 9PL, UK

\textsuperscript{b}Facultad de Ciencias, Universidad Autónoma del Estado de Morelos, Avenida Universidad 1001, Chamilpa, Cuernavaca, Morelos 62209, México

\textsuperscript{c}Sección de Posgrado e Investigación, Escuela Superior de Ingeniería Mecánica y Eléctrica Culhuacan-IPN, Av. Santa Ana 1000, Col. San Francisco Culhuacan Coyoacan 04430, México D.F.

Abstract

When making the connection between the thermodynamics of irreversible processes and the theory of stochastic processes through the fluctuation-dissipation theorem, it is necessary to invoke a postulate of the Einstein-Boltzmann type. For convective processes hydrodynamic fluctuations must be included, the velocity is a dynamical variable and although the entropy cannot depend directly on the velocity, $\delta^2S$ will depend on velocity variations. Some authors do not include velocity variations in $\delta^2S$, and so have to introduce a non-thermodynamic function which replaces the entropy and does depend on the velocity. At first sight, it seems that the introduction of such a function requires a generalisation of the Einstein-Boltzmann relation to be invoked. We review the reason why it is not necessary to introduce such a function, and therefore why there is no need to generalise the Einstein-Boltzmann relation in this way. We then obtain the fluctuation-dissipation theorem which shows some differences as compared with the non-convective case. We also show that $\delta^2S$ is a Liapunov function when it includes velocity fluctuations.
1 INTRODUCTION

Velocity fluctuations play an important role in a variety of non-equilibrium phenomena. Mention can be made, for instance, of time dependent diffusion processes in binary liquid mixtures, where they are the principal mechanism leading to anomalously large fluctuations in concentration [1]. Also, the coupling between temperature and transverse-velocity fluctuations in the well known case of a horizontal fluid layer heated from below may be associated with a small convective heat transfer below the Rayleigh-Bénard instability [2]. It is natural to consider these kind of problems from the point of view of irreversible thermodynamics. However, there is no prescription for how to introduce the velocity fluctuations into the formalism.

The standard method of introducing fluctuations into irreversible thermodynamics is through the Einstein-Boltzmann relation $P_S \sim \exp \{\frac{\delta^2 S}{2k_B}\}$, where $P_S$ is the stationary probability distribution and $\delta^2 S$ is the second variation of the local entropy [3]. In this paper we will be interested in convective processes where the velocity is included as a dynamical variable, and in the explicit form for $\delta^2 S$ in this case. It should be noted, and is widely appreciated, that the entropy does not depend directly on the velocity of the system: velocity is a hydrodynamic, but not a thermodynamic variable. Therefore some authors, notably Glansdorff and Prigogine [4], do not include velocity variations in the expression for $\delta^2 S$.

A solution to this problem could be to introduce a new function which is essentially a generalisation of the entropy which does depend on the velocity. This would not be a thermodynamic function, but it would then be necessary to generalise the Einstein-Boltzmann relation in such a way that entropy would be replaced by this new function. Such a function has been introduced some time ago by Glansdorff and Prigogine, but in the context of thermodynamic and hydrodynamic stability [4]. They suggested defining a new function $z \equiv s - \frac{v^2}{2T_0}$, where $s$ is the entropy per unit mass, $v$ is the barycentric velocity and $T_0$ is the temperature in the reference state (for example, the temperature in equilibrium). The analogous quantity for the system as a whole will be denoted by $Z$ and is given by $Z = \int \rho z dV$, just as $S = \int \rho s dV$. This function has not been utilised a great deal, perhaps in part because among those who explicitly use the $Z$-function [4]-[7], most do not consistently use the definition given above, sometimes using the (varying) temperature $T$ in place of the (non-varying) reference temperature $T_0$.

