

Generalized Gibbs Entropy, Irreversibility and Stationary States

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Abstract

A generalization of the Gibbs entropy postulate is proposed, based on the BBGKY hierarchy as the non-equilibrium entropy for a system of N interacting particles. This entropy satisfies the basic principles of thermodynamics in the sense that it reaches its maximum at equilibrium and is coherent with the second law. By using this entropy and the methods of non-equilibrium thermodynamics in the phase space, a generalization of the Liouville equation describing the evolution of the distribution vector in the form of a master equation is obtained. After neglecting correlations in this master equation, the Boltzmann equation was obtained. Moreover, this entropy remains constant in non-equilibrium stationary states and leads to macroscopic hydrodynamics. Non-equilibrium Green-Kubo type relations and the probability for the non-equilibrium fluctuations are also derived

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1. Introduction

According to the mechanistic interpretation of the physical world, the basic laws of nature are deterministic and time reversible. However, at the macroscopic level, we observe irreversible processes related to energy degradation which generate entropy. How do we reconcile the 'spontaneous production of entropy' with the time reversibility of the microscopic equations of motion? At the end of the nineteenth century, Boltzmann tried to answer this question from a probabilistic point of view. According to him, entropy is a measure of the lack of knowledge of the precise state of matter and can be defined as a function of the probability of a given state of matter. This function associates a number $S_B(X) = \log |\Gamma_{M(X)}|$ to each microstate X of a macroscopic system, with $|\Gamma_M|$ being the volume of the region of the phase space Γ_M corresponding to the macrostate $M = M(X)$. The macrostate M is all of a group of states Y such that $M(Y) = M(X) = M$. In this sense, the Boltzmann entropy is a function of the microstate which at equilibrium coincides with the thermodynamic entropy. All systems in their irreversible evolution tend to a state of maximum probability or maximum entropy -the state of equilibrium.

In contrast to the Boltzmann entropy, the Gibbs entropy is not a function of the individual microstate but rather a function of the probability distribution in a statistical ensemble of systems with both entropies coinciding at equilibrium. As a consequence of the incompressible character of the flow of points representing the natural evolution of the statistical ensemble in phase space, the Gibbs entropy is a constant of motion. Thus, it has been argued that the relevant entropy for understanding thermodynamic irreversibility is the Boltzmann entropy and not the Gibbs entropy (Lebowitz, 1999a; Lebowitz, 1999b; Goldstein, 2001).

In addition, the problem of the diverging character of the Gibbs entropy related to the negative sign of the entropy production in non-equilibrium stationary states apparently excludes the use of the Gibbs entropy in the statistical description of non-equilibrium systems (Andrey, 1985; Hoover, 1992). This raises the question as to how to define the non-equilibrium entropy and if possible, to give a thermodynamic description of non-equilibrium fluctuations. In other words: can thermodynamics describe systems far from equilibrium (Gallavotti, 2004; Ruelle, 1999)?

Thus, from the moment when Gibbs first postulated his entropy formula, the definition of the non-equilibrium entropy, and its relation to

irreversibility, has been an outstanding problem, now compounded by the fact that the entropy production is negative in non-equilibrium stationary states in apparent violation of the second law of thermodynamics (Evans, 1994; Wang, 2002). This constitutes an open problem which must be solved.

A huge amount of work has been done on this subject, trying to address the problem. On the one hand, there have been attempts to extend the equilibrium entropy (Rondoni, 2000; Ruelle, 2003; Tuckerman, 1997; Gaspard, 1997) to non-equilibrium situations in order to avoid the divergence of the Gibbs entropy. On the other hand, work has been done to establish fluctuation theorems for the probability of the entropy production fluctuations (Evans, 2002). In a previous work (Pérez-Madrid, 2004), we showed a way to circumvent the difficulty of reconciling the second law of thermodynamics with the reversible microscopic equations of motion in the framework of the BBGKY hierarchy. We proposed a functional of the set of s-particle reduced distribution functions as the entropy for a system of N interacting particles. This entropy does not enter into contradiction with thermodynamics, and as shown here, in addition to being time-dependent, it enables the performance of a thermodynamic analysis of the stationary non-equilibrium states. In this sense, our theory constitutes an extension of the scope of thermodynamics to systems away from equilibrium.

