GIBBS ENTROPY AND IRREVERSIBILITY

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Abstract

This contribution is dedicated to dilucidating the role of the Gibbs entropy in the discussion of the emergence of irreversibility in the macroscopic world from the microscopic level. By using an extension of the Onsager theory to the phase space we obtain a generalization of the Liouville equation describing the evolution of the distribution vector in the form of a master equation. This formalism leads in a natural way to the breaking of the BBGKY hierarchy. As a particular case we derive the Boltzmann equation.
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 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 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, i.e. it is a function of the microstate. 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 a function of the probability distribution in a statistical ensemble of systems, both 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], [2], [3].

But in our opinion, this is not the end of the story. It is our contention here to show that depending on the representation we use to describe the state of the system, the Gibbs entropy is a good definition of the nonequilibrium entropy which increases in the approach to equilibrium and is compatible with the Boltzmann’s account for irreversibility. To accomplish that goal, we will use the methods of mesoscopic nonequilibrium thermodynamics MNET [4], [5] in addition to the generalized Liouville description of dynamical systems in terms of the distribution vector.

The paper is organized as follows. In Section II we introduce the representation of the state of the isolated system in terms of the hierarchy of reduced distribution functions. Sec-
tion III, is devoted to developing the thermodynamic analysis, and to deriving the entropy production. Here, we draw kinetic equations as one of the consequences, in particular the Boltzmann equation. In section IV, we stress our main conclusions.

**Distribution vector dynamics.**—Let us think of a dynamical system having N interacting degrees of freedom \((q_1, ..., q_2, p_1, ..., p_N)\), where \(q_i\) and \(p_i\) are the generalized coordinate and conjugated momentum corresponding to the \(i\)-th degree of freedom. Let \(H(\{q^N, p^N\})\) be the Hamiltonian of the system, given by

\[
H = \sum_{j=1}^{N} \left\{ \frac{p_j^2}{2m} + \phi^e(q_j) \right\} + \frac{1}{2} \sum_{j \neq k=1}^{N} \phi(|q_j - q_k|),
\]

(1)

where \(m\) is the mass, \(\phi^e(q_j) \equiv \phi^e_j\) is an external potential, and \(\phi(|q_j - q_k|) \equiv \phi_{jk}\) is the interaction potential. The state of the system is completely specified at a given time by the N-particle distribution function \(F(\{q^N, p^N\}; t)\), 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 \([6]\]

\[
f \equiv \{f_o, f_1(x_1), f_2(x_1, x_2), ..., f_N(x_1, x_2, ..., x_N)\},
\]

(2)

which represents the set of all the reduced \(s\)-particle distribution functions \(f_s(x_1, x_2, ..., x_s)\) \((s = 0, ..., N)\), defined through

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

(3)

where \(x_j \equiv (q_j, p_j)\). This function is normalized according to

\[
\int f_s \, dx_1...dx_s = \frac{N!}{(N-s)!}.
\]

(4)

The evolution equations of the \(s\)-particle distribution functions can be obtained by integrating the Liouville equation constituting a set of coupled equations: the BBGKY hierarchy.

An arbitrary component equation of this hierarchy is

\[
\frac{\partial}{\partial t} f_s(x_1, ..., x_s) = \left( \sum_{j=1}^{s} L^o_j + \sum_{j<n=1}^{s} L'_{j,n} \right) f_s(x_1, ..., x_s)
+ \sum_{j=1}^{s} \int L'_{j,s+1} f_{s+1}(x_1, ..., x_{s+1}) \, dx_{s+1},
\]

(5)
which shows that the time derivative of \( f_s \) depends both on \( f_s \) and on the higher-order functions \( f_{s+1} \). Here

\[
L^o_j = [H^o_j, \ldots]^P ,
\]

where \([\ldots, \ldots]^P\) is the Poisson bracket, \( H^o_j = \frac{p^2_j}{2m} + \phi^o_j \), and

\[
L'_{j,n} = [H'_{j,n}, \ldots]^P ,
\]

with \( H'_{j,n} = \frac{1}{2} \phi_{j,n} \).

