Molecular Theory of Irreversibility

A. Pérez-Madrid

Departament de Física Fonamental,
Facultat de Física, Universitat de Barcelona,
Diagonal 647, 08028 Barcelona, SPAIN

Abstract

A generalization of the Gibbs entropy postulate is proposed based on the BBGKY [Bogolyubov-Born-Green-Kirkwood-Yvon] hierarchy of equations as the nonequilibrium 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 a generalization of the Liouville equation describing the evolution of the distribution vector, it is demonstrated that the entropy production is a non-negative quantity. Moreover, following the procedure of non-equilibrium thermodynamics a transport matrix is introduced and a microscopic expression for this is derived. This framework allows one to perform the thermodynamic analysis of non-equilibrium steady states with smooth phase space distribution functions which, as proven here, constitute the states of minimum entropy production when one considers small departures from stationarity.

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I. INTRODUCTION

According to the mechanicistic 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 generates 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 $\Gamma_M$ 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$^{1-3}$.

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$^{4-5}$. 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$^{6-7}$.

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. 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 one hand, there have been attempts to extend the equilibrium entropy 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. In a previous work 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 Bogolyubov-Born-Green-Kirkwood-Yvon (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 we show here, in addition to being time-dependent it enables one to perform 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 an isolated system in terms of the hierarchy of reduced distribution functions. Afterwards, in section 3, we introduce a generalization of the Gibbs entropy postulate as the non-equilibrium entropy and derive the entropy production. After that, in section 4, we give the thermodynamic analysis of the non-equilibrium steady states of the system and establish a minimum principle for those states having obtained a phenomenological transport matrix previously. Finally, in section 5, we stress our main conclusions.

II. HAMILTONIAN DYNAMICS

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

$$H_N = \sum_{j=1}^{N} \frac{p_j^2}{2m} + \frac{1}{2} \sum_{j \neq k=1}^{N} \phi \left( |q_j - q_k| \right),$$  \hspace{1cm} (1)$$

where $m$ is the mass and $\phi \left( |q_j - q_k| \right) \equiv \phi_{jk}$ is the interaction potential. The state of the system is completely specified at a given time by the N-particle distribution function
$F \left( \{ q^N, p^N \} ; t \right)$ which evolves in time according to the Liouville equation. Nonetheless, an strictly equivalent alternative description of the state of the system can be given in terms of the distribution vector$^{16}$

$$f \equiv \{ f_o, f_1(\Gamma_1), f_2(\Gamma_2), \ldots, f_N(\Gamma_N) \} ,$$

with $\Gamma_s = (x_1, x_2, \ldots, x_s)$ and $x_j \equiv (q_j, p_j)$. Additionally, the set of quantities $\Gamma_s$ can be grouped as the vector $\Gamma \equiv \{ \Gamma_1, \Gamma_2, \ldots, \Gamma_N \}$, and correspondingly $H \equiv \{ H_1, H_2, \ldots, H_N \}$ 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 $f_s(\Gamma_s) \ (s = 0, \ldots, N)$, defined through

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

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$^{15}$

$$\left( \frac{\partial}{\partial t} - \mathcal{P} \mathcal{L} \right) f(t) = \mathcal{Q} \mathcal{L} f(t) ,$$

with

$$\langle s | \mathcal{P} \mathcal{L} | s' \rangle = \delta_{s,s'} \left\{ \sum_{j=1}^{s} L^s_j + \sum_{j<n=1}^{s} L'_{j,n} \right\}$$

$$= \delta_{s,s'} [H_s, \ldots]_P ,$$

and

$$\langle s | \mathcal{Q} \mathcal{L} | s' \rangle = \delta_{s',s+1} \int \left\{ \sum_{j=1}^{s} L'_{j,s+1} \right\} \, dx_{s+1} .$$

where $| \, s \rangle$ represents the s-particle state defined through $\langle \Gamma_s | s \rangle = f_s(\Gamma_s)$ and where the projection operators $\mathcal{P}$ and $\mathcal{Q}$, its complement with respect to the identity, give the diagonal and non-diagonal part of the generalized Liouvillian $\mathcal{L}$, respectively. Here, $L^s_j = [H^s_j, \ldots]_P$ , where $[\ldots, \ldots]_P$ is the Poisson bracket, $H^s_j = \frac{p^2}{2m}$, and $L'_{j,n} = [H'_{j,n}, \ldots]_P$ , with $H'_{j,n} = \frac{1}{2} \phi_{j,n}$. 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.
III. NON-EQUILIBRIUM ENTROPY AND IRREVERSIBILITY