We begin this contribution introducing in Section 2 the representation of the state of the isolated system in terms of the hierarchy of reduced distribution functions. Afterwards in Section 3 we develop the thermodynamic analysis and derive the entropy production which enables us to draw kinetic equations, in particular the Boltzmann equation. Section 4 is devoted to the analysis of the non-equilibrium stationary states of the system. Finally in Section 5 we stress the main conclusions.

2. Hamiltonian Dynamics

Let's consider a dynamical system of N identical particles whose Hamiltonian $H_N(\{\mathbf{q}^N, \mathbf{p}^N\})$ is given by

$$H_N = \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m} + \frac{1}{2} \sum_{j \neq k=1}^N \phi(|\mathbf{q}_j - \mathbf{q}_k|) \quad (1)$$

where m is the mass and $\phi(|\mathbf{q}_j - \mathbf{q}_k|) \equiv \phi_{jk}$ is the interaction potential. The state of the system is completely specified at a given time by the N-particle distribution function $F(\{\mathbf{q}^N, \mathbf{p}^N\}; t)$ which evolves in time according to the Liouville

equation. Nonetheless, an alternative description of the state of the system can be given in terms of the distribution vector (Balescu, 1975)

$$\mathbf{f} \equiv \{f_0, f_1(\Gamma_1), f_2(\Gamma_2), \dots, f_N(\Gamma_N)\} \quad (2)$$

with $\Gamma_s = (x_1, x_2, \dots, x_s)$ and $x_j \equiv (\mathbf{q}_j, \mathbf{p}_j)$. Additionally, the set of quantities Γ_s can be grouped as the vector $\Gamma \equiv \{\Gamma_1, \Gamma_2, \dots, \Gamma_N\}$, and correspondingly $\mathbf{H} \equiv \{H_1, H_2, \dots, H_N\}$ can be defined with H_s being the s-particle Hamiltonian. The distribution vector represents the set of all the s-particle reduced distribution functions $f_s(\Gamma_s)$ ($s=0, \dots, N$), defined through

$$f_s = \frac{N!}{(N-s)!} \int F(x_1, \dots, x_s, x_{s+1}, \dots, x_N) dx_{s+1} \dots dx_N \quad (3)$$

The evolution equations of these functions can be obtained by integrating the Liouville equation, thereby constituting a set of coupled equations: the BBGKY hierarchy which can be written in a compact way as a generalized Liouville equation (Pérez-Madrid, 2004)

$$\left(\frac{\partial}{\partial t} - \mathbf{PL} \right) \mathbf{f}(t) = \mathbf{QLf}(t) \quad (4)$$

with

$$\begin{aligned} \langle s | \mathbf{PL} | s' \rangle &= \delta_{s, s'} \left\{ \sum_{j=1}^s L_j^0 + \sum_{j < n=1}^s L'_{j, n} \right\} \\ &= \delta_{s, s'} [H_s, \dots]_p \end{aligned} \quad (5)$$

and

$$\langle s | \mathbf{QL} | s' \rangle = \delta_{s', s+1} \int \left\{ \sum_{j=1}^s L'_{j, s+1} \right\} dx_{s+1} \quad (6)$$

where $|s\rangle$ represents the s-particle state defined through $\langle \Gamma_s | s \rangle = f_s(\Gamma_s)$ and where the projection operators \mathbf{P} and \mathbf{Q} , its complement with respect to the identity, give the diagonal and nondiagonal part of the generalized Liouvillian \mathbf{L} , respectively. Here, $L_j^0 = [H_j^0, \dots]_p$ where $[\dots, \dots]_p$ is the Poisson bracket, $H_j^0 \equiv \mathbf{p}_j^2 / 2m$, and $L'_{j, n} = [H'_{j, n}, \dots]_p$, with $H'_{j, n} = \phi_{j, n} / 2$. In the next section we will show that irreversibility is manifested in the dynamics of the system when the adequate description, *i.e.* in terms of the distribution vector, is used.