From Eq. (5) one can infer the evolution equation for the distribution vector

\[
\frac{\partial}{\partial t} f(t) = \mathbf{L} f(t) ,
\]

which constitutes the generalized Liouville equation, and \( \mathbf{L} \) is the generalized Liouvillian. This equation should be equivalent to Eq. (5), thus, the matrix elements \( \langle s | \mathbf{L} | s' \rangle \) must have the following values:

\[
\begin{align*}
\langle s | \mathbf{L} | s' \rangle &= \delta_{s,s'} \left\{ \sum_{j=1}^{s} L^o_j + \sum_{j<n=1}^{s} L'_{j,n} \right\} \\
&\quad + \delta_{s',s+1} \int \left\{ \sum_{j=1}^{s} L'_{j,s+1} \right\} dx_{s+1} ,
\end{align*}
\]

and

\[
\langle 0 | \mathbf{L} | s' \rangle = 0 ,
\]

where \( | s \rangle \) represents the \( s \)-particle state. At this point, it is convenient to introduce the operator \( \mathcal{P} \) providing the diagonal part of a matrix, and \( \mathcal{Q} \), its complement which gives the nondiagonal part. Thus, by using these operators we can rewrite Eq. (8) as follows

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

with

\[
\begin{align*}
\langle s | \mathcal{P} \mathbf{L} | s' \rangle &= \delta_{s,s'} \left\{ \sum_{j=1}^{s} L^o_j + \sum_{j<n=1}^{s} L'_{j,n} \right\} ,
\end{align*}
\]
\[
\langle s | \mathcal{Q} \mathcal{L} | s' \rangle = \delta_{s',s+1} \int \left\{ \sum_{j=1}^{s} L'_{j,s+1} \right\} dx_{s+1}.
\] (13)

The left-hand side of Eq. (11) is invariant under time reversal whereas this symmetry is broken in the right-hand side term, as one can convince oneself changing \(t\) by \(-t\) and taking into account Eqs. (12) and (13). Thus, the diagonal part of the generalized Liouvillian accounts for the reversible evolution of the distribution vector, and the nondiagonal part introduces irreversibility in the dynamics of \(f\) leading to dissipation, this fact will be show adequately in the section that follows. Hence, in the sense that the time reversal invariance is broken, the generalized Liouville equation given through Eqns. (8) or (11) is irreversible. Irreversibility is manifested in the dynamics of the system when we use the adequate description, \(i.e.\) in terms of the distribution vector, this description brings with itself certain degree of coarse graining.

**Mesoscopic nonequilibrium thermodynamics.—** The MNET constitutes the mesoscopic generalization of the macroscopic formalism of the non-equilibrium thermodynamics [8]. Here, the entropy is a functional of the distribution vector in the phase space given by the Gibbs entropy postulate [7]. Moreover, we apply the principles of equilibrium thermodynamics at a local level in phase space, and we follow the general scheme of non-equilibrium thermodynamics in order to compute the entropy production from the Gibbs entropy postulate. One then postulates the linear phenomenological equations relating fluxes and thermodynamic forces occurring therein. Immediately afterwards, by substituting this phenomenological equations in the generalized Liouville equation written in the form given in Eq. (11), one derives master equations for the distribution vector. Therefore, the entropy of the system, in analogy to the Gibbs entropy postulate, is given by

\[
S = -k_B Tr \left\{ f \log \left( \frac{f^{-1}}{f_0} \right) \right\} + S_o
= -k_B \sum_{s=1}^{N} \int f_s \log \frac{f_s}{f_0} dx_1 \ldots dx_s + S_o ,
\] (14)

where \(k_B\) is the Boltzmann constant, \(S_o\) the equilibrium entropy, and \(f_0\) is assumed to
be the equilibrium distribution vector satisfying $\mathcal{L}f_o = 0$. The rate of change of $S$ can be obtained by differentiating Eq. (14)

$$\frac{dS}{dt} = -k_BTr \left\{ \frac{\partial f}{\partial t} \log \left( \frac{f^{-1}f_o}{f_o} \right) \right\} ,$$

which for small deviations from the equilibrium reduces to

$$\frac{dS}{dt} = -k_BTr \left\{ \frac{\partial f}{\partial t} \frac{f^{-1}f_o}{f_o} \left( f_o - f \right) \right\} .$$

Here, the only contribution to the entropy production comes from the irreversible change of the distribution vector since the change reversible contributes to zero entropy production. The reversible change of the distribution vector is given by the mainstream current induced by the s-Hamiltonian flow in each one of the s-particle subspaces of the total phase space, and it is known that the Hamiltonian flow does not create entropy. According to the Onsager theory [8], [9] from Eq. (16) we infer the linear relation

$$\frac{\partial f}{\partial t} = M \left\{ \frac{f^{-1}f_o}{f_o} \left( f_o - f \right) \right\} \equiv MX ,$$

where the master or mobility matrix $M$ acts on an arbitrary vector $Y$ according to

$$\langle s | M | s' \rangle \langle s' | Y \rangle = \int M(s|s')Y_s'(x'_1, ..., x'_s') dx'_1.....dx'_s .$$

