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Non-equilibrium thermodynamics

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Abstract. Non-equilibrium statistical thermodynamics is discussed again from the information theory viewpoint of Jaynes. The outlook of Ingarden and Kossakowski is reviewed and analysed, with the result that a particular solution of the Liouville equation is derived, this solution being capable of describing non-equilibrium processes. This solution of Liouville's equation is split in a fashion which enables statistical mean values to be evaluated at any time in the history of a system in terms of mean values evaluated using the statistical index which, at that time, maximises the information entropy subject to various mean value constraints. The theory developed herein is then used to derive, under certain approximations, the formalism of irreversible thermodynamics, the approximations made delineating the validity of the resulting theory. A brief comparison is made with other formalisms arising in non-equilibrium statistical thermodynamics.

1. Introduction

Irreversible processes may be split into two camps: those which may be regarded as caused by mechanical perturbations, and those which are caused by inhomogeneities in the system. (Though attempts have been made to express the latter in terms of the former; see Chester's review article for details [1].) It is the latter with which we will be most concerned here, i.e. systems in which diffusion, thermal conductivity and viscosity are of interest. In the succeeding sections of this paper we will develop a new theory of non-equilibrium processes, based on information thermodynamics as described in section 2, and apply it to various types of transport in a fluid. The theory will enable us to give also a microscopic derivation of the equations of irreversible thermodynamics, although the general theory which we develop in section 3 will not be limited merely to discussions of transport in fluids.

There are many methods which are used to describe such transport processes as mentioned above. However, they are all concerned with showing that equations like the relation

$$J_i(\boldsymbol{r}, t) = \sum_k \int \mathrm{d}\boldsymbol{r}'\, L_{ik}(\boldsymbol{r}, \boldsymbol{r}', t) \cdot X_k(\boldsymbol{r}') \tag{1.1}$$

between the currents J_i and the thermodynamic forces X_k (which are assumed to cause the transport in the system) are valid. It must also be possible to derive closed expressions for the transport coefficients L_{ik}. Kirkwood [2] and Green [3] were the first to succeed in obtaining substantial results in the general theory of irreversible processes, using the theory of stochastic processes and the Fokker-Planck equation.

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In particular, Kirkwood and Green obtained the relation between the transport coefficients and time correlation functions. For a classical system this is written as

$$L_{ik}(\mathbf{r}, \mathbf{r}', t) = \int \mathrm{d}t' \langle j_i(\mathbf{r}) j_k(\mathbf{r}', t-t') \rangle_0 \tag{1.2}$$

where the $j_i(j_k)$ are the appropriate flux densities and $\langle \cdot \rangle_0$ denotes a statistical mean value. This method was later improved by Mori and Kubo [4–6]. More recently Zwanzig and Nordholm have written a definitive paper using Zwanzig's projection operator technique [7] (see also [8, 9]).

Apart from the indirect methods from the theory of linear response to a perturbation, see e.g. Kubo *et al* [10], there are two other main methods not necessarily directly involving the information theory approach: that of Mori [11], which is based on the use of a local-equilibrium distribution as an initial condition for the Liouville equation, and that of Zubarev and McLennan, in which an expression is derived for the solution of the Liouville equation (or a variant thereof) called by Zubarev [12] the method of Gibbs' statistical ensembles for non-equilibrium systems. Zubarev's theory is based on the construction of local integrals of the motion [13], while McLennan's theory is based on the calculation of the influence of a thermostat in terms of non-conservative forces [14, 15]. Both theories give the same results. (It should be mentioned in passing that the theories of McLennan and Zubarev are not entirely independent of information theory ideas. In particular, the work of Zubarev and Kalashnikov should be referred to in this matter [16]. More will be said about this in section 5.) The reader may be referred also to the review article of Zubarev [17] and to Zubarev's book [18].

The theory to be developed in this paper also includes a Gibbs' statistical ensemble for non-equilibrium systems. Basically the theory involves writing a solution of the Liouville equation in a particular form which turns out to be very useful for the application of a so-called 'cumulant expansion' [19]. In this cumulant expansion, mean values over $\rho^*(t)$, the solution of the Liouville equation under specified initial conditions, are expressed in terms of mean values over $\tilde{\rho}(t)$, the statistical index with maximum entropy subject to given mean value constraints at time t. The initial conditions mentioned above may be summarised by the single initial condition $\rho^*(t_0) = \tilde{\rho}(t_0)$ for some initial time $t_0 \neq t$.

Until recently not much work seems to have been done on applying the information theory approach to non-equilibrium statistical thermodynamics. Most of the early published work appears to have been done by Robertson using his time-dependent projection operator technique (see [20, 21]) with which non-local equations of motion are derived for $\rho(t)$ and the statistical mean values of a particular set of operators (called an r set in section 2). Other work which was done in and around the time of Robertson's initial publications was mentioned in a review by Zwanzig. Zwanzig [22] reported work by Jaynes and an unpublished thesis by Scalapino. With the exception of certain formal relationships [23, 24] this work remained unpublished for over a decade and these formal relationships were not (publicly) applied to any specific problems. Finally, in a seminal article [25] Jaynes published a fuller account of his ideas and sketched the application to non-equilibrium thermodynamics. Jaynes has since followed this up with other publications (see [26–29]) again sketching developments of the basic theory and reporting previously unpublished material, e.g. Michelson's theory of macroscopic sources [28] (see also the footnote in [21]).

The major review was left to another, however, when Grandy published his authoritative overview 'Principle of Maximum Entropy and Irreversible Processes' [30]. Again though, Grandy's article refers to unpublished work, e.g. [30, refs [66] and [91] therein]. Grandy has since followed this article with a major book on the subject [31]. Other work that needs to be mentioned is Robertson's more recent paper [32] and the work of Levine and his collaborators [33]. (See also the work based on Levine's that is detailed in [34] and references cited therein.)

The general outline of the paper is as follows. In section 2 the approach of Ingarden and Kossakowski is presented for field operators. That is, in section 2 the formalism and terminology of information thermodynamics for position-dependent observables are developed. Section 2 is a formal development of the work of Kossakowski [35] and Ingarden and Kossakowski [36] appearing already in the work of Robertson [20, 32] for example, and Ramshaw [37] among others (especially Zubarev and McLennan, though in these works [13, 15] from a different viewpoint). The formalism of information thermodynamics provides a structure to hang non-equilibrium thermodynamics on, as well as a clearly defined language with which we may discuss non-equilibrium processes in general. In section 3 the formalism of information thermodynamics is extended by clarifying the relationship between the two main statistical indexes of the theory, $\rho^*(t)$ and $\tilde{\rho}(t)$, mentioned already in the above discussion. Essentially, mean values over $\rho^*(t)$ may be expressed instead as mean values over $\tilde{\rho}(t)$. Section 4 sees the application of this extended formalism of information thermodynamics in the form of a derivation of the formalism of non-equilibrium thermodynamics. This is done for the case of a simple fluid as discussed by Grandy [30] and by Zubarev [17]. The reader is referred also to the original work by Mori [4, 11] for a clear and detailed discussion of the idealisations and assumptions that are inherent in this approach in general, and in particular the validity of treating the fluid system as isolated so that the fluid system's temporal development is determined by a Hamiltonian. In the final section, section 5, the present formalism is compared with other similar cases, i.e. the work of McLennan and Zubarev cited already.

2. Information thermodynamics

In this section we present a particular account of the information theory approach to statistical mechanics following the work of Kossakowski and Ingarden [35, 36]. The account presented below will be essentially non-rigorous in that mathematical existence properties will, in general, be ignored. This has not always been the case, however, and in the next subsection an informal review of this subject is presented which is intended also to act as an introduction to some of the wider mathematical aspects that Jaynes' basic formalism gives rise to. Section 2.1 is both complementary to, and introductory to, the rest of this section as well. It must be stressed once again though that the review in section 2.1 is informal and not exhaustive.

2.1. *A partial overview of information theory and statistical mechanics*

In 1957 Jaynes put forward the idea [38] that by using concepts from information theory it should be possible to treat statistical mechanics as a form of statistical inference, rather than as an attempt to derive the bulk laws of matter directly from the microscopic laws of physics, which until then had been the usual philosophy. (For a contemporary review of this situation we refer to ter Haar [39]; for a more recent account see [40].) The method Jaynes proposed; he considered to be a generalisation of Laplace's principle of indifference (though see [41] for some further thoughts on this point), i.e. that, if there is no evidence to the contrary, then all possibilities are equally probable. This is generalised to 'Jaynes' principle': statistical inferences on the basis of incomplete information should be founded on the most unbiased probability assumptions compatible with the given information.