3. Non-Equilibrium Thermodynamics

As the expression for the non-equilibrium

entropy, we propose

$$\begin{aligned}
 S &= -k_B \text{tr} \left\{ \mathbf{f} \ln \left(\mathbf{f}_{\text{eq}}^{-1} \mathbf{f} \right) \right\} + S_{\text{eq}} \\
 &= -k_B \sum_{n=1}^N \frac{1}{n!} \int f_n \\
 &\quad \ln \frac{f_n}{f_{\text{eq}, n}} dx_1 \dots dx_n + S_{\text{eq}}
 \end{aligned} \tag{7}$$

a functional of \mathbf{f} , analogous with the Gibbs entropy postulate (de Groot, 1984; van Kampen, 1990), is based on the fact that the distribution vector determines the state of the system. Here, k_B is the Boltzmann constant, $\mathbf{f}_{\text{eq}} = \{f_{\text{eq}, 0}, f_{\text{eq}, 1}, f_{\text{eq}, 2}, \dots\}$ is assumed to be the equilibrium distribution vector which corresponds with the equilibrium entropy $S_{\text{eq}} = S_B$, satisfying $\mathbf{L} \mathbf{f}_{\text{eq}} = 0$ (*i.e.* the Yvon-Born-Green hierarchy) whereas $\mathbf{f}_{\text{eq}}^{-1}$ denotes the vector whose components are the inverse of the reduced equilibrium distribution functions, $f_{\text{eq}, n}^{-1}$. Moreover, S is maximum at equilibrium when $\mathbf{f} = \mathbf{f}_{\text{eq}}$ giving $S = S_{\text{eq}}$, which can be proven by taking the first and second variation of S with respect to \mathbf{f} while S_{eq} and \mathbf{f}_{eq} remain fixed. This entropy is also coherent with the second law according to which S increases in irreversible processes such as the relaxation to equilibrium from an initially non-equilibrium state. This expression based on the BBGKY hierarchy is different from other developments in the literature, such as the paper by Green and Nettleton (Nettleton, 1958). Therefore, the rate of change of S which can be obtained by differentiating equation (7) with the help of equation (4) is

$$\begin{aligned}
 \frac{dS}{dt} \equiv \sigma &= -k_B \text{tr} \left\{ \frac{\partial \mathbf{f}}{\partial t} \ln \left(\mathbf{f}_{\text{eq}}^{-1} \mathbf{f} \right) \right\} \\
 &= -k_B \text{tr} \left\{ \mathbf{L} \mathbf{f} \ln \left(\mathbf{f}_{\text{eq}}^{-1} \mathbf{f} \right) \right\} \geq 0
 \end{aligned} \tag{8}$$

where use has been made of the fact that $\mathbf{P} \mathbf{L} + \mathbf{Q} \mathbf{L} = \mathbf{L}$. Thus, equation (8) constitutes the entropy production corresponding to the relaxation passing from a non-equilibrium state to equilibrium.

The explicit expression of σ can be obtained by using equations (5), (6) and (8). We get two contributions

$$\begin{aligned}
 \sigma_1 &= -\frac{1}{T} \sum_{n=1}^N \frac{1}{n!} \sum_{j=1}^n \int f_n \mathbf{p}_j \cdot \\
 &\quad \nabla_j \left(-k_B T \ln f_{\text{eq}, n} \right) dx_1 \dots dx_n \\
 &\quad -\frac{1}{T} \sum_{n=1}^N \frac{1}{n!} \sum_{j \neq i}^n \int f_n \mathbf{p}_i \cdot \mathbf{F}_{ij} dx_1 \dots dx_n
 \end{aligned} \tag{9}$$

where $\mathbf{F}_{ij} = -\nabla_i \phi_{ij}$ is the force on particle i due to particle j and

$$\begin{aligned}
 \sigma_2 &= -\frac{1}{T} \sum_{n=1}^N \frac{1}{n!} \sum_{j=1}^n \int f_n \mathbf{F}_j \cdot \\
 &\quad \mathbf{p}_j dx_1 \dots dx_n
 \end{aligned} \tag{10}$$

where \mathbf{F}_j is the force on particle j pertaining to the n -th cluster from outside this cluster

$$\mathbf{f}_n \mathbf{F}_j(\underline{q}_j) = \int \mathbf{F}_{j, n+1} f_{n+1} dx_{n+1} \tag{11}$$