The main reason why the function $Z$ has not been widely used is no doubt the demonstration by Oono [6] that $\delta^2 S$ does in fact contain velocity variations, even though the entropy does not depend on the velocity. In fact, the entropy may be written in terms of the velocity if other variables are introduced which exactly cancel out the velocity dependence [8]. To see this
let us write \[ dU = T dS - pdV + \mu_\gamma dN_\gamma, \] (1)

where \( U \) is the internal energy, \( V \) the volume, \( N_\gamma \) the number of moles of the \( \gamma \)-chemical species, \( p \) the pressure, and \( \mu_\gamma \) the chemical potential of the \( \gamma \)-species. In addition, let \( E_T \) be the total energy:

\[ E_T = U + m v_\mu v_\mu / 2, \] (2)

\( v_\mu \) being the barycentric velocity and \( m \) the mass. We assume that the changes in potential energy due to altitude, for instance, are negligible. Therefore we omit a potential term in this definition. Then Eq. (1) can be written as

\[ dE_T = T dS - pdV + \mu_\gamma dN_\gamma + m v_\mu dv_\mu. \] (3)

Now note that in Eq. (3) the term \( dE_T - m v_\mu dv_\mu \) does not depend on velocity in accordance with the definition of the total energy Eq.(2). So the entropy in Eq. (3) does not depend on the velocity and the thermodynamic consistency of this form of Gibbs relation Eq.(1) is ensured.

Oono also showed that \( \delta^2 Z \) is nothing else but \( \delta^2 S \). However, mention must be made of the fact that \( \delta^2 S \) and \( \delta^2 Z \) are only equal within approximation schemes where \( T \) can be replaced by \( T_0 \). There is also a lack of consensus as to whether \( \delta^2 S \) is a Liapunov function in systems where velocity is a dynamical variable: some authors believe it is \[9\], others believe it is not \[4\]. Some of this confusion involves matters of principle, some involves matters of notation (for instance, \( \delta^2 S \) meaning two entirely different things), and some involves inconsistencies in definitions of key quantities. Our objective in this paper is to clarify many of these points, by examining their consequences in the context of linear theories of irreversible thermodynamics, and to obtain the explicit form of the fluctuation-dissipation theorem for convective processes. We remark in passing that there are a whole set of different subtleties and controversies in extending these ideas to the non-linear regime \[5 \text{–} 10\], but we do not explore these here.

2 IRREVERSIBLE THERMODYNAMICS AND STOCHASTIC PROCESSES

A fluid being described within linear irreversible thermodynamics (LIT) requires five local variables: the volume per unit mass \( v \), the barycentric velocity \( v_\mu \) and the temperature \( T \) \[3\], but our conclusions will be more widely applicable, for example applying also to a fluid in extended irreversible thermodynamics (EIT), which requires 14 dynamic variables \[11\]. To keep the notation general, we will denote the fluctuations in the independent dynamic
variables as \( a_b(r, t) \), where \( b = 1, \ldots, N \) and assume that they satisfy a set of Langevin-type equations:

\[
\frac{\partial a_b(r, t)}{\partial t} = - \sum_c \int d\mathbf{r}' G_{bc}(\mathbf{r}, \mathbf{r}') a_c(\mathbf{r}', t) + \tilde{f}_b(\mathbf{r}, t). \tag{4}
\]

Here the first term on the right-hand side is a result of the linearization of the macroscopic equation about the stationary state and \( \tilde{f}_b(\mathbf{r}, t) \) is a stochastic term that represents fluctuations in the system. For the particular case of a fluid within LIT \( N = 5 \) and the five local variables \( a_1, \ldots, a_5 \) are the scaled versions of fluctuations in \( \{v, v_\mu, T\} \). Specifically if the equilibrium state is denoted by \( \{v_0, 0, T_0\} \), and fluctuations away from this state by \( \{v_1, v_\mu, T_1\} \), then we define the \( a_b \) by \([9, 12]\):

\[
a_1 = -\rho_0^{\frac{4}{3}} v_1, \quad a_{\mu+1} = \rho_0^{1/2} v_\mu, \quad a_5 = \left( \frac{\rho_0 C_v}{T_0 c_T^2} \right)^{\frac{1}{2}} T_1, \tag{5}
\]

with \( \mu = 1, 2, 3 \). Here \( \rho_0 \) is the mass density, \( c_T \) the isothermal speed of sound and \( C_v \) the specific heat at constant volume, all in equilibrium. These rescalings simplify the algebraic structure of the results. We use the same notation for the velocity and the velocity fluctuations, since no confusion should arise.