To implement this principle, Jaynes borrowed the idea, from Shannon [42], of a measure of the 'uncertainty' associated with any statistical index—probability density function or density matrix—corresponding to the 'lack of information' inherent in any probabilistic description. If we denote this measure by S, it turns out that in statistical mechanics S is just the 'entropy' of a probability density function or density matrix. That is,

$$S(\rho) = -K \int \rho \log \rho \, \mathrm{d}s \tag{2.1a}$$

or

$$S(\rho) = -K \operatorname{Tr} \rho \log \rho. \tag{2.1b}$$

In (2.1a), the classical case, ρ is a probability density function and s an appropriate Lebesgue measure [43]. In (2.1b) ρ is a density matrix with Tr denoting the trace [44]. In both cases K is a positive constant. For a thorough review of the entropy concept see Wehrl [45]. Jaynes assumed also that the given information was the measured values of several properties of the system under investigation which were to be represented by the mean values of the respective observables (phase functions or operators). Using these concepts Jaynes now considered that the most unbiased probability assumption to make was to choose the probability density function or density matrix which was consistent with the given information and had the maximum entropy. That is, we use that probabilistic description which is consistent with our knowledge and maximally non-committal about our ignorance.

By treating this 'maximum entropy principle' as a variational problem, Katz in his book on the subject [46] showed that the earlier work of Jaynes [23, 38] could be put on a firmer mathematical basis. As well as rederiving the generalised canonical ensemble (see (2.10)) he gave necessary conditions for the Lagrange multipliers to exist and to be unique. (In the language of information thermodynamics Katz required the dynamical variables to be 'thermodynamically regular' and to be 'informationally independent'.)

There were various other existence problems not treated by Katz. These were investigated in the context of quantum mechanics by Wichmann [47], for the finite-dimensional Hilbert space case, and further developed to the case of infinite-dimensional Hilbert spaces by Ochs and Bayer [48]. Ochs and Bayer also utilised the earlier work of Ingarden and Urbanik [49] and Kossakowski [35]. Specifically investigated were the domains and ranges of the mappings defined by the statistical mean values, the 'generalised partition function' and the 'entropy' of a 'macrostate' (these concepts are defined in the next subsection to which we refer for details). Also investigated were the analytic properties (convexity, differentiability) of the generalised partition function and the macrostate entropy.

There are treatments other than those mentioned above, see e.g. [50–53]; these last four references all discuss finite-dimensional quantum systems. Particularly interesting is the approach of Mackey [50] who uses the theory of Laplace transforms to give an account of statistical thermodynamics in which only the mean energy (i.e. one physical quantity) is considered.

The information theory approach to statistical mechanics was further generalised to include field operators by Robertson [20] (see also [21, 33]) and made use of recently by Ramshaw [37] and is indeed implicit in Zubarev's approach [16]. There does not appear to be the same attempt to justify the general theory in the field format rigorously as there was in the straightforward operator approach, and in what follows we will assume that all analytical processes are valid (though some assumptions are explicitly made). Of course this is not the whole story since Jaynes [25] has developed the theory along different lines from Robertson and Ramshaw (see Hobson's book [54] and previous references to Jaynes and Grandy).

We are in a position now to discuss the information theory approach to statistical mechanics which has been called, by Kossakowski [35], 'information thermodynamics'.

2.2. Quantum information thermodynamics

We proceed now to develop the quantum information thermodynamics, the classical theory follows in a well known manner [35]. We deal with a quantum Hamiltonian system with Hamiltonian H, assumed time independent. The state of our quantum Hamiltonian system is assumed to be represented by a density matrix $\rho(t)$ satisfying the Liouville equation

$$\frac{\partial \rho(t)}{\partial t} = -\frac{\mathrm{i}}{\hbar}[H, \rho(t)] = -\mathrm{i}L\rho(t) \tag{2.2}$$

where $[A, B] = AB - BA$ is, as usual, the commutator of the two operators A and B and the 'Liouville superoperator' L is defined as

$$\mathrm{i}L = \frac{\mathrm{i}}{\hbar}[H, \;]. \tag{2.3}$$

The statistical mean values of the Hermitian operator, $A, B, \ldots$, are at time t given by, e.g.

$$\langle A \rangle_t = \mathrm{Tr}\, A\rho(t) \tag{2.4}$$

with $\rho(t)$ the relevant solution of (2.2). The quantum entropy of a density matrix ρ is, from section 2.1,

$$S(\rho) = -K\, \mathrm{Tr}\, \rho \log \rho \tag{2.5}$$

with K a real positive constant. $S(\rho)$ as given by (2.5) is, in fact, the only measure of information or uncertainty compatible with certain axiomatic characterisations [55, 56, 45] which is invariant under all unitary transformations in the underlying Hilbert space.

To avoid certain existence and uniqueness problems (and redundancy difficulties) it is necessary to restrict the type of operators for which information thermodynamics is defined. Suppose then we have a set of operators $A_i = A_i(\boldsymbol{r})$, $i = 1, 2, \ldots, r$ which may be spatially dependent as they are in their second quantised from (see e.g. Robertson [57], Zubarev [17], Grandy [30 or 58]) then we make the following assumption about the 'allowable' class of (possibly non-commuting) operators.

Definition 2.1. A set of (possibly non-commuting) Hermitian operators

$$\mathcal{S}=\{A_i(\boldsymbol{r}),\ i=0,1,2,\ldots,r,\ A_0=I \text{ and } r=1,2,3\ldots\}$$

is said to be a thermodynamic r set if and only if the following conditions are satisfied:

(i) The A_i are linearly independent.

(ii) The operators $A_i(\boldsymbol{r})$, $i=1,\ldots,r$, are 'thermodynamically regular'. This condition implies the existence of real functions $\beta_1(\boldsymbol{r}),\ldots,\beta_r(\boldsymbol{r})$ such that the 'generalised partition functional' $Z(\boldsymbol{\beta})$ satisfies the inequality

$$Z(\boldsymbol{\beta})=\operatorname{Tr}\exp\left(-\sum_{k=1}^{r}\int_{R_k}\mathrm{d}\boldsymbol{r}'\,\beta_k(\boldsymbol{r}')A_k(\boldsymbol{r}')\right)<\infty \tag{2.6}$$

for each region R_k, $k=1,\ldots,r$.

(iii) $Z(\boldsymbol{\beta})$ is sufficiently often differentiable (in a generalised sense) as is necessary.

Condition (i) guarantees the existence of the inverse matrix G_{ij} of (2.15) below [46]. Also, if condition (i) is violated then the A_i will not be 'informationally independent' [35, 36]. If the A_i are informationally independent then it is not possible to calculate the mean value of any one from the mean values of the others ($\langle I\rangle=\operatorname{Tr}\rho=1$ expresses the normalisation of the density matrix ρ). To see this we assume that $\Sigma_{i=0}^{r}\alpha_iA_i=0$, but that $\Sigma_{i=1}^{r}\alpha_i^2\neq 0$. Then since the A_i satisfy a linear equation their mean values will also satisfy the same equation. That is

$$\alpha_0+\sum_{k=1}^{r}\alpha_k a_k=0 \tag{2.7}$$

where $a_k=\operatorname{Tr}A_k(\boldsymbol{r})\rho$. In this case we see that by rearranging (2.7) we may calculate the mean value of any A_k from the mean values of the others.

Condition (ii) ensures the existence of the entropy (maximum information entropy) of the 'macrostate', as will become clearer later on. Condition (iii) is the first of a number of technical assumptions that are necessary if the full formalism of information thermodynamics is to be developed.

In the next definition we formalise the concept of a macrostate, i.e. a state of macroscopic knowledge compatible with a large number of microscopic descriptions.

Definition 2.2. Let $\mathcal{S}$ be a thermodynamic r set, $a_i(i=1,\ldots,r)$ be real numbers. Then the set of density matrices

$$M=\{\rho\colon \operatorname{Tr}\rho=1,\operatorname{Tr}A_i(\boldsymbol{r})\rho=a_i(\boldsymbol{r}),\ i=1,2,\ldots,r\} \tag{2.8}$$

is said to be the macrostate with respect to $\mathcal{S}$, $a_i(\boldsymbol{r})(i=1,2,\ldots,r)$ and the underlying Hilbert space. The numbers, or rather functions, $a_i(\boldsymbol{r})$ are assumed to be defined over regions $R_i(i=1,2,\ldots,r)$.