Both contributions, σ_1 and σ_2 , vanish when the distribution function f_n coincides with its equilibrium value $f_{\text{eq}, n}$. In any other case these should not necessarily be zero. One has, then

$$\sigma = \sigma_1 + \sigma_2 \tag{12}$$

For small deviations from equilibrium, equation (8) becomes

$$\sigma = -k_B \text{tr} \left\{ \frac{\partial \mathbf{f}}{\partial t} \mathbf{X} \right\} \tag{13}$$

where $\mathbf{X} = \mathbf{f}_{\text{eq}}^{-1} (\mathbf{f} - \mathbf{f}_{\text{eq}})$ is the thermodynamic force conjugated with the current $\partial \mathbf{f} / \partial t$. Following the methods of non-equilibrium thermodynamics (de Groot, 1984; Bedeaux and Mazur, 2001) in the phase space, from equation (13) the linear relation

$$\frac{\partial \mathbf{f}}{\partial t} = -\mathbf{M} \mathbf{X} \tag{14}$$

is inferred, where the master or mobility matrix \mathbf{M} acts on an arbitrary vector \mathbf{Y} according to

$$\begin{aligned}
 \langle s | \mathbf{M} | s' \rangle \langle s' | \mathbf{Y} = \int M(s | s') \\
 Y_{s'}(x'_1, \dots, x'_s) dx'_1 \dots dx'_s
 \end{aligned} \tag{15}$$

Note that in view of the orthogonal character of the operators \mathbf{P} and \mathbf{Q} , equation (14) leads to $\mathbf{Q} \mathbf{M} \mathbf{X} = \mathbf{Q} \mathbf{L} \mathbf{f}$ and $\mathbf{P} \mathbf{M} \mathbf{X} = \mathbf{P} \mathbf{L} \mathbf{f}$.

Substituting the linear relation equation (14) into equation (13) and using the cyclic invariance of the trace, the entropy production is

$$\text{tr}(\mathbf{X} \mathbf{M} \mathbf{X}) \geq 0 \tag{16}$$

according to the second law of thermodynamics. Therefore, \mathbf{M} is a positive semidefinite matrix. In addition, the master matrix should be

Hermitian

$$M(s|s') = M^\dagger(s|s') = M^*(s'|s) \quad (17)$$

as predicted by the Onsager symmetry relations. Here \dagger refers to the Hermitian conjugate and $*$ stands for the complex conjugated. Furthermore, due to the fact that \mathbf{f} should be normalized, $\text{tr}(\mathbf{f})$ is a constant quantity which is a function of N . It can be inferred from equation (14) that $\text{tr}(\mathbf{M}\mathbf{X})=0$ which, when the Hermitian character of the master matrix is taken into account, leads to the following constraints

$$\int M(s|s') dx_1 \dots dx_s = \int M^\dagger(s|s') dx'_1 \dots dx'_{s'} = 0 \quad (18)$$

Hence, by using equation (14), the generalized Liouville equation, equation (4), can be written as

$$\left(\frac{\partial}{\partial t} - \mathbf{P}\mathbf{L} \right) \mathbf{f} = \mathbf{Q}\mathbf{M}\mathbf{X} \quad (19)$$

with

$$\langle s|\mathbf{Q}\mathbf{M}|s'\rangle \langle s'|\mathbf{X} = \delta_{s',s+1} \int M(s+1|s') X_s dx'_1 \dots dx'_s dx_{s+1} \quad (20)$$

written in analogy with equation (6). It should be mentioned that the presence of the master matrix in equation (19) notably simplifies the BBGKY hierarchy. In fact, the master matrix introduces a relaxation time scale. Hence, our theory is equivalent to a relaxation time approach to the study of the BBGKY hierarchy valid when there is a broad separation between the hydrodynamic and microscopic scales.