The analysis of the fluctuations is made more transparent if we adopt an abbreviated form where the continuous labels \( r \) and \( r' \) are replaced by the discrete labels \( j \) and \( k \) and where the summation convention is assumed. In this case, (4) becomes

\[
\dot{a}_j^b(t) + G_{jk}^{bc} a_k^c(t) = \tilde{f}_j^b(t); \quad b, c = 1, \ldots, N. \tag{6}
\]

To complete the specification of the stochastic dynamics, the statistics of the stochastic terms \( \tilde{f}_j^b(t) \) need to be given. We will take them to have a Gaussian distribution with mean zero and correlator

\[
\langle \tilde{f}_j^b(t) \tilde{f}_k^c(t') \rangle = 2Q_{jk}^{bc} \delta(t - t'). \tag{7}
\]

The requirement that they have zero mean follows from the fact that we ask that the \( a_b \) have zero mean: \( \langle a_b^2 \rangle = 0 \). The matrix \( Q \) is real, symmetric and positive semidefinite. We will not give an explicit form for the matrix \( G \) here: it may be straightforwardly derived by a linearization of the macroscopic equations \([9]\). As will be discussed below, the matrix \( Q \) may be given in terms of the matrix \( G \) and another matrix \( E \), which is the covariant matrix of the \( a_k^c \) in the stationary state:

\[
\langle a_k^c a_m^f \rangle_S = (E^{-1})_{cf}. \tag{8}
\]
Therefore the stochastic dynamics will be completely specified if we can determine the matrix $E$. Clearly we need some new information from which to find it. This is the Einstein-Boltzmann relation.

The Gaussian assumption determines the class of phenomena to be dealt with. In general, the Gaussian assumption is valid for a wide range of conditions in which the physical variables do not change too fast with time [3]. It may be said that the sufficient condition for the validity of this assumption is the local equilibrium hypothesis. Nevertheless, the system may be in a non-equilibrium non-stationary state in which such a hypothesis is not satisfied and yet will be well described throughout using the Gaussian assumption.

We now introduce the fluctuation-dissipation theorem by recalling that another way of specifying the stochastic process defined by Eqs. (6) and (7) is through the Fokker-Planck equation [14, 15]

$$\frac{\partial P(\mathbf{a}, t)}{\partial t} = \frac{\partial}{\partial a^b} \left[ G^{jk}_{bc} a^c_k P(\mathbf{a}, t) \right] + \frac{\partial^2}{\partial a^b \partial a^k_c} \left[ Q^{jk}_{bc} P(\mathbf{a}, t) \right],$$

where $P(\mathbf{a}, t)$ is the probability distribution function of the local variables $\mathbf{a}$. This is a linear Fokker-Planck equation and so the solution is a Gaussian which may be written down explicitly as [16]

$$P(\mathbf{a}, t) = \mathcal{N} (\text{det } \Xi(t))^{-1/2} \times \exp \left\{ -\frac{1}{2} \mathbf{a}^T \Xi(t)^{-1} \mathbf{a} \right\},$$

where $\mathcal{N}$ is a normalisation constant and where the matrix $\Xi(t)$ is given by

$$\Xi(t-t_0) = 2 \int_{t_0}^t e^{-(t-t')G} Q e^{(t-t')G} dt'.$$

Here initial conditions have been set at $t = t_0$ and we have made use of the fact that $\langle a^b_0 \rangle = 0$. By letting $t_0 \rightarrow -\infty$, we find the stationary distribution. It has the form (10), but with $\Xi(t)$ replaced by

$$\Xi(\infty) = 2 \int_{-\infty}^t e^{-(t-t')G} Q e^{(t-t')G} dt'$$

$$= 2 \int_0^\infty e^{-\rho G} Q e^{\rho G} d\rho.$$

To make use of the Einstein-Boltzmann relation, let us observe that since the $a^k_b$ have zero mean, and since they are linearly related to the $f^k_b$ which are Gaussian, they also have a Gaussian distribution with a stationary probability distribution of the form:

$$P_S(\mathbf{a}) = \mathcal{N} \exp \left\{ -\frac{1}{2} a^b_d E^{jk}_{bc} a^k_c \right\}.$$
Here $\mathbf{a} = (a^1, a^2, \ldots)$ where $a^i = (a^i_1, \ldots, a^i_N)$ and $N$ is a normalisation constant. By comparing (13) with (10) when $t_0 \to -\infty$, we can make the identification

$$E^{-1} = \Xi(\infty) = 2 \int_0^\infty e^{-\rho G} Q e^{\rho G} \, d\rho.$$  \hspace{1cm} (14)

Performing the integral in (14) gives the result [16]

$$2Q_{ij} = G_{ik}^{ac}(E^{-1})_{cb}^{kj} + (E^{-1})_{ac}^{ik}G_{cb}^{T kj},$$ \hspace{1cm} (15)

where $T$ denotes transpose. This is the fluctuation-dissipation theorem of the theory. It is the required relationship which gives the matrix $Q$ in terms of the matrices $G$ and $E$.

### 3 THE FLUCTUATION-DISSIPATION THEOREM FOR CONVECTIVE SYSTEMS

The result (13) may be compared directly [12] with the Einstein-Boltzmann relation

$$P_S(\mathbf{a}) \sim \exp \left\{ \delta^2 S/2k_B \right\},$$ \hspace{1cm} (16)

so that

$$S(\mathbf{a}) = S_{eq} - \frac{1}{2}k_B a^2_b E_{bc}^{ij} a^k_c.$$ \hspace{1cm} (17)

The indices $b$ and $c$ in (13) or (17) run from 1 to $N$ (from 1 to 5 in LIT) and include the velocity as a variable. However, if only specific volume (or density) and temperature are included as variables in $\delta^2 S$ [1, 13], then it apparently seems that Eqs. (13) and (16) cannot be compared to determine the $E_{bc}^{ij}$ matrix. Thus, it seems clear that the $\delta^2 S$ which we need to use in the Einstein-Boltzmann relation is the one which allows for variations in the velocity. In fact, as shown by Oono [6],

$$\delta^2 S = \delta \left( \frac{1}{T} \right) \delta U + \delta \left( \frac{p}{T} \right) \delta V - \frac{m\delta v_\mu \delta v_\mu}{T},$$ \hspace{1cm} (18)

where $\delta^2 S|_{\nu}$ is $\delta^2 S$ with no variation in the velocity. Using $\delta^2 S$, rather than $\delta^2 S|_{\nu}$ allows Eqs. (13) and (16) to be compared and the matrix $E$ determined. It should be noted that (i) in Ref. [12] the additional term to be added to $\delta^2 S|_{\nu}$ was given as $m\delta v_\mu \delta (-v_\mu/T)$, and (ii) in Ref. [6] it was stated that $\delta^2 Z = \delta^2 S$ — whereas from the definition of $z$ we see that

$$\delta^2 Z = \delta^2 S|_{\nu} - \frac{m\delta v_\mu \delta v_\mu}{T_0}.$$ \hspace{1cm} (19)
Both the results (i) and (ii) are true in the linear regime, where $T^{-1}$ may be replaced by $T^{-1}_0$, but they are not true in general; the correct form for $\delta^2 S$ is given in Eq. (18), and $\delta^2 Z$ is not equal to $\delta^2 S$, it is given by Eq. (19). A consequence of this is that in the linear regime the Einstein-Boltzmann relation may also be written as $P_S \sim \exp \left\{ \frac{\delta^2 S}{2k_B} \right\}$. This means that if we were to use $\delta^2 S|_v$, as Glansdorff and Prigogine do, we would need to invoke this latter form of the Einstein-Boltzmann relation to identify the matrix $E$ and so make the connection between irreversible thermodynamics and the theory of stochastic processes, at least in the linear regime. However, as we have stressed there is no need to introduce this extra postulate, and we may use the usual form $P_S \sim \exp \left\{ \frac{\delta^2 S}{2k_B} \right\}$, as long as the correct form of $\delta^2 S$ (18) is used.