Our problem, i.e. the basic problem of statistical thermodynamics, is encapsulated in the definition of a macrostate. We have a set of density matrices M constrained by the conditions (2.8) and we require a criterion to choose which one to use, i.e. the one that agrees with the 'data' (the $a_i(\boldsymbol{r})$) and assumes nothing else. The criterion for choosing the density matrix is Jaynes' maximum entropy principle which assumes the following form.

Maximum entropy principle. If the available information about the statistical state of a quantum (Hamiltonian) system does not distinguish a unique density matrix (or 'microstate') but is compatible with a whole class of density matrices (the macrostate), then the system must be described by the density matrix which has the maximum entropy (as defined by (2.5)) subject to the conditions defining the class (2.8).

This principle leads us naturally to the next definition.

Definition 2.3. The 'entropy' $S(M)$ of the macrostate M defined by relation (2.8) is the maximum entropy concerning microstate ρ when the macrostate M is known, i.e.

$$S(M)=\sup\{S(\rho)\colon \rho\in M\} \tag{2.9}$$

where $S(\rho)$ is given by (2.5).

We are now in a position to state the main results of information thermodynamics which we summarise by theorem 2.1.

Theorem 2.1. Let M be a macrostate as defined by (2.8). Then there exists a unique microstate $\rho^*\in M$ such that

$$\rho^*=\rho^*(\boldsymbol{\beta})=\{Z(\boldsymbol{\beta})\}^{-1}\exp\{-\boldsymbol{\beta}\cdot\boldsymbol{A}\} \tag{2.10}$$

where

$$\boldsymbol{\beta}\cdot\boldsymbol{A}=\sum_{k=1}^{r}\int_{R_k}\mathrm{d}\boldsymbol{r}'\,\beta_k(\boldsymbol{r}')A_k(\boldsymbol{r}')$$

and

$$-\infty<S(M)=S(\rho^*)=K\log Z(\boldsymbol{\beta})+K\boldsymbol{\beta}\cdot\boldsymbol{a}<\infty \tag{2.11}$$

with

$$\boldsymbol{\beta}\cdot\boldsymbol{a}=\sum_{k=1}^{r}\int_{R_k}\mathrm{d}\boldsymbol{r}'\,\beta_k(\boldsymbol{r}')a_k(\boldsymbol{r}').$$

Further, the functions $\beta_1(\boldsymbol{r}), \beta_2(\boldsymbol{r}), \ldots, \boldsymbol{\beta}(\boldsymbol{r})$ are the unique solutions of the equations

$$a_i(\boldsymbol{r})=-\frac{\delta}{\delta\beta_i}\log Z(\boldsymbol{\beta}) \tag{2.12}$$

$i=1,2,\ldots,r$ and

$$K\beta_i(\boldsymbol{r})=\frac{\delta S(M)}{\delta a_i(\boldsymbol{r})}\qquad i=1,2,\ldots,r. \tag{2.13}$$

Finally we have the reciprocity relationship between the 'covariance functions' $K_{ij}(\boldsymbol{r},\boldsymbol{r}')$:

$$K_{ij}(\boldsymbol{r},\boldsymbol{r}')=-\frac{\delta a_j(\boldsymbol{r}')}{\delta\beta_i(\boldsymbol{r})}=\frac{\delta^2\log Z}{\delta\beta_i(\boldsymbol{r})\delta\beta_j(\boldsymbol{r}')} \tag{2.14}$$

and their functional inverses

$$G_{ij}(\boldsymbol{r},\boldsymbol{r}')=\frac{\delta\beta_j(\boldsymbol{r}')}{\delta a_i(\boldsymbol{r})}=\frac{1}{K}\frac{\delta^2 S}{\delta a_i(\boldsymbol{r})\delta a_j(\boldsymbol{r}')}. \tag{2.15}$$

That is

$$\frac{1}{K}\sum_{k=1}^{r}\frac{\delta^2\log Z}{\delta\beta_i(\boldsymbol{r})\delta\beta_k(\boldsymbol{r}')}\cdot\frac{\delta^2 S(M)}{\delta a_k(\boldsymbol{r})\delta a_j(\boldsymbol{r}')}=-\delta_{ij}\delta(\boldsymbol{r}-\boldsymbol{r}'). \tag{2.16}$$

This completes the basic formalism of information thermodynamics. We consider now the time evolution of the microstates, via (2.2), and develop the theory for arbitrary times. We assume the existence of a macrostate at some initial time t_0 say, M_{t_0}, and define the concept of a macrostate at time t with $t \geqslant t_0$, M_t.

Definition 2.4. We define the macrostate at time $t \geqslant t_0$ with respect to an r set $\mathscr{S}$ and initial $(t = t_0)$ mean values $a_1(\boldsymbol{r}), a_2(\boldsymbol{r}), \ldots, a_r(\boldsymbol{r})$ as the set of density matrices:

$$M_t = \{\rho\colon \operatorname{Tr} \rho = 1, \operatorname{Tr} A_i(\boldsymbol{r})\rho = \operatorname{Tr} A_i(\boldsymbol{r})\rho^*(t) = a_i(\boldsymbol{r}, t), (i = 1, 2, \ldots, r)\} \tag{2.17}$$

where $\rho^*(t)$ is the time evolved value (via (2.2)) of ρ^*.

The fact that we need only consider microstates with finite entropies follows from theorem 2.1 with the following definitions and assumptions. To begin with, the 'entropy' of the macrostate M_t is defined analogously to definition 2.3.

Definition 2.5. The 'entropy' $S(M_t)$ of the macrostate M_t is the maximum entropy concerning microstate ρ when the macrostate M_t is known, i.e.

$$S(M_t) = \sup\{S(\rho)\colon \rho \in M_t\} \tag{2.18}$$

where $S(\rho)$ is given by (2.5).

Further, we define the 'generalised partition functional at time $t'(t \geqslant t_0)$ as

$$Z(\beta_1(\boldsymbol{r}, t), \ldots, \beta_r(\boldsymbol{r}, t)) = \operatorname{Tr} \exp\left(-\sum_{k=1}^{r} \int_{R_k} \mathrm{d}\boldsymbol{r}'\, \beta_k(\boldsymbol{r}', t) A_k(\boldsymbol{r}')\right) \tag{2.19}$$

or, in vector notation,

$$Z(\boldsymbol{\beta}(t)) = \operatorname{Tr} \exp\{-\boldsymbol{\beta}(t) \cdot \boldsymbol{A}\}. \tag{2.20}$$

We also assume that, if $Z(\boldsymbol{\beta}(t_0))$ is thermodynamically regular, $Z(\boldsymbol{\beta}(t))$ is also.

Using the above definitions and assumptions, theorem 2.1 tells us that the maximum entropy of the microstates $\rho \in M_t$ is finite. Continuing to use theorem 2.1 we have for every time $t \geqslant t_0$ a representative microstate $\tilde{\rho}(t)$ for the macrostate M_t of the form

$$\tilde{\rho}(t) = \tilde{\rho}(\boldsymbol{\beta}(t)) = [Z(\boldsymbol{\beta}(t))]^{-1} \exp[-\boldsymbol{\beta}(t) \cdot \boldsymbol{A}] \tag{2.21}$$

where again we have

$$a_i(\boldsymbol{r}, t) = -\frac{\delta}{\delta\beta(\boldsymbol{r}, t)} \log Z \tag{2.22}$$

where $a_i(\boldsymbol{r}, t) = \operatorname{Tr} A_i(\boldsymbol{r})\tilde{\rho}(t)$, $i = 1, \ldots, r$.

Thus, $\tilde{\rho}(t)$ retains a 'generalised canonical' form at all times and the macrostate entropy at time t is

$$S(M_t) = S(\rho(t)) = K \log Z(\boldsymbol{\beta}(t)) + K\boldsymbol{\beta}(t) \cdot \boldsymbol{a}(\boldsymbol{r}, t) \tag{2.23}$$

so that upon differentiating we have

$$K\beta_i(\boldsymbol{r}, t) = \frac{\delta S(M_t)}{\delta a_i(\boldsymbol{r}, t)} \qquad i = 1, 2, \ldots, r. \tag{2.24}$$

Note that

$$\tilde{\rho}(t_0) = \rho^*(t_0) = \rho^* \tag{2.25}$$

but for $t \geqslant t_0$, $\tilde{\rho}(t)$ and $\rho^*(t)$ can be different.