Here, equation (19) can be put into a more common form by introducing a new function \mathbf{W} defined through (Meixner, 1957)

$$f_{0,s'} W(s'|s) = -M(s|s') + \delta(x'_1 - x_1) \dots \delta(x'_{s'} - x_s) \psi_s(x_1, \dots, x_s) \quad (21)$$

where the auxiliary function ψ_s is not arbitrarily selectable because of the constraints given by equation (18). Instead

$$\psi_s(x_1, \dots, x_s) = f_{0,s}(x_1, \dots, x_s) \int W(s|s') dx'_1 \dots dx'_{s'} \quad (22)$$

can be applied. Thus, equation (19) may be written in terms of the transition matrix as follows

$$\left(\frac{\partial}{\partial t} - \mathbf{P}\mathbf{L} \right) \mathbf{f}(t) = \mathbf{Q}\mathbf{W}\mathbf{f}(t) \quad (23)$$

where

$$\langle s|\mathbf{Q}\mathbf{W}|s'\rangle \langle s'|\mathbf{f} = \delta_{s',s+1} \int \{f_{s'}(x'_1, \dots, x'_{s'}) W(s'|s+1) - f_{s+1}(x_1, \dots, x_{s+1}) W(s+1|s')\} dx'_1 \dots dx'_{s'} dx_{s+1} \quad (24)$$

The introduction of the transition matrix enables us to write equation (19) as a master equation.

A particularly interesting case corresponds to $s=1$ where equations (23) and (24) reduce to

$$\left(\frac{\partial}{\partial t} - L_1^0 \right) f_1(x_1) = \int \{f_2(x'_1, x'_2) W(x_1, x_2 | x'_1, x'_2) - f_2(x_1, x_2) W(x_1, x_2 | x'_1, x'_2)\} dx'_1 dx'_2 dx_2 \quad (25)$$

This is not yet a kinetic equation; however, its uncorrelated part can be written as

$$\left(\frac{\partial}{\partial t} - L_1^0 \right) f_1(x_1) = \int \{f_1(x'_1) f_1(x'_2) W(x'_1, x'_2 | x_1, x_2) - f_1(x_1) f_1(x_2) W(x_1, x_2 | x'_1, x'_2)\} dx'_1 dx'_2 dx_2 \quad (26)$$

which is the famous Boltzmann equation. Analogous procedure can be followed to obtain the kinetic equations for the correlations coming from the components of \mathbf{f} of an order higher than one.

Although the generalized Liouville equation.(4) is reversible, the generalized Gibbs entropy (7) we propose is a monotonous functional of the distribution vector. We have shown that unlike the conventional belief an external manipulation of the system like coarse graining procedures is not necessary in order to obtain irreversibility. This is based on the fact that the generalized Gibbs entropy given by equation (7), which is formally analogous to the relative or Kullback entropy, is a concave functional of the distribution vector. In addition the generalized Liouville dynamics introduces a trace preserving linear transformation in the set of distribution vectors related to a compressible flow in Γ -space. Thus, in general, the compressible character of the flow associated to the generalized Liouville equation causes a non-vanishing rate of change of the generalized entropy that will never decrease under a trace

preserving linear transformation (Schlögl, 1980; Wehr, 1978).

4. Non-Equilibrium Stationary States

Let us assume that a nonconservative field h_o acts on the system, modifying the Hamilton equations of motion

$$\begin{aligned}\dot{\mathbf{q}}_i &= \frac{\partial H_N}{\partial \mathbf{p}_i} + \mathbf{C}_i(x_1, \dots, x_N) h_o \\ \dot{\mathbf{p}}_i &= -\frac{\partial H_N}{\partial \mathbf{q}_i} + \mathbf{D}_i(x_1, \dots, x_N) h_o\end{aligned}\quad (27)$$

where $\mathbf{C}_i(x_j)$ and $\mathbf{D}_i(x_j)$ are coupling functions. This drive introduces a compressible contribution to the flow in the phase space which is reflected in the Liouville equation characterizing the phase space flow

$$\frac{\partial}{\partial t} F - [H_N, F]_P = -\frac{\partial}{\partial \Gamma_N} \cdot \dot{\Gamma}_N^{\text{nc}} F \quad (28)$$