We can now come back to the task of determining the matrix $E$. Let us first write down the expression for $\delta^2 S$ without velocity variations in terms of the scaled versions of $v_1$ and $T_1$, namely $a_1$ and $a_5$ to see explicitly where the process fails. After some straightforward manipulations [12] of this standard result [13], we obtain, using the Einstein-Boltzmann relation,

$$P_S(a) \sim \exp \left\{ \frac{c_T^2}{2k_BT_0} \left[ -a_1^ja_1^j - a_5^ja_5^j \right] \right\}. \quad (20)$$

If this result were to be compared with (13) then it would imply that $E$ would be diagonal, but with entries corresponding to the velocity fluctuations being zero. This is clearly not correct since, for instance, the velocity-velocity correlation function in equilibrium (8) would be formally infinite. Using instead the form of $\delta^2 S$ allowing for velocity variation we find

$$P_S(a) \sim \exp \left\{ \frac{c_T^2}{2k_BT_0} \left[ -a_1^ja_1^j \right] \right\}, \quad (21)$$

since $v_\mu = (c_T^2/\rho_0)^{1/2}a_\mu+1$ and where $b = 1, ..., 5$. A comparison with (8) gives the identification

$$E_{jk}^{bc} = \frac{c_T^2}{k_BT_0} \delta_{jk} \delta_{bc}. \quad (22)$$

This now gives a consistent result, which when used in conjunction with the fluctuation-dissipation theorem [15], completely specifies the stochastic dynamics described by (6) and (7) or by (9). An explicit expression for matrix $Q$ is obtained by substituting Eq. (22) into Eq. (15). The result is

$$Q_{jk}^{bc} = \frac{k_BT_0}{A} S_{jk}^{bc}. \quad (23)$$

where $S_{jk}^{bc}$ represents the symmetric part of the dynamic matrix $G$:

$$S_{\mu+1,\nu+1}(r,r') = \frac{1}{\rho_0} \left[ 2\mu X_{\mu\rho\nu\sigma} + \zeta \delta_{\mu\rho} \delta_{\nu\sigma} \right] \frac{\partial^2}{\partial x_\rho \partial x'_\sigma} \delta(r-r'), \quad (24)$$
\[ S_{55}(r, r') = \frac{1}{\rho_0 C} \lambda \delta_{\mu \nu} \frac{\partial^2}{\partial x_\mu \partial x'_\nu} \delta(r - r'), \tag{25} \]

with all other \( S_{bc}(r, r') \), including \( S_{11}(r, r') \), equal to zero. The tensor \( X_{\mu \nu \rho \sigma} \) is defined by

\[ X_{\mu \nu \rho \sigma} = \frac{1}{2} \left( \delta_{\mu \rho} \delta_{\nu \sigma} + \delta_{\mu \sigma} \delta_{\nu \rho} - \frac{2}{3} \delta_{\mu \nu} \delta_{\rho \sigma} \right). \tag{26} \]

In Eqs. (24) and (25), the continuum limit has been taken so that the discrete spatial variables \( j, k \) have been replaced by \( r, r' \). As mentioned above, all the matrices in Eq. (15) are \( 5 \times 5 \) in the convective case, unlike in the non-convective case where they are \( 2 \times 2 \).

The discussion above took place within the framework of LIT which contains 5 dynamical variables, but the idea is more general. We have already mentioned EIT where the dissipative fluxes are raised to the same status as the thermodynamic variables. In this case \( \delta^2 S \) (where \( S \) now denotes the corresponding non-equilibrium thermodynamic potential in place of the local equilibrium entropy) contains terms involving these fluxes, as well as the more conventional thermodynamical variables, but not the velocity variables \[11\]. Written in terms of scaled variables it has the form \[12\]

\[ P_S(\mathbf{a}) \sim \exp \left\{ \frac{c_T^2}{2k_B T_0} \left[ -a_j^i a_j^i - a_j^5 a_j^5 - \frac{1}{2} a_j^\mu a_j^\mu a_j^\nu a_j^\nu - a_j^{\mu+10} a_j^{\mu+10} - a_j^{14} a_j^{14} \right] \right\}. \tag{27} \]