As the expression for the non-equilibrium entropy we propose

\[
S = -k_B Tr \left\{ \frac{f}{f_o} \log \left( \frac{f}{f_o} \right) \right\} + S_o
\]

\[
= -k_B \sum_{n=1}^{N} \frac{1}{n!} \int f_n \log \frac{f_n}{f_{o,n}} \, dx_1 ... dx_n + S_o ,
\]

(7)

a functional of \( f \), generalizing the Gibbs entropy postulate\(^{17,18} \), based on the fact that the distribution vector determines the state of the system. The Gibbs entropy postulate is also known as relative or Kullback entropy\(^{19,20} \). Here, \( k_B \) is the Boltzmann constant, \( S_o \) the equilibrium entropy and \( f_o \) is assumed to be the equilibrium distribution vector which corresponds with \( S_o \), satisfying \( \mathcal{L} f_o = 0 \), the Yvon-Born-Green (YBG) hierarchy. Moreover, \( S \) is maximum at equilibrium when \( f = f_o \), giving \( S = S_o \), which can be proven by taking the first and second variation of \( S \) with respect to \( f \) while \( S_o \) and \( f_o \) remain fixed

\[
\delta S = -k_B Tr \left\{ \delta f \log \left( \frac{f}{f_o} \right) \right\}
\]

(8)

showing that \( \delta S = 0 \) at equilibrium when \( f = f_o \) and

\[
\delta^2 S = -\frac{1}{2} k_B Tr \left\{ f_o \left( f_o^{-1} \delta f \right)^2 \right\}
\]

(9)

which is a negative quantity.

As known the Gibbs entropy is a functional of the full phase-space distribution function. Since the flow of points representing the natural evolution of an isolated system in phase space is incompressible, this entropy is a constant of motion under the standard Liouville dynamics which is not the case for the generalized Gibbs entropy \(^{17} \). This entropy is 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. To prove this we compute the rate of change of \( S \) which can be obtained by differentiating Eq. \(^{17} \) with the help of Eq. \(^{4} \)

\[
\frac{dS}{dt} \equiv \sigma = -k_B Tr \left\{ \frac{\partial f}{\partial t} \log \left( \frac{f}{f_o} \right) \right\}
\]

(10)

\[
= -k_B Tr \left\{ \mathcal{L}_f \log \left( \frac{f}{f_o} \right) \right\} \geq 0 .
\]
This constitutes the entropy production corresponding to the relaxation passing from a non-equilibrium state to equilibrium. Two contributions to the entropy production $\sigma$ can be distinguished

$$\sigma_1 = -k_B Tr \left\{ \mathcal{P} \mathcal{L} f \log \left( f^{-1}_n \right) \right\} = -\frac{1}{T} \sum_{n=1}^{N} \frac{1}{n!} \sum_{j=1}^{n} \int f_n p_j \cdot \left(-k_B T \nabla_j \log f_{o,n} + \sum_{j \neq i=1}^{n} E_{j,i} \right) dx_1...dx_n , \quad (11)$$

where $T$ is the equilibrium kinetic temperature, taking into account that the dependence of $f_{o,n}$ in the velocities is given through a local Maxwellian and $E_{j,i} = -\nabla_j \phi_{j,i}$. The second contribution is

$$\sigma_2 = -k_B Tr \left\{ \mathcal{Q} \mathcal{L} f \log \left( f^{-1}_o \right) \right\} = k_B \sum_{n=1}^{N} \frac{1}{n!} \int \left( \sum_{j=1}^{n} E_{j,n+1} \cdot \frac{\partial}{\partial p_j} f_{n+1} \right) \times \log \frac{f_n}{f_{o,n}} dx_1...dx_n dx_{n+1} . \quad (12)$$