where $\dot{\Gamma}_N^{\text{nc}} = (\dot{x}_1^{\text{nc}}, \dots, \dot{x}_N^{\text{nc}})$, $\dot{x}_i^{\text{nc}} = (\mathbf{C}_i(x_j), \mathbf{D}_i(x_j)) h_o$ and F is assumed to be a smooth function. To equation (28) corresponds

$$\left(\frac{\partial}{\partial t} - \mathbf{P}(\mathbf{L} - \mathbf{G}) \right) \mathbf{f} = \mathbf{Q}\mathbf{L}\mathbf{f} \quad (29)$$

for the distribution vector, where $\mathbf{G}\mathbf{f} = \partial \dot{\Gamma}_N^{\text{nc}} \mathbf{f} / \partial \Gamma$ and $\langle s' | \mathbf{P}\mathbf{G}\mathbf{f} | s \rangle = \delta_{s, s'} \partial \dot{\Gamma}_s^{\text{nc}} f_s / \partial \Gamma_s$. Equation (28) admits a stationary solution satisfying

$$[H_N, F_{\text{st}}]_P = \frac{\partial}{\partial \Gamma_N} \cdot \dot{\Gamma}_N^{\text{nc}} F_{\text{st}} \quad (30)$$

or equivalently

$$\dot{\Gamma}_N \cdot \frac{\partial}{\partial \Gamma_N} \ln F_{\text{st}} - \frac{\partial}{\partial \Gamma_N} \cdot \dot{\Gamma}_N^{\text{nc}} = 0 \quad (31)$$

Up to order one with respect to the external force, equation (31) becomes $[H_N, \ln F_{\text{st}}]_P = \partial \dot{\Gamma}_N^{\text{nc}} / \partial \Gamma_N$. To this stationary distribution function F_{st} , there is a corresponding stationary distribution vector \mathbf{f}_{st} which can be obtained as a solution of the stationary version of equation (29) or computed directly from F_{st} by using equation (3), $\mathbf{f}_{\text{st}} \neq \mathbf{f}_{\text{eq}}$.

In this stationary state the rate of change of the internal energy $U = \int H_N(x_1, \dots, x_N) F(x_1, \dots, x_N) dx_1 \dots dx_N$, is given by

$$\begin{aligned}\frac{dU_{\text{st}}}{dt} &= \int H_N(x_1, \dots, x_N) \\ &\times \frac{\partial}{\partial t} F_{\text{st}}(x_1, \dots, x_N) dx_1 \dots dx_N = 0\end{aligned}\quad (32)$$

i.e. the energy is constant. Moreover, the total rate of change of the entropy is given by

$$\begin{aligned}\frac{dS_{\text{st}}}{dt} &= -k_B \text{tr} \left\{ \frac{\partial \mathbf{f}_{\text{st}}}{\partial t} \ln(\mathbf{f}_{\text{eq}}^{-1} \mathbf{f}_{\text{st}}) \right\} \\ &= k_B \text{tr} \left\{ \mathbf{G}\mathbf{f}_{\text{st}} \right. \\ &\left. \ln(\mathbf{f}_{\text{eq}}^{-1} \mathbf{f}_{\text{st}}) \right\} + \sigma_{\text{st}} = 0\end{aligned}\quad (33)$$

which is also constant, showing that entropy does not diverge. Hence, the stationary state coincides with the state of constant internal energy and entropy. In fact, in general the stationary average of any phase function remains constant. According to equation (33), the entropy production (8) reduces to

$$\begin{aligned}\sigma_{\text{st}} &= -k_B \text{tr} \left\{ \mathbf{G}\mathbf{f}_{\text{st}} \ln(\mathbf{f}_{\text{eq}}^{-1} \mathbf{f}_{\text{st}}) \right\} \\ &= k_B \text{tr} \left\{ \mathbf{f}_{\text{st}} \dot{\Gamma}^{\text{nc}} \frac{\partial}{\partial \Gamma} \ln(\mathbf{f}_{\text{eq}}^{-1} \mathbf{f}_{\text{st}}) \right\}\end{aligned}\quad (34)$$