Here the variables \( a_j^\mu, a_j^{\mu+10} \) and \( a_j^{14} \) are scaled versions of the traceless stress tensor, the heat flux and the trace of the stress tensor, respectively. The result (27) suffers from the same defect as (20), but if we now include the velocity variations in \( \delta^2 S \) then we again obtain (21), but now with \( b = 1, \ldots, 14 \). Therefore the matrix \( E \) can be consistently identified, and again is given by (22).

### 4 VELOCITY FLUCTUATIONS AND THE LIAPUNOV FUNCTION

Finally, within the context of LIT or EIT, we can investigate the claim that \( \delta^2 Z \) is a Liapunov function, but that \( \delta^2 S \) can no longer be adopted as a Liapunov function when velocity is included as a dynamical variable \[4\]. In the language we have been using in this paper, the former is \( \delta^2 S \) and the latter is \( \delta^2 S|_{\nu} \), and this is the notation we will use in what follows. To investigate whether these functions are Liapunov functions, we begin from the form of \( \delta^2 S \) sufficiently near equilibrium that LIT will apply:

\[ \delta^2 S = -\frac{c_T^2}{T_0} a_j^i(t) a_j^i(t). \tag{28} \]
Here the $a^i_b$ are averaged variables, that is, non-fluctuating variables which obey the hydrodynamic balance equations. From Eq. (28) we see that $\delta^2 S \leq 0$ with equality if and only if $a^i_b(t) = 0$. Differentiating Eq. (28) with respect to time gives

$$
\frac{d}{dt} (\delta^2 S) = - \frac{2c_r^2}{T_0} a^i_b(t) a^j_a(t) = \frac{2c_r^2}{T_0} G^{jk}_{bc} a^k_c(t) a^i_b(t)$$

$$= \frac{2c_r^2}{T_0} S^{jk}_{bc} a^k_c(t) a^i_b(t), \quad (29)$$

where $S^{jk}_{bc}$ is the symmetric part of $G^{jk}_{bc}$. Using the expressions for $S^{jk}_{bc}$, Eqs. (24) and (25), and integrating by parts gives

$$
\frac{d}{dt} (\delta^2 S) = \frac{2c_r^2}{\rho_0 T_0} \int d\mathbf{r} \left( 2\mu \frac{\delta}{\partial x} \frac{\delta a_{\mu\nu} + \partial a_{\nu\mu}}{\partial x} + \lambda \frac{\partial a_5}{\partial x} \frac{\partial a_5}{\partial x} \right) \geq 0, \quad (30)
$$

where we have gone back to an explicit notation for the continuous space variable $\mathbf{r}$. In Eq. (30), $\lambda$, $\zeta$ and $\mu$ are the thermal conductivity, the bulk viscosity and the shear viscosity, respectively, $D_{\mu\nu}$ is the symmetric part of the scaled velocity gradient and $D_{\mu\nu}$ its traceless form:

$$D_{\mu\nu} = \frac{1}{2} \left( \frac{\partial a_{\mu+1}}{\partial x_{\nu}} + \frac{\partial a_{\nu+1}}{\partial x_{\mu}} \right), \quad \delta D_{\mu\nu} = D_{\mu\nu} - \frac{1}{3} D_{\rho\rho} \delta_{\mu\nu}. \quad (31)$$

This shows explicitly, when $\delta^2 S$ is defined in terms of the averaged variables, that it is a Liapunov function, as suggested by Glansdorff and Prigogine [4]. However, this calculation is identical to one carried out in Ref. [9], where $dS/dt$ was evaluated and shown to be non-negative. Since all of these calculations have been carried out in the linear regime, and $dS/dt = (1/2) d(\delta^2 S)/dt = (1/2) d(\delta^2 Z)/dt$ this is not surprising. Note that the inequality in Eq. (30) is an equality if and only if $D_{\mu\nu} = 0$, $D_{\mu\nu} = 0$ and $\partial a_5/\partial x_\mu = 0$. From the constitutive relations for LIT this corresponds to the vanishing of the traceless stress tensor and its trace and of the heat flux. This condition corresponds to the thermodynamic equilibrium state and it is equivalent to the condition $a^i_b(t) = 0$ found when $\delta^2 S$ given by Eq. (28) is equal to zero.