After partial integration Eq. (12) gives

$$\sigma_2 = -k_B \sum_{n=1}^{N} \frac{1}{n!} \int \sum_{j=1}^{n} \left( \int E_{j,n+1} f_{n+1} dx_{n+1} \right) \cdot \frac{\partial}{\partial p_j} \log \frac{f_n}{f_{o,n}} dx_1...dx_n$$

$$\sigma_2 = -k_B \sum_{n=1}^{N} \frac{1}{n!} \sum_{j=1}^{n} \int f_n E_{j}(q_j) \cdot \frac{\partial}{\partial p_j} \log \frac{f_n}{f_{o,n}} dx_1...dx_n , \quad (13)$$

where $f_n E_{j}(q_j) = \int E_{j,n+1} f_{n+1} dx_{n+1}$. Hence,

$$\sigma_2 = -k_B \sum_{n=1}^{N} \frac{1}{n!} \sum_{j=1}^{n} \int E_{j} \cdot \left( \frac{\partial f_n}{\partial p_j} - f_n \frac{\partial \log f_{o,n}}{\partial p_j} \right) dx_1...dx_n$$

$$\sigma_2 = -\frac{1}{T} \sum_{n=1}^{N} \frac{1}{n!} \sum_{j=1}^{n} \int f_n E_{j} \cdot p_j dx_1...dx_n . \quad (14)$$

Therefore,

$$\sigma = \sigma_1 + \sigma_2 . \quad (15)$$

At equilibrium when we substitute $f_{o,n}$ for $f_n$, $\sigma_1$ and $\sigma_2$ becomes zero, while in any other case these are not necessarily zero. Hence, the interaction among the different particles causing the correlations introduces the irreversibility into the system which is accompanied
by a creation of entropy. Entropy should explicitly contain all the correlations among the particles through the reduced distribution functions according to Eq. (7). This is our most important result in this paper. Although one can find somewhat related analyses\textsuperscript{21−23}, as far as we know, this expression (7) based on the BBGKY hierarchy has no direct counterpart in the previous literature.

As compared to other definitions of entropy, Eq. (7) does not contain any coarse-graining since this would imply some kind of time-averaging in order to subsum a certain number of time-scales, a procedure absent in Eq. (7). In addition, the generalized Gibbs entropy (7) is not a constant of motion under the Liouville dynamics given by Eq. (4). This dynamics introduces a trace-preserving transformation which in concomitance with the fact that Eq. (7) is a concave functional of the distribution vector leads to the positive character of the entropy production. In this framework we have shown in Ref.\textsuperscript{15} that by using the methods of the non-equilibrium thermodynamics it is possible to recover the kinetic Boltzmann equation. In the light of these facts not contained in other definitions of the entropy in the literature the strength of our definition (7) resides. Hence, it seems that the generalized Gibbs entropy (7) built in the framework of the BBGKY hierarchy which explicitly incorporates the correlations between all particles clusters in the system constitutes the appropriate description leading to irreversibility at the macroscopic level.

In appendix A we give the local version constituting the valance equation of the specific entropy.

IV. NON-EQUILIBRIUM STEADY STATES

As a way of demonstrating the applicability of the framework established in the previous section which enables us to describe irreversibility in a N-body system, let us assume that a non-conservative field $h(t)$ acts on this system, modifying the Hamilton equations of motion

\begin{align}
\dot{q}_i &= \frac{\partial H_N}{\partial p_i} + C_i(x_1, ... x_N)h(t) , \\
\dot{p}_i &= -\frac{\partial H_N}{\partial q_i} + D_i(x_1, ... x_N)h(t) ,
\end{align}

where $C_i(x_j)$ and $D_i(x_j)$ are coupling functions which are assumed to be analytic. 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