Here in analogy with Brownian motion (Meixner, 1957), the entropy production given by equation (34) describes a diffusion process in Γ -space for which $\mathbf{f}_{\text{st}} \dot{\Gamma}^{\text{nc}}$ can be interpreted as the diffusion current \mathbf{J} and $\ln(\mathbf{f}_{\text{eq}}^{-1} \mathbf{f}_{\text{st}}) = \mu / k_B T_{\text{st}}$, μ being the chemical potential and T_{st} the stationary temperature in such a way that $\partial \mu / \partial \Gamma$ plays the role of the corresponding thermodynamic force \mathbf{X}_J conjugated to the current \mathbf{J} . Thus, the entropy production can be rewritten as

$$\sigma_{\text{st}} = \frac{1}{T_{\text{st}}} \text{tr} \{ \mathbf{J}\mathbf{X}_J \} \quad (35)$$

>From this equation, the following phenomenological law can be inferred

$$\mathbf{J} = \frac{1}{T_{\text{st}}} \mathbf{L}_{JX} \mathbf{X}_J \quad (36)$$

where \mathbf{L}_{JX} is a phenomenological coefficient. The phenomenological law (36) enables us to express the generalized velocity $\dot{\Gamma}^{\text{nc}}$ as

$$\dot{\Gamma}^{\text{nc}} = k_B T_{\text{st}} \mathbf{B} \frac{\partial}{\partial \Gamma} \ln(\mathbf{f}_{\text{eq}}^{-1} \mathbf{f}_{\text{st}}) \quad (37)$$

where $\mathbf{B} = (\mathbf{f}_{\text{st}} T_{\text{st}})^{-1} \mathbf{L}_{JX}$ is a mobility matrix. Moreover, $k_B T_{\text{st}} \mathbf{B}$ is a diffusion coefficient \mathbf{D} . Thus,

$$\frac{\partial}{\partial \Gamma} \ln(\mathbf{f}_{\text{eq}}^{-1} \mathbf{f}_{\text{st}}) = \mathbf{D}^{-1} \dot{\Gamma}^{\text{nc}} \quad (38)$$

and equation (34) becomes

$$\sigma_{\text{st}} = k_B \text{tr} \left\{ \mathbf{f}_{\text{st}} \dot{\Gamma}^{\text{nc}} \mathbf{D}^{-1} \dot{\Gamma}^{\text{nc}} \right\} \square h_o^2 \quad (39)$$

Thus, we can assume that for small deviations from the stationary state

$$\dot{\sigma} \equiv \frac{dS}{dt} - \sigma = -k_B \text{tr} \left\{ \mathbf{f} \dot{\Gamma}^{\text{nc}} \mathbf{D}^{-1} \dot{\Gamma}^{\text{nc}} \right\} \quad (40)$$

Therefore, following Boltzmann, the probability of the non-equilibrium fluctuations can be defined as

$$P_{\tau}(\dot{\Gamma}^{\text{nc}}, t) \sim \exp(\dot{\sigma}\tau) = \exp\left(-\text{tr} \left\{ \mathbf{f} \dot{\Gamma}^{\text{nc}} \mathbf{D}^{-1} \dot{\Gamma}^{\text{nc}} \right\}\right) \quad (41)$$

where τ is a macroscopic time. This probability enables us to compute the average value of any phase function $\Psi(\dot{\Gamma}^{\text{nc}})$, as for example the compressibility factor \mathbf{G} .

Finally, by approximating \mathbf{D} by its average value $D = \text{tr} \{ \mathbf{f}_{\text{st}} \mathbf{D} \}$ and using equation (8), we find

$$D = \frac{\text{tr} \left\{ \mathbf{f}_{\text{st}} \dot{\Gamma}^{\text{nc}} \dot{\Gamma}^{\text{nc}} \right\}}{-\text{tr} \left\{ \mathbf{L} \mathbf{f}_{\text{st}} \ln \left(\mathbf{f}_{\text{eq}}^{-1} \mathbf{f}_{\text{st}} \right) \right\}} \quad (42)$$

which constitutes a kind of Green-Kubo relation.