A similar calculation may be carried out for EIT. In this case Eqs. (28) and (29) also hold, but now with the indices $b$ and $c$ running from 1 to 14. The form of the $S^{jk}_{bc}$ are different for EIT — in some ways they are simpler, since they do not involve derivatives, and so no integration by parts is required to obtain an explicit expression for the time derivative of $\delta^2 S$. Using the expressions for $S^{jk}_{bc}$ given in Ref. [12] for EIT one finds that

$$
\frac{d}{dt} (\delta^2 S) = \frac{2c_r^2}{T_0} \int d\mathbf{r} \left( \frac{1}{2} \tau_{2-1} \delta_{\mu\nu} a_{\nu\mu} + \tau_{-1} a_{14} a_{14} + \tau_{-1} a_{\mu+10} a_{\mu+10} \right) \geq 0, \quad (32)
$$
where the $\tau_i, i = 0, 1, 2$ are the relaxation times of the various fluxes. Once again $\delta^2 S$ is seen to be a Liapunov function, with the inequality in Eq. (32) becoming an equality if and only if $a_{\mu\nu} = 0$, $a_{14} = 0$ and $a_{\mu+10} = 0$. These are just scaled versions of the traceless stress tensor and its trace, and of the heat flux, and so equality is obtained when these vanish, just as for LIT. If we use this method to try and show that $\delta^2 S|_v$ is a Liapunov function, we find, for example in the case of LIT,

$$\delta^2 S|_v = -\frac{c^2}{T_0} \left( a^i_1(t)a^j_1(t) + a^i_2(t)a^j_2(t) \right),$$

(33)

and differentiating with respect to time gives

$$\frac{d}{dt} \left( \delta^2 S|_v \right) = -\frac{2c^2}{T_0} \left( \dot{a}^i_1(t)a^j_1(t) + \dot{a}^i_2(t)a^j_2(t) \right)$$

$$= \frac{2c^2}{T_0} \left( G_{i_1c}^k a^k_1(t) a^i_1(t) + G_{i_2c}^k a^k_2(t) a^i_2(t) \right).$$

(34)

Substituting the actual expressions for $G_{i_1c}^k$ in Eq. (34), does not give an expression which is manifestly positive semi-definite. This is no doubt what Glansdorff and Prigogine meant by saying that $\delta^2 S$ loses its properties as a Liapunov function when velocity is included as a dynamical variable. However, since we are assuming that $v$ is fixed in the definition of $\delta^2 S$ it might be more consistent to take $v$ to be a constant in the balance equations. If we do this we find that only the third term in the parentheses in Eq. (30) is present. It now follows that $d(\delta^2 S|_v)/dt \geq 0$

5 CONCLUSIONS

In summary, when studying fluctuations in irreversible thermodynamics using the formalism of Langevin or Fokker-Planck equations, velocity is included as a variable. When making use of the Einstein-Boltzmann relation to determine the exact form of the fluctuation-dissipation relation the form of $\delta^2 S$ where velocity variation is allowed must be used. Although $S$ and $\delta S$ may be written in forms that do not involve velocity, $\delta^2 S$ does depend on the velocity variation. If, as some authors do, $\delta^2 S$ is taken not to include velocity variations — using what we have called $\delta^2 S|_v$ — then these velocity variations have to be introduced by some other means, for example, by the introduction of the $Z$ function. However, in this case an added postulate of the form $P_S \sim \exp \{\delta^2 Z/2k_B\}$ has to be introduced. Clearly, this is unnecessary since the usual Einstein-Boltzmann relation, with the correct use of $\delta^2 S$, that is, including velocity variations, may be used without contradiction to complete the link between thermodynamic and hydrodynamic fluctuations and the theory of stochastic processes.
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