Theorem 2.2. Let M_{t_0} be a macrostate known at time $t = t_0$, the initial time say. Then the following inequality holds for all $t \geqslant t_0$:

$$S(M_t) \geqslant S(M_{t_0}) \tag{2.26}$$

where M_t is the 'time-ordered' macrostate of definition 2.4.

The proof of theorem 2.2 follows immediately from definition 2.5 of the macrostate entropy and by the dynamical invariance of $S(\rho^*(t))$ [23, 59], i.e.

$$-K \operatorname{Tr} \tilde{\rho}(t) \log \tilde{\rho}(t) \geqslant -K \operatorname{Tr} \rho^*(t) \log \rho^*(t) = K \operatorname{Tr} \rho^* \log \rho^*.$$

Thus

$$S(M_t) \geqslant S(M_{t_0}) \tag{2.27}$$

the equality holding if and only if $\tilde{\rho}(t) = \rho^*(t)$.

It is a consequence of theorem 2.2 and the discussion in Wu's paper [60] that $\tilde{\rho}(t)$ is not necessarily governed by an equation which satisfies reversible dynamical laws. Jaynes [59] has used theorem 2.2 as a basis for a proof of the second law of thermodynamics.

Levine [33] and his collaborators have investigated the problem of forcing $\tilde{\rho}(t) = \rho^*(t)$ for all values of $t \geqslant t_0$. (See also the papers of Duering *et al* [34].) The requirement that $\tilde{\rho}(t) = \rho^*(t)$, $t \geqslant t_0$, leads to a set of conditions (differential equations) for the parameters $\boldsymbol{\beta}(t)$ [33, 34].

3. Non-equilibrium information thermodynamics

In this section we describe the general method that we are proposing be used in solving problems in non-equilibrium statistical mechanics. We have seen in the previous section that information thermodynamics is characterised by the existence of two statistical indices: the representative microstate at time t, $\tilde{\rho}(t)$, which maintains a generalised canonical form for all values of t, and the solution of the Liouville equation, $\rho^*(t)$, which is subject to the initial condition that at some initial time t_0, $\rho^*(t_0) = \tilde{\rho}(t_0)$. It is apparent that $\rho^*(t)$ and $\tilde{\rho}(t)$ are related since $\tilde{\rho}(t)$ is defined using $\rho^*(t)$ which in turn depends upon $\tilde{\rho}(t_0)$ and the dynamics. Below, we will further elucidate the relationship between these two statistical indices, $\tilde{\rho}(t)$ and $\rho^*(t)$, and develop a general approach to handling non-equilibrium situations described by macrostates.

We assume the existence of a macrostate at some initial time t_0, M_{t_0}, and consider the time-evolved macrostate M_t. From section 2 we know that M_t is represented by the microstate $\tilde{\rho}(t)$ where

$$\tilde{\rho}(t) = [Z(\boldsymbol{\beta}(t))]^{-1} \exp[-\boldsymbol{\beta}(t) \cdot \boldsymbol{A}] \tag{3.1}$$

with, in the more general case,

$$\boldsymbol{\beta}(t) \cdot \boldsymbol{A} = \sum_{k=1}^{r} \int_{R_k} \beta_k(\boldsymbol{r}, t) A_k(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r}. \tag{3.2}$$

Equation (3.2) enables spatial dependence of the operators to be taken into account. If the operators are not spatially varying, then we drop the integral and are left with a sum only. $Z(\boldsymbol{\beta}(t))$ is, of course, the generalised partition function(al) and is obtained from the normalisation condition for $\tilde{\rho}(t)$. Thus, since $\mathrm{Tr}\,\rho(t)=1$,

$$Z(\boldsymbol{\beta}(t))=\mathrm{Tr}\exp[-\boldsymbol{\beta}(t)\cdot \boldsymbol{A}]. \tag{3.3}$$

The mean value of any operator is given by

$$\langle A\rangle_{t+s}=\mathrm{Tr}\,A\rho^*(t+s) \tag{3.4}$$

where $\rho^*(t)$ is the solution of the Liouville equation under the initial condition $\rho^*(t_0)=\tilde{\rho}(t_0)$. Since

$$\rho^*(t+s)=\exp(-\mathrm{i}Ls)\rho^*(t) \tag{3.5}$$

(3.5) may be rewritten in an 'intermediate' representation

$$\langle A\rangle_{t+s}=\langle A(s)\rangle_t \tag{3.6}$$

with

$$A(s)=\exp(\mathrm{i}Ls)A \tag{3.7a}$$

i.e.

$$A(s)=\exp\left(\frac{\mathrm{i}H}{\hbar}s\right)A\exp\left(-\frac{\mathrm{i}H}{\hbar}s\right). \tag{3.7b}$$

If A is a member of the r set associated with the macrostate M_{t_0}, then the mean values calculated using $\rho^*(t)$ and $\tilde{\rho}(t)$ will coincide by definition. However, if A is any arbitrary operator this may not be so. Even so, the mean value over $\tilde{\rho}(t)$ will still be instantaneously the best estimate possible given M_t.

The essence of the method presented below is to cast $\rho^*(t)$ into a form in which the mean values over $\rho^*(t)$ may be expressed in terms of mean values over $\tilde{\rho}(t)$ using a form of cumulant expansion. In this way, we will have developed more fully a non-equilibrium information thermodynamics since, using (3.6), we have

$$\langle \dot{A}(s)\rangle_t=\mathrm{Tr}\,\dot{A}(s)\rho^*(t) \tag{3.8}$$

where

$$\dot{A}(s)=\mathrm{i}LA(s)=\frac{\mathrm{i}}{\hbar}[H, A(s)] \tag{3.9}$$

from which it will be possible to estimate the equations of motion of the mean values via the cumulant expansion.

We consider again the solution to the Liouville equation

$$\frac{\partial\rho^*(t)}{\partial t}=-\mathrm{i}L\rho^*(t) \tag{2.2}$$

subject to the initial condition $\rho^*(t_0)=\tilde{\rho}(t_0)$ with

$$\tilde{\rho}(t)=[Z(\boldsymbol{\beta}(t))]^{-1}\exp[-\boldsymbol{\beta}(t)\cdot\boldsymbol{A}] \tag{2.21}$$

with the notation of sections 2 and 3. Defining

$$U(t, t')=\exp[-\mathrm{i}L(t-t')] \tag{3.10}$$

we see that

$$\rho^*(t)=U(t, t_0)\rho(t_0) \tag{3.11a}$$

i.e.

$$\rho^*(t) = \exp\left(-\frac{\mathrm{i}H}{\hbar}(t-t_0)\right)\rho(t_0)\exp\left(\frac{\mathrm{i}H}{\hbar}(t-t_0)\right). \tag{3.11b}$$

Therefore

$$\rho^*(t) = [Z(\beta(t_0))]\exp[-\boldsymbol{\beta}(t_0)\cdot\boldsymbol{A}(t_0-t)] \tag{3.12}$$

where

$$\boldsymbol{A}(t_0-t) = \exp\left(\frac{\mathrm{i}H}{\hbar}(t_0-t)\right)\boldsymbol{A}\exp\left(-\frac{\mathrm{i}H}{\hbar}(t_0-t)\right). \tag{3.13}$$

However, since $\mathrm{Tr}\,\rho^*(t) = 1$ at all times, we have

$$\rho^*(t) = \exp[-\boldsymbol{\beta}(t_0)\cdot\boldsymbol{A}(t_0-t)]\{\mathrm{Tr}\exp[-\boldsymbol{\beta}(t_0)\cdot\boldsymbol{A}(t_0-t)]\}^{-1} \tag{3.14}$$

which follows also from

$$\exp\left(\frac{\mathrm{i}H}{\hbar}(t_0-t)\right)\exp\left(-\frac{\mathrm{i}H}{\hbar}(t_0-t)\right) = I \tag{3.15}$$

and the cyclic invariance of the trace. Finally, since

$$\boldsymbol{\beta}(t_0)\cdot\boldsymbol{A}(t_0-t) = \boldsymbol{\beta}(t)\cdot\boldsymbol{A} - \int_{t_0}^{t} \mathrm{d}t'\frac{\partial}{\partial t'}[\boldsymbol{\beta}(t')\cdot\boldsymbol{A}(t'-t)] \tag{3.16a}$$

i.e.