5. Conclusions

Here, we have proposed a generalization of the Gibbs entropy postulate based on the BBGKY-hierarchy as the non-equilibrium entropy for an N-body system. This entropy, which at equilibrium coincides with the thermodynamic entropy, is a concave functional of the distribution vector. In addition, the distribution vector representing the set of all the s-particle reduced distribution functions evolves according to the generalized Liouville equation, a compact way of writing the BBGKY hierarchy of equations which introduces a trace-preserving linear transformation in the set of distribution vectors.

Our generalized Gibbs entropy is formally analogous to the relative or Kullback entropy. Thus, due to the compressible character of the flow in Γ -space induced by the generalized Liouville equation and to the fact that this equation is a trace-preserving linear transformation, the generalized Gibbs entropy will never decrease. This is crucial to show that our approach constitutes the most appropriate description leading to irreversibility at the macroscopic level. No coarse graining procedures are necessary in order to obtain irreversibility.

On the other hand, by applying the methods of non-equilibrium thermodynamics in phase space, *i.e.* in the framework of the mesoscopic non-equilibrium thermodynamics MNET, a theory which has been proved to be successful in deriving kinetic transport equations in some

particular cases (Pérez-Madrid, 1994; Mayorga, 2002), we obtain a linear relation between the irreversible rate of change of the distribution vector and the conjugated thermodynamic force which introduces a master matrix which should satisfy the properties required by the Onsager theory. This result simplifies the BBGKY hierarchy and enables us to break the hierarchy by neglecting higher order correlations, thus obtaining the Boltzmann equation for the one-particle distribution function. This last result constitutes a test of our theory. Hence, based on the MNET, we have founded a way for deriving kinetic equations.

Our approach enables us to describe macroscopic stationary states. In this sense we have also shown that the entropy defined in terms of the distribution vector remains constant in a non-equilibrium stationary state; hence, divergences reported in the recent literature are avoided and the second law is satisfied. Also a kind of Green-Kubo relation was derived for a transport coefficient that can be defined in the system relating the power supplied to the system with the entropy production with the aid of a stationary temperature. Finally, following the Boltzmann principle, we derive the expression of the probability for the non-equilibrium fluctuations. Therefore, the answer to the question raised at the beginning: can thermodynamics describe systems far from equilibrium? is obviously yes if one works at the adequate level of description, which corresponds to the distribution vector.

Nomenclature

\mathbf{q}_j	position vector of the j-th point particle
\mathbf{p}_j	momentum of the j-th point particle
	$\mathbf{x}_j \equiv (\mathbf{q}_j, \mathbf{p}_j)$
ϕ_{jk}	interaction potential between the j-th and k-th particles
F	full space distribution function
\mathbf{f}	distribution vector
Γ_s	6s-dimensional phase space
H_s	s-particle Hamiltonian
f_s	s-particle reduced distribution function
\mathbf{L}	generalized Liouvillian
\mathbf{P}	projection operator onto the diagonal part of the generalized Liouvillian
\mathbf{Q}	projection operator onto the non-diagonal part of the generalized Liouvillian
S	entropy
S_{eq}	equilibrium entropy
S_B	Boltzmann entropy
\mathbf{f}_{eq}	equilibrium distribution vector
$f_{\text{eq}, n}$	equilibrium n-particle reduced distribution function
σ	entropy production

T	temperature
\mathbf{M}	mobility matrix
\mathbf{X}	thermodynamic force
$M(s s')$	s, s' component of the mobility matrix
\mathbf{W}	transition matrix
$W(s s')$	s, s' component of the transition matrix
h_o	external field
$C_i(x_j)$ and $D_i(x_j)$	coupling functions between the external field and the system
$\dot{\Gamma}^{nc}$	non-conservative generalized velocity
\mathbf{G}	generalized gradient
F_{st}	stationary full space distribution function
S_{st}	stationary entropy
\mathbf{f}_{st}	stationary distribution vector
σ_{st}	stationary entropy production
T_{st}	stationary temperature
μ	generalized chemical potential
\mathbf{J}	thermodynamic current
\mathbf{X}_J	thermodynamic force conjugated to the current \mathbf{J}
T_{st}	stationary temperature
L_{JX}	phenomenological coefficient
\mathbf{D}	diffusion coefficient

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