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

(17)

where $\dot{\Gamma}_N^{nc} = (\dot{x}_1^{nc}, ..., \dot{x}_N^{nc})$, $\dot{x}_i^{nc} = (C_i(x_j), D_i(x_j)) h(t)$ . Here, the full phase-space distribution function $F$ should be an smooth function in order that Eq. (17) be applicable. This function is defined through

$$F(\Gamma_N, t) = \frac{1}{M} \sum_{m=1}^{M} \delta(\Gamma_N - \gamma_m(t)),$$  

(18)

with $\gamma_m(t)$ being one among the $M$ realizations ($m = 1, ..., M$) in the statistical mechanical ensemble associated to our $N$-body system, so that $MF(\Gamma_N, t) d\Gamma_N$ equals the number of realizations contained in the infinitesimal phase space volume $d\Gamma_N$ at time $t$.24

In this context, some simulations have shown multifractal phase-space distributions.25–27 Although the multifractal nature of the phase space distribution functions has been stated,28,29 apparently this is not always the case. In fact, it has been shown that in the case of the Galton staircase30,31 an initial strong fractal phase space portrait becomes smooth when the system is coupled to a more ergodic Hoover-Holian thermostat.

To Eq. (17) corresponds

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

(19)

for the distribution vector, where $Q f = \frac{\partial}{\partial \Gamma} \left( \dot{\Gamma}_N^{nc} f \right)$ and $\langle s' | P G f | s \rangle = \delta_{s,s'} \frac{\partial}{\partial \Gamma_s} \cdot \left( \dot{\Gamma}_N^{nc} f_s \right)$. The total rate of change of the entropy is given now by

$$\frac{dS}{dt} = k_B Tr \left\{ G f \log \left( f^{-1} f \right) \right\} + \sigma.$$  

(20)

For a constant field $h$ a steady state, $dS/dt = 0$, can be reached when both contributions appearing in the right hand side of the previous equation balance each other. In such a case, the distribution vector is $f_{st}$ and the entropy production (10) reduces to

$$\sigma_{st} = -k_B Tr \left\{ G f_{st} \log \left( f_{st}^{-1} f_{st} \right) \right\}$$

$$= k_B Tr \left\{ f_{st} \frac{\partial}{\partial \Gamma} \dot{\Gamma}_N^{nc} \log \left( f_{st}^{-1} f_{st} \right) \right\}.$$  

(21)
In an attempt to study the stability of this non-equilibrium steady state we come back to Eq. (10). From this equation we infer the phenomenological law
\[
\frac{\partial f}{\partial t} \equiv -M \log (f^{-1} \hat{f}) \tag{22}
\]
in analogy with non-equilibrium thermodynamics, where $M$ is a transport matrix which in general might depend on the state of the system. Thus
\[
\sigma = k_B Tr \left\{ \log (f^{-1} \hat{f}) M \log (f^{-1} \hat{f}) \right\} , \tag{23}
\]
expressing $\sigma$ as a positive semidefinite quadratic form. Therefore, in light of our result corresponding to Eq. (10) one can state that $M$ is a positive semidefinite matrix which in addition should be Hermitian
\[
M(s|s') = M^\dagger(s|s') = M^c(s'|s) , \tag{24}
\]
as predicted by the Onsager symmetry relations. Here $^\dagger$ refers to the Hermitian conjugate and $^c$ stands for the complex conjugated. By comparing Eqs. (15) and (23) we can obtain a microscopic expression for $M$
\[
Tr \left\{ \log (f^{-1} \hat{f}) M \log (f^{-1} \hat{f}) \right\}
= \sigma_1 + \sigma_2 , \tag{25}
\]
where $\sigma_1$ and $\sigma_2$ are given by Eqs (11) and (14), respectively. In order to get a Lyapunov function for this system we can develop the expression (23) as follows
\[
\sigma = k_B Tr \left\{ \log (f^{-1} \hat{f}) M \log (f^{-1} \hat{f}) \right\}
+ 2k_B Tr \left\{ \log (f_{st}^{-1} \hat{f}_{st}) M \log (f_{st}^{-1} \hat{f}_{st}) \right\}
+ k_B Tr \left\{ \log (\hat{f}_{st}^{-1} f_{st}) M \log (\hat{f}_{st}^{-1} f_{st}) \right\} . \tag{26}
\]
Notice that the second and third terms on the right hand side of this equation vanishes in view to the fact that $M \log (f_{st}^{-1} \hat{f}_{st}) = 0$ according to Eq. (22). On the other hand, for small departures from the steady state we can assume that $M$ coincides with its value at the steady state. Thus, the remaining non-zero term in Eq. (26) provides us the desired Lyapunov function
\[
L(t) \equiv k_B Tr \left\{ \log (f_{st}^{-1} \hat{f}) M \log (f_{st}^{-1} \hat{f}) \right\} \tag{27}
\]
which is a positive semidefinite quadratic form having its minimum value at the stationary state $f_{st}$. Hence, the steady state is the state of minimum entropy production. This is a result analogous to the one of the principle of minimum entropy production by I. Prigogine\textsuperscript{33}, nonetheless, the later was formulated in the framework of the classical non-equilibrium thermodynamics applicable in the linear regime.