$$\boldsymbol{\beta}(t_0)\cdot\boldsymbol{A}(t_0-t) = \boldsymbol{\beta}(t)\cdot\boldsymbol{A} - \int_{t_0}^{t} \mathrm{d}t'[\dot{\boldsymbol{A}}(t'-t)\cdot\boldsymbol{\beta}(t') + \boldsymbol{A}(t'-t)\cdot\dot{\boldsymbol{\beta}}(t')] \tag{3.16b}$$

where

$$A_k(t'-t) = \exp[\mathrm{i}L(t'-t)]A_k \tag{3.17a}$$

i.e.

$$A_k(t'-t) = \exp\left(\frac{\mathrm{i}H}{\hbar}(t'-t)\right)A_k\exp\left(-\frac{\mathrm{i}H}{\hbar}(t'-t)\right) \tag{3.17b}$$

with

$$\dot{A}_k(t'-t) = \frac{\mathrm{i}}{\hbar}[H, A(t'-t)] \qquad k = 1, 2, \ldots, r \tag{3.18}$$

and

$$\dot{\beta}_k(t') = \frac{\partial\beta_k(t')}{\partial t'} \qquad k = 1, 2, \ldots, r. \tag{3.19}$$

Substituting (3.16*b*) into (3.14) we obtain

$$\rho^*(t) = [Q(t)]^{-1}\exp\left(-\boldsymbol{\beta}(t)\cdot\boldsymbol{A} + \int_{t_0}^{t} \mathrm{d}t'[\dot{\boldsymbol{A}}(t'-t)\cdot\boldsymbol{\beta}(t') + \boldsymbol{A}(t'-t)\cdot\dot{\boldsymbol{\beta}}(t')]\right) \tag{3.20}$$

and

$$Q(t) = \mathrm{Tr}\exp\left(-\boldsymbol{\beta}(t)\cdot\boldsymbol{A} + \int_{t_0}^{t} \mathrm{d}t'[\dot{\boldsymbol{A}}(t'-t)\cdot\boldsymbol{\beta}(t') + \boldsymbol{A}(t'-t)\cdot\dot{\boldsymbol{\beta}}(t')]\right). \tag{3.21}$$

This argument follows substantially that given by Wilcox [61].

Now, if we examine $\rho^*(t)$ as given by (3.20) in conjunction with (3.21), we see that $\rho^*(t)$ is of the general form

$$\rho = \exp(A+B)[\operatorname{Tr}\exp(A+B)]^{-1} \tag{3.22}$$

where A and B are arbitrary operators. The idea of the cumulant expansion, which we now introduce, is to consider a second simpler density matrix

$$\rho_0 = \exp(A)[\operatorname{Tr}\exp(A)]^{-1} \tag{3.23}$$

and to express any mean value over ρ in terms of mean values over ρ_0.

We have outlined already how this expansion will be applied: any mean value over $\rho^*(t)$ is to be expressed in terms of mean values over $\tilde{\rho}(t)$—the representative micro-state—which are supposed to be the least biased estimates possible in a situation where our knowledge is represented by M_t (M_{t_0}). The idea of expressing any mean value over one density matrix and discussed above is due to Jaynes and Heims [19]. Jaynes and Heims did not, however, apply the idea in the manner that we are going to. Neither have Jaynes or Grandy in more recent publications [25, 30, 31] applied the expansion (introduced below) in the manner discussed in this paper. In the above quoted papers the cumulant expansion of Jaynes [19] is used purely as a calculational tool to approximate mean values over ρ and not as a (self-consistant) principle as used here (although the expansion is used approximately as well). That is, all mean values are to be calculated on the basis of the information thermodynamics approach and the cumulant expansion tells us how to do this, in principle at least, exactly. The results of the perturbation/cumulant expansion are summarised in the following theorem. The proof of theorem 3.1 is given, e.g. in Jaynes and Heims [19] the theorem itself is given in a slightly modified form presented in [25].

Theorem 3.1 (perturbation/cumulant expansion). The mean value of an arbitrary observable, C say, over ρ:

$$\rho = \exp(A+B)[\operatorname{Tr}\exp(A+B)]^{-1} \tag{3.22}$$

may be expressed in terms of mean values over ρ_0:

$$\rho_0 = \exp(A)[\operatorname{Tr}\exp(A)]^{-1}. \tag{3.23}$$

Thus, if

$$\langle C\rangle = \operatorname{Tr} C\rho \qquad \langle C\rangle_0 = \operatorname{Tr} C\rho_0 \tag{3.24}$$

then

$$\langle C\rangle - \langle C\rangle_0 = \sum_{n=1}^{\infty} (\langle W_n C\rangle_0 - \langle W_n\rangle_0\langle C\rangle_0) \tag{3.25}$$

where $W_1 = V_1$ and

$$W_n \equiv V_n - \sum_{k=1}^{n-1} \langle W_k\rangle_0 V_{n-k} \qquad n>1 \tag{3.26}$$

with the V_n defined via

$$V_n = \int_0^1 \mathrm{d}x_1 \int_0^{x_1} \mathrm{d}x_2 \ldots \int_0^{x_{n-1}} \mathrm{d}x_n\, B(x_1)\ldots B(x_n) \qquad n\geqslant 1 \tag{3.27}$$

where

$$B(x) \equiv \mathrm{e}^{-xA} B\, \mathrm{e}^{xA}. \tag{3.28}$$

The linear term will be of most importance in the next section. It is

$$\langle C\rangle-\langle C\rangle_0=\int_0^1 \mathrm{d}x(\langle \mathrm{e}^{-xA}B\,\mathrm{e}^{xA}C\rangle_0-\langle B\rangle_0\langle C\rangle_0). \tag{3.29}$$

It is a simple matter to apply theorem 3.1 with $\rho^*(t)$ replacing ρ and $\tilde{\rho}(t)$ replacing ρ_0. We simply identify

$$\begin{aligned} &\langle C\rangle\equiv\mathrm{Tr}\,C\rho^*(t) \qquad \langle C\rangle_0\equiv\mathrm{Tr}\,C\tilde{\rho}(t)\\ &A\equiv-\boldsymbol{\beta}(t)\cdot\boldsymbol{A}\\ &B\equiv\int_{t_0}^{t}\mathrm{d}t'[\dot{\boldsymbol{A}}(t'-t)\cdot\boldsymbol{\beta}(t')+\boldsymbol{A}(t'-t)\cdot\dot{\boldsymbol{\beta}}(t')]\end{aligned} \tag{3.30}$$

and we may evaluate any non-equilibrium expression that arises in information thermodynamics, involving the mean values of observables over $\rho^*(t)$, to arbitrary order in terms of mean values estimated using $\tilde{\rho}(t)$. In this way we see that we have extended the information thermodynamics approach to non-equilibrium statistical mechanics.

4. Transport phenomena

We will now apply the expansion of theorem 3.1 in conjunction with (3.29) and (3.30) to the discussion of transport phenomena in a simple fluid, as defined by Grandy [30], and hence to irreversible thermodynamics. We consider the state of a system (a fluid) which is macroscopically defined by given fields of temperature, chemical potential and velocity, i.e. by the densities of energy, particle number and momentum, as functions of the space (and possibly time) coordinates. Thus we consider a situation in which energy, mass and momentum occurs, no electric or magnetic fields are applied and no phase transitions occur.

The chosen parameters are assumed sufficient for a macroscopic description of the system. Further, it is assumed [17] 'that the system is in thermal, material and mechanical contact with a combination of thermostats and reservoirs, maintaining the given distribution of parameters'. In fact, we will be considering essentially just the system alone as we will be trying to obtain a description of non-equilibrium processes within the system only. This idea is discussed in detail by Mori [4, 11] and was used by Zubarev [12, 13] who, as Robertson and Mitchell point out [21] '...obtains an expression for a non-equilibrium statistical density that depends only upon the conjugate variables of the system alone, with no reference to the reservoirs. [...] this nonequilibrium statistical density is easily shown to satisfy the Liouville equation for the isolated system alone'. With the above in mind, we will apply the formalism of the previous section where we assume in particular that H, the Hamiltonian of the liquid, does not include the interaction with the reservoirs [11].