Substituting the linear relation Eq. (17) into Eq. (15) and using the cyclic invariance of the trace, we find for the entropy production

$$Tr (XMX) \geq 0 ,$$

according to the second law of Thermodynamics. This relation imposes the Hermitian character of the master matrix

$$M(s|s') = M(s'|s)\dagger ,$$

as predicted by the Onsager symmetry relations. Here $\dagger$ refers to the Hermitian conjugate. Furthermore, due to the fact that $f$ should be normalized $Tr(f)$ is a constant quantity which
is a function of $N$, from Eq. (17) we infer that $Tr(MX) = 0$, which, when we take into account the Hermitian character of the master matrix, leads to the following constraints

$$\int M(s | s') dx_1 \ldots dx_s = \int M(s | s')^\dagger dx'_1 \ldots dx'_{s'} = 0 . \quad (21)$$

Hence, by using the generalized Liouville equation (8) and Eq. (17) it comes to be that Eq. (11) can be written in a more convenient form

$$\left( \frac{\partial}{\partial t} - PL \right) f(t) = Q \frac{\partial f}{\partial t} = QMX , \quad (22)$$

with

$$\langle s | QM | s' \rangle \langle s' | X$$

$$= \delta_{s',s+1} \int M(s+1 | s') X_{s'} dx'_1 \ldots dx'_{s'} dx_{s+1} , \quad (23)$$

written in analogy with Eq. (13). It should be mentioned that the presence of the master matrix in Eq. (22) 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, Eq. (22) can be brought into a more common form, by introducing a new function $W$ defined through [10]

$$f_{a,s} W (s' | s) = - M (s | s')$$

$$+ \delta (x'_1 - x_1) \ldots \delta (x'_{s'} - x_s) \psi_s (x_1, \ldots, x_s) , \quad (24)$$

where the auxiliary function $\psi_s$ is not arbitrarily selectable because of the constraints given by Eq. (21). Rather applies

$$\psi_s (x_1, \ldots, x_s) = f_{a,s}(x_1, \ldots, x_s) \int W(s | s') dx'_1 \ldots dx'_{s'} . \quad (25)$$

Thus, Eq. (22) may be written in terms of the transition matrix as follows

$$\left( \frac{\partial}{\partial t} - PL \right) f(t) = QWf(t) , \quad (26)$$
where

\[ \langle s | QW | s' \rangle \langle s' | f = \delta_{s',s+1} \int \{ f_s'(x_1', \ldots, x_{s'}') W(s'|s + 1) - f_{s+1}(x_1, \ldots, x_{s+1}) W(s+1 | s') \} dx_1' \ldots dx_{s'}' dx_{s+1} . \]

(27)

It should be stressed that the introduction of the transition matrix leads to a deeper physical insight of our result.

A particularly interesting case corresponds to \( s = 1 \) where Eqs. (26) and (27) reduce to

\[
\left( \frac{\partial}{\partial t} - L_1^o \right) f_1(x_1) = \int \{ f_2(x_1', x_2') W(x_1', x_2'|x_1, x_2) - f_2(x_1, x_2) W(x_1, x_2 | x_1', x_2') \} dx_1' dx_2' dx_2 .
\]

(28)

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

\[
\left( \frac{\partial}{\partial t} - L_1^o \right) f_1(x_1) = \int \{ f_1(x_1') f_1(x_2) W(x_1', x_2'|x_1, x_2) - f_1(x_1) f_1(x_2) W(x_1, x_2 | x_1', x_2') \} dx_1' dx_2' dx_2 ,
\]

(29)

which is the famous Boltzmann equation. The correlated part of Eq. (28) does not matter because the correlated part of each side of this equation is identically zero. Analogous procedure can be followed to obtain the kinetic equations for the correlations coming from the components of \( f \) of an order higher than one.

The quantum generalization of our classical treatment can be done in terms of the Wigner distribution vector [6], defined as the set of all the \( s \)-particle Wigner functions. This quantum approach follows the same lines as the previous classical approach, but with the unavoidable differences in the algebraic manipulations.

**Discussion.**—Here, we have presented a representation of the statistical description of a many-body system in terms of the distribution vector, which reveals the irreversible component of the motion of this system. This component is hidden when we work with the standard Liouville equation but at the level of the generalized Liouville equation which entails a certain degree of coarse graining, this irreversible component becomes obvious. 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 represents a contraction of the statistical description. But, as we have mentioned in section II, the full statistical description in terms of the phase space distribution function is equivalent to the description in terms of the set of all the reduced s-particle distribution functions. In this scenario, we show that the Gibbs entropy given by the Gibbs entropy postulate is a non-conserved quantity throughout the motion in phase space. This entropy should increase until its maximum value at equilibrium according to the second law. The consequences we have drawn from the Gibbs entropy are compatible with the explanation of irreversibility which follows from Boltzmann’s entropy postulate.

By applying Onsager’