V. CONCLUSIONS

Here we have shown a representation of the statistical description of a many-body system in terms of the distribution vector which reveals the irreversible manifestation of the motion of this system at the macroscopic level. This manifestation is hidden when one works with the standard Liouville equation but at the level of the generalized Liouville equation this irreversibility becomes evident. The Liouville equation is a closed equation for the phase space distribution function while the generalized Liouville equation encloses a set of coupled equations, each one in itself representing a contraction of the statistical description. But, as I have mentioned previously, the full statistical description in terms of the phase space distribution function is entirely equivalent to the description in terms of the set of all the reduced s-particle distribution functions, the distribution vector, with no loss of information. In this scenario, we show that the entropy given through the proposed generalization of the Gibbs entropy postulate is not conserved throughout the motion in phase space. The key point is that our entropy contains all the correlations among the particles through the reduced distribution functions. We have proven that this entropy reaches its maximum value at the equilibrium state where it coincides with the thermodynamic entropy and that the entropy production is positive according to the second law.

By applying the methods of non-equilibrium thermodynamics in phase space, \textit{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\textsuperscript{34–37}, we have obtained a phenomenological transport matrix relating the rate of change of the distribution vector with its conjugated thermodynamic force. We have proven that this is a positive semidefinite Hermitian matrix satisfying a kind of Green-Kubo relation. In this scenario, assuming that the full phase-space distribution function is adequately smoothed we have performed the thermodynamic description of the non-equilibrium steady states. We
have derived a minimum principle for those stationary states satisfied by the corresponding Lyapounov function which coincides with the entropy production referred to the steady distribution vector.

Therefore, in our opinion we have reconciled the reversibility of the microscopic level of description with the irreversible macroscopic behavior giving a molecular basis to the Non-equilibrium thermodynamics not restricted to the linear range. This enables us to perform the thermodynamic description of non-equilibrium steady states that can be far away from equilibrium, avoiding divergences and possible violations of the second law referred to in the previous literature. Hence, 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.

Appendix: local form

The local form corresponding to Eq. (14) is

$$\frac{\partial}{\partial t} f_1(x, t)s(x, t) = \frac{1}{T} \sum_{n=1}^{N} \frac{1}{n!} \sum_{j=1}^{n} \int f_n p_j \cdot \left( -k_B T \nabla_j \log f_{o,n} + F_j + \sum_{j \neq i=1}^{n} F_{j,i} \right) \delta(x_1 - x)dx_1......dx_n$$  \hspace{0.5cm} (28)

or

$$\frac{\partial}{\partial t} \rho(q, t)s(q, t) = \frac{1}{T} \sum_{n=1}^{N} \frac{1}{n!} \sum_{j=1}^{n} \int f_n p_j \cdot \left( -k_B T \nabla_j \log f_{o,n} + F_j + \sum_{j \neq i=1}^{n} F_{j,i} \right) \delta(x_1 - x)dx_1......dx_n dp$$,  \hspace{0.5cm} (29)

where $\rho(q, t)$ is the density and $s(q, t)$ the specific entropy.

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