Mathematically, this situation is described by an r set consisting of $H(\boldsymbol{r})$, $\boldsymbol{p}(\boldsymbol{r})$ and $n_j(\boldsymbol{r})(j=1,\ldots,r-2)$ which are, respectively, the density operators for energy, momentum and particle number ($r-2$ species). The macrostate deals with the mean values of these quantities which are assumed known over some common volume V at an initial time t_0. The representative microstate for this situation is therefore

$$\tilde{\rho}(t)=[Z(\boldsymbol{\beta}(\boldsymbol{r},t))]^{-1}\exp\left(-\sum_{k=1}^{n}\int_V \beta_k(\boldsymbol{r},t)A_k(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}\right) \tag{4.1}$$

where (note that, as defined in (4.2) and (4.3), A_2 and β_2 are vectors, while the other A_k and β_k are scalars)

$$\begin{aligned} &A_1(\boldsymbol{r}) \equiv H(\boldsymbol{r}) \\ &A_2(\boldsymbol{r}) \equiv \boldsymbol{p}(\boldsymbol{r}) \\ &A_{k+2}(\boldsymbol{r}) \equiv n_j(\boldsymbol{r}) \qquad (j, k = 1, \ldots, r-2). \end{aligned} \tag{4.2}$$

In this case, since the $\beta_k(\boldsymbol{r}, t)$ are determined from

$$a_k(\boldsymbol{r}, t) = \frac{\delta \log Z(\beta(\boldsymbol{r}, t)}{\delta \beta_k(\boldsymbol{r}, t)} \qquad (k-1, \ldots, r) \tag{4.3}$$

we have (Jaynes [23], Zubarev [17])

$$\begin{aligned} &\beta_1(\boldsymbol{r}, t) = \beta(\boldsymbol{r}, t) \\ &\beta_2(\boldsymbol{r}, t) = -\beta(\boldsymbol{r}, t)\boldsymbol{V}(\boldsymbol{r}, t) \\ &\beta_{k+2}(\boldsymbol{r}, t) = -\beta(\boldsymbol{r}, t)[\mu_j(\boldsymbol{r}, t) - \tfrac{1}{2}m_j V^2(\boldsymbol{r}, t)] \end{aligned} \tag{4.4}$$

with $\beta(\boldsymbol{r}, t)$ the inverse temperature, $\mu_j(\boldsymbol{r}, t)(j = 1, \ldots, r-2)$ the chemical potentials and $\boldsymbol{V}(\boldsymbol{r}, t)$ the bulk velocity of the fluid. The 'non-equilibrium ensemble' (3.20) is in this case therefore given by

$$\begin{aligned} \rho^*(t) = \{Q(t)\}^{-1} \exp\Bigg(-\sum_{k=1}^{r} \int_V \mathrm{d}\boldsymbol{r}\, \beta_k(\boldsymbol{r}, t) A_k(\boldsymbol{r}) + \int_{t_0}^{t} \mathrm{d}t' \sum_{k=1}^{r} \int_V \mathrm{d}\boldsymbol{r} \\ \times [\dot{A}_k(\boldsymbol{r}, t'-t)\beta_k(\boldsymbol{r}, t') + A_k(\boldsymbol{r}, t'-t)\dot{\beta}_k(\boldsymbol{r}, t')]\Bigg) \end{aligned} \tag{4.5}$$

with the A_k and β_k given by (4.2) and (4.4), respectively.

To discuss the transport processes in the fluid, we shall begin from the laws of conservation of energy, particle number and momentum in local form (for details of the exact form of the quantities appearing in the conservation laws and in relations (4.2) we refer to Zubarev [17] or Grandy [30]) which may be written:

$$\begin{aligned} &\dot{H}(\boldsymbol{r}) + \nabla \boldsymbol{j}_H(\boldsymbol{r}) = 0 \\ &\dot{\boldsymbol{p}}(\boldsymbol{r}) + \nabla \cdot T(\boldsymbol{r}) = 0 \\ &\dot{n}_j(\boldsymbol{r}) + \nabla \cdot \boldsymbol{j}_{n_j}(\boldsymbol{r}) = 0 \qquad (j = 1, \ldots, r-2). \end{aligned} \tag{4.6}$$

In (4.6) $\boldsymbol{j}_H$ is the energy flux density, $T(\boldsymbol{r})$ is the stress tensor (assumed symmetric) and $\boldsymbol{j}_{n_j}(\boldsymbol{r})$ is the particle flux density of the jth species of particle. Equations (4.6) have classical equivalents, see e.g. McLennan [15]. Equations (4.6) may be rewritten in a more compact form:

$$\dot{A}_k(\boldsymbol{r}) + \nabla \cdot j_k(\boldsymbol{r}) = 0 \qquad k = 1, \ldots, r \tag{4.7}$$

where $A_k(\boldsymbol{r})(k = 1, \ldots, r)$ are defined by (4.2) and

$$\begin{aligned} &j_1(\boldsymbol{r}) \equiv \boldsymbol{j}_H(\boldsymbol{r}) \\ &j_2(\boldsymbol{r}) \equiv T(\boldsymbol{r}) \\ &j_{k+2}(\boldsymbol{r}) \equiv \boldsymbol{j}_{n_j} \qquad j, k = 1, \ldots, r-2. \end{aligned} \tag{4.8}$$

It follows from definitions (4.2) and (4.8) that the densities $A_k(\boldsymbol{r})$ may be scalars or vectors and the fluxes $j_k(\boldsymbol{r})$ vectors or tensors. (The dot after the nabla operator in (4.7) denotes a scalar product, i.e. the divergence of a vector or tensor.) Note that the momentum density and the related particle fluxes are assumed to be related according to

$$\boldsymbol{p}(\boldsymbol{r}) = \sum_{j=1}^{r-2} m_j \boldsymbol{j}_{n_j}(\boldsymbol{r}) \tag{4.9}$$

where m_j is the particle mass of the jth species.

We wish to express the non-equilibrium ensemble (4.5) in terms of the fluxes. To do this we rewrite (4.7) in the Heisenberg representation:

$$\dot{A}_k(\boldsymbol{r}, t'-t) = -\nabla \cdot j_k(\boldsymbol{r}, t'-t) \qquad k = 1, \ldots, r \tag{4.10}$$

substitute (4.10) into (4.5) and integrate. Thus, since

$$-\int_V \mathrm{d}\boldsymbol{r}\, \nabla \cdot j_k(\boldsymbol{r}, t'-t)\beta_k(\boldsymbol{r}, t') = \int_V \mathrm{d}\boldsymbol{r}\, j_k(\boldsymbol{r}, t'-t) \cdot \nabla\beta_k(\boldsymbol{r}, t') \tag{4.11}$$

where the identity

$$\nabla \cdot (\beta_k j_k) = (\nabla\beta_k) \cdot j_k + \beta_k(\nabla \cdot j_k) \tag{4.12}$$

has been used, and the surface integral

$$\int_V \mathrm{d}\boldsymbol{r}\, \nabla \cdot (\beta_k j_k) = \int_{\partial V} (\beta_k j_k) \cdot \mathrm{d}\boldsymbol{S} \tag{4.13}$$

has been neglected [30], where ∂V is the surface enclosing V and $\mathrm{d}\boldsymbol{S}$ is an element of ∂V. The non-equilibrium ensemble now becomes:

$$\rho^*(t) = [Q(t)]^{-1} \exp\biggl(-\sum_{k=1}^{r} \int_V \mathrm{d}\boldsymbol{r}'\, \beta_k(\boldsymbol{r}', t)A_k(\boldsymbol{r}') + \int_{t_0}^{t} \mathrm{d}t' \sum_{k=1}^{r} \int \mathrm{d}\boldsymbol{r}' \\ \times [j_k(\boldsymbol{r}', t'-t) \cdot \nabla\beta_k(\boldsymbol{r}', t') + A_k(\boldsymbol{r}', t-t)\dot{\beta}_k(\boldsymbol{r}', t')]\biggr) \tag{4.14}$$

with

$$Q(t) = \mathrm{Tr}\exp\biggl(-\sum_{k=1}^{r} \int_V \mathrm{d}\boldsymbol{r}'\, \beta_k(\boldsymbol{r}', t)A_k(\boldsymbol{r}') + \int_{t_0}^{t} \mathrm{d}t' \sum_{k=1}^{r} \int_V \mathrm{d}\boldsymbol{r}' \\ \times [j_k(\boldsymbol{r}', t'-t) \cdot \nabla\beta_k(\boldsymbol{r}', t') + A_k(\boldsymbol{r}', t'-t)\dot{\beta}_k(\boldsymbol{r}', t')]\biggr). \tag{4.15}$$

The fluxes of energy, particles and momentum through the surface of the system which we have neglected correspond to the 'non-conservative forces' which McLennan introduced to describe the influence of a thermostat (Zubarev [17]). Implicit in this assumption is the idea that at the end of the calculations we take the thermodynamic limit. We refer to Grandy [30] for a further discussion of this point, and also to Mori [4, 11] who relates the requirement of large volumes to the existence of various relaxation timescales in the system.

The equations of motion when expressed in terms of the mean fluxes over (4.14) are

$$\dot{a}_k(\boldsymbol{r}, t) = -\nabla \cdot \mathrm{Tr}\, j_k(\boldsymbol{r})\rho^*(t) \tag{4.16}$$

which follows from (4.7).

We will use the expansion of theorem 3.1 to express the mean fluxes $\langle j_k(\boldsymbol{r})\rangle = \operatorname{Tr} j_k(\boldsymbol{r})\rho^*(t)$ in terms of mean values over the representative microstate $\tilde{\rho}(t)$, denoted by $\langle\,.\,\rangle_0$. We will assume that the gradients in the fields and their time rate of change (the 'thermodynamic forces'—Zubarev [12]) are small enough so that we may consider the first order, i.e. linear, terms in the expansion of theorem 3.1 only. Indeed, as Jaynes has pointed out: 'Physically [. . .] one can argue that, in most experimentally realisable cases, irreversible flows (A) are already 'in progress' at the time the experiment is started, and (B) take place slowly, so that the low order distribution functions and expectation values of measurable quantities must be already slowly-varying functions of time and position' [25, p 93].

From (3.29) we have

$$\langle C\rangle - \langle C\rangle_0 = \int_0^1 \mathrm{d}x(\langle \mathrm{e}^{-xA} B\, \mathrm{e}^{xA} C\rangle_0 - \langle B\rangle_0\langle C\rangle_0). \tag{4.17}$$

When we identify

$$C \equiv j_k(\boldsymbol{r})$$

$$B \equiv \int_{t_0}^{t} \mathrm{d}t' \sum_{k=1}^{r} \int_V \mathrm{d}\boldsymbol{r}'[j_k(\boldsymbol{r}', t'-t)\cdot\nabla\beta_k(\boldsymbol{r}', t') + A_k(\boldsymbol{r}', t'-t)\dot{\beta}_k(\boldsymbol{r}', t')] \tag{4.18}$$

and

$$A = -\sum_{k=1}^{r} \int_V \mathrm{d}\boldsymbol{r}'\, \beta_k(\boldsymbol{r}', t')A_k(\boldsymbol{r}')$$

we find that (4.17) becomes

$$\begin{aligned}\langle j_i(\boldsymbol{r})\rangle = \langle j_i(\boldsymbol{r})\rangle_0 + \int_{t_0}^{t} \mathrm{d}t' \sum_{k=1}^{r} \int_V \mathrm{d}\boldsymbol{r}' \int_0^1 \mathrm{d}x \\ \times\{\langle j_i(\boldsymbol{r}) \exp(Ax)(j_k(\boldsymbol{r}', t'-t) - \langle j_k(\boldsymbol{r}', t'-t)\rangle_0) \exp(-Ax)\rangle_0 \cdot \nabla\beta_k(\boldsymbol{r}', t') \\ + \langle j_i(\boldsymbol{r}) \exp(Ax)(A_k(\boldsymbol{r}', t'-t) - \langle A_k(\boldsymbol{r}', t'-t)\rangle_0) \\ \times \exp(-Ax)\rangle_0\dot{\beta}_k(\boldsymbol{r}', t')\}.\end{aligned} \tag{4.19}$$

Note that, to obtain (4.19), we have used the fact that

$$\begin{aligned}\int_0^1 \mathrm{d}x\langle \exp(-Ax)(j_k(\boldsymbol{r}', t'-t) - \langle j_k(\boldsymbol{r}', t'-t)\rangle_0) \exp(Ax) j_i(\boldsymbol{r})\rangle_0 \\ = \int_0^1 \mathrm{d}x\langle j_i(\boldsymbol{r}) \exp(Ax)(j_k(\boldsymbol{r}', t'-t) - \langle j_k(\boldsymbol{r}', t'-t)\rangle_0) \exp(-Ax)\rangle_0.\end{aligned} \tag{4.20}$$

The equality (4.20) is readily obtained by changing the integration variable x to $1-x$ after invoking the cyclic invariance of the trace.

If we introduce the notation

$$\langle F, G\rangle_0 = \int_0^1 \mathrm{d}x\langle F \exp(Ax)(G - \langle G\rangle_0) \exp(-Ax)\rangle_0 \tag{4.21}$$

where F and G are arbitrary operators, we may rewrite (4.19) as

$$\begin{aligned}\langle j_i(\boldsymbol{r})\rangle = \langle j_i(\boldsymbol{r})\rangle_0 + \int_{t_0}^{t} \mathrm{d}t' \sum_{k=1}^{r} \int \mathrm{d}\boldsymbol{r}'[\langle j_i(\boldsymbol{r}), j_k(\boldsymbol{r}', t'-t)\rangle_0 \cdot \nabla\beta_k(\boldsymbol{r}', t') \\ + \langle j_i(\boldsymbol{r}), A_k(\boldsymbol{r}', t'-t)\rangle_0\dot{\beta}_k(\boldsymbol{r}', t')].\end{aligned} \tag{4.22}$$

Following Grandy [30] we note that: 'In general, determinations of transport coefficients are carried out in stationary processes, and so we employ the steady-state scenario . . . '.

For the steady state, $\dot{\beta}_k(\boldsymbol{r}', t') = 0$, $k = 1, 2, \ldots, r$, and (4.22) reduce to

$$\langle j_i(\boldsymbol{r})\rangle = \langle j_i(\boldsymbol{r})\rangle_0 + \sum_{k=1}^{r} \int_V \mathrm{d}\boldsymbol{r}'\, L_{ij}(\boldsymbol{r}, \boldsymbol{r}', t) \cdot \nabla \beta_k(\boldsymbol{r}') \tag{4.23}$$

with

$$L_{ik}(\boldsymbol{r}, \boldsymbol{r}', t) = \int_{t_0}^{t} \mathrm{d}t' \langle j_i(\boldsymbol{r}), j_k(\boldsymbol{r}', t' - t)\rangle_0 \tag{4.24}$$

the 'transport coefficients'.

Equations (4.19)-(4.24) exhibit non-local dependence of the fluxes at a point on conditions throughout the surrounding medium and on earlier times. They are similar to equations derived by Zubarev [12, 13] and also by McLennan [15]; they in fact become equivalent to the results of Zubarev and McLennan in the limit $t_0 \to -\infty$. The transport coefficients L_{ik} become then, changing variables from t' to $\tau = t' - t$,

$$L_{ik}(\boldsymbol{r}, \boldsymbol{r}') = \int_{-\infty}^{0} \mathrm{d}\tau \langle j_i(\boldsymbol{r}), j_k(\boldsymbol{r}', \tau)\rangle_0 \tag{4.25}$$

and in the classical case when all quantities commute

$$L_{ik}(\boldsymbol{r}, \boldsymbol{r}') = \int_{-\infty}^{0} \mathrm{d}\tau \langle j_i(\boldsymbol{r})(j_k(\boldsymbol{r}', \tau) - \langle j_k(\boldsymbol{r}', \tau)\rangle_0)\rangle_0 . \tag{4.26}$$

The expression (4.25) for the transport coefficients is identical to that of Zubarev [13] while that of (4.26) corresponds to McLennan's results [15].

As mentioned previously, Robertson derived an expression similar to (4.26) for the heat conductivity coefficient and in his more recent article [32] has extended these considerations. Grandy [30] and Jaynes [25] have derived similar formalisms to that discussed above.

Again, the formal extension of the interval $t - t_0 \to \infty$ is discussed by Mori [11]. The argument is that the correlation functions $\langle j_i(\boldsymbol{r}), j_k(\boldsymbol{r}', \tau)\rangle_0$ '. . . decay approximately exponentially to zero in times comparable to the mean free time of molecules.' See also the work of Robertson [20], Jaynes [25] and Grandy [30, 31] where this assumption is used in the information theory approach.

To expose the connection with irreversible thermodynamics, we will simplify the discussion somewhat by considering, from now on, systems in which only energy and mass transport occurs. That is, we will ignore the momentum transport. In this situation the r set is contracted as is the argument of the representative microstate. If we further restrict ourselves to stationary processes ($\dot{\beta}_k = 0$) then $\rho(t)$ reduces to, in the case of one-particle species,

$$\rho = \{Z(\beta(\boldsymbol{r}'), \mu(\boldsymbol{r}')\}^{-1} \exp\left(-\int_V \beta(\boldsymbol{r}')[H(\boldsymbol{r}') - \mu(\boldsymbol{r}')n(\boldsymbol{r}')]\, \mathrm{d}\boldsymbol{r}'\right) \tag{4.27}$$

which is the so-called 'local equilibrium' density matrix.

It is well known (see e.g. Chester [1]) that the average fluxes, calculated with the local equilibrium density matrix are zero. This means that, if we carry through the analysis of the preceding part of this section with ρ defined by (4.27), that (4.22) will become

$$\langle j_i(\boldsymbol{r})\rangle = \sum_{k=1}^{2} \int_V \mathrm{d}\boldsymbol{r}' L_{ik}(\boldsymbol{r}, \boldsymbol{r}') \cdot \nabla\beta_k(\boldsymbol{r}') \tag{4.28}$$

with

$$L_{ik}(\boldsymbol{r}, \boldsymbol{r}') = \int_{-\infty}^{0} \mathrm{d}\tau \int_0^1 \mathrm{d}x \langle j_i(\boldsymbol{r}) \exp(Ax) j_k(\boldsymbol{r}', \tau) \exp(-Ax)\rangle_0 \tag{4.29}$$

and

$$\begin{aligned} \beta_1(\boldsymbol{r}) &= \beta(\boldsymbol{r}) \\ \beta_2(\boldsymbol{r}) &= -\beta(\boldsymbol{r})\mu(\boldsymbol{r}). \end{aligned} \tag{4.30}$$

From (3.13) and (4.16) we have for the 'entropy production'

$$\dot{S}(M_t) = K \sum_{i=1}^{2} \int_V \mathrm{d}r\, \beta_i(\boldsymbol{r}) \dot{a}_i(\boldsymbol{r}, t) \tag{4.31}$$

i.e.,

$$\dot{S}(M_t) = -K \sum_{i=1}^{2} \int_v \mathrm{d}r\, \beta_i(\boldsymbol{r}) \nabla \cdot \langle j_i(\boldsymbol{r})\rangle \tag{4.32}$$

since $S(M_t) = K\langle -\log \rho\rangle_0 = K\langle -\log \rho\rangle$. Using the identity

$$\nabla \cdot (\beta_i j_i) = \beta_i(\nabla \cdot j_i) + (\nabla\beta_i) \cdot j_i \tag{4.33}$$

and ignoring the surface integrals [30], (4.32) becomes

$$\dot{S}(M_t) = K \sum_{i=1}^{2} \int_V \mathrm{d}\boldsymbol{r}\, \nabla\beta_i(\boldsymbol{r}) \cdot \langle j_i(\boldsymbol{r})\rangle. \tag{4.34}$$

However, since $\langle j_i(\boldsymbol{r})\rangle$ is given by (4.28), in the linear approximation with small gradients in the fields, we have, finally, for the entropy production:

$$\dot{S}(M_t) = K \sum_{i,k=1}^{2} \int_V \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}' \nabla\beta_i(\boldsymbol{r}) \cdot L_{ik}(\boldsymbol{r}, \boldsymbol{r}') \cdot \nabla\beta_k(\boldsymbol{r}'). \tag{4.35}$$

According to Zubarev [12] and McLennan [62] the L_{ik} satisfy the Onsager relations [26] and the entropy production, as given by (4.35), is positive (retarded solution of Liouville's equation having so far been chosen).

5. Discussion and conclusions

The theory that we have outlined above has some minor advantages over the related theories of Zubarev and McLennan. Zubarev [17] arrived at a statistical index almost identical to relation (3.20), and hence relation (4.14), by his theory of 'quasi-integrals of the motion'. Again, McLennan [15] constructed a probability distribution function almost identical to (3.20) by explicit consideration of non-conservative forces describing the influence of a thermostat [14]. Specifically, Zubarev arrived at the expression [16]

$$\rho(t) = \exp\left(-\widetilde{\Phi(t)} - \varepsilon \int_{-\infty}^{0} \mathrm{d}t'\, \mathrm{e}^{\varepsilon t'} \boldsymbol{\beta}(t+t') \cdot \boldsymbol{A}(t')\right) \tag{5.1}$$

where

$$\widetilde{\Phi(t)} = \log \operatorname{Tr} \exp\left(-\varepsilon \int_{-\infty}^{0} \mathrm{d}t'\, \mathrm{e}^{\varepsilon t'}(\boldsymbol{\beta}(t+t') \cdot \boldsymbol{A}(t')\right). \tag{5.2}$$

By evaluating the integrals appearing in (5.1) and (5.2) by parts we arrive at expressions that are very similar to (3.20) and (3.21) [17]. At the end of a calculation using (5.1) and (5.2) one must let $\varepsilon \to 0$. Equation (5.1) can be shown to satisfy the Liouville equation with a weight [63]

$$\frac{\partial \rho(t)}{\partial t} + \mathrm{i}L\rho(t) = -\varepsilon(\rho(t) - \tilde{\rho}(t)). \tag{5.3}$$

In passing, we note that the work of Zubarev has been generalised by Algarte *et al* [64]. In [64] a non-equilibrium density matrix is constructed that includes both Zubarev's work and that of Green and Mori [8] as special cases.

McLennan's operator is of the form

$$\rho(t) = \tilde{\rho}(t) \exp(D(t)) \tag{5.4}$$

where

$$D(t) = \int_{-\infty}^{t} \mathrm{d}t' \int_{V} \mathrm{d}\boldsymbol{r}[\dot{\boldsymbol{A}}(t'-t) \cdot \boldsymbol{\beta}(t') + \boldsymbol{A}(t'-t) \cdot \dot{\boldsymbol{\beta}}(t')] \tag{5.5}$$

and $\rho(t) \to \tilde{\rho}(t)$ as $t \to -\infty$. Equation (5.4) satisfies the Liouville equation with external sources. Although the three theories have an almost identical formalism, this formalism has, of course, an entirely different origin in all three cases. The theory presented in this paper does though have certain advantages.

First, in order to fix the value of $\beta(t)$ which appears in (5.1) and (5.3) Zubarev and McLennan are forced to assume the validity of (2.22) as an added assumption. In the present approach, relations (2.22) are built into the formalism from the beginning.

Secondly, the lower limit in the time integrals of equations (5.1), (5.2) and (5.5) which arise in the theories of Zubarev and McLennan are only the special case of $t_0 \to -\infty$ of the present approach; this is equivalent to the initial condition

$$\rho(t \to -\infty) = \tilde{\rho}(t \to -\infty). \tag{5.6}$$

While (5.6) has the advantage of definiteness in a calculation, it is nevertheless quite a severe logical restriction because $\rho^*(t_0) = \tilde{\rho}(t_0)$ is the mathematical description of the imposition of constraints in an experiment. Robertson has also criticised the appearance of the weighting factor $\mathrm{e}^{\varepsilon t}$ in Zubarev's approach; indeed this factor appears also in the work of McLennan [15, 62]. However, as Grandy has pointed out [30] such a factor may be essential to ensure the convergence of the infinite time integrals. The convergence factor $\mathrm{e}^{\varepsilon t}$ may be incorporated into the current approach.

If we consider that we are dealing with slowly varying functions of time and position, then we may consider the steady state to be approached as a limit by defining $\beta_k(\boldsymbol{r}, t) = \exp(\varepsilon_k t)\beta_k(\boldsymbol{r})$ with $\varepsilon_k \to 0$, $k = 1, 2, \ldots, r$. From this we get $\dot{\beta}_k = \varepsilon_k \beta_k \to 0$ as $\varepsilon_k \to 0$. So, provided the appropriate integrals converge, the third term on the right-hand side of (4.22) will vanish as $\varepsilon_k \to 0$ and we will be left with (4.23) with the L_{ik} defined by

$$L_{ik}(\boldsymbol{r}, \boldsymbol{r}', t) = \lim_{\varepsilon_k \to 0} \int_{t_0}^{t} \mathrm{d}t' \langle j_i(\boldsymbol{r}), j_k(\boldsymbol{r}', t'-t)\rangle_0 \exp(\varepsilon_k t'). \tag{5.7}$$

In (5.7) it is assumed that we let $\varepsilon_k \to 0$ before taking the thermodynamic limit [17]. (Note that similar assumptions may be made for closed systems undergoing relaxation hydrodynamic processes from an initial steady state [20, 25].)

A third factor, connected with the first point mentioned in the first paragraph of this section, is the identification of the thermodynamic entropy with the macrostate entropy which leads in a natural fashion to the expression (4.35) for the entropy production. This indeed has an interpretation of relevant information leaking from the macrostate, an idea due to Nordholm and Zwanzig [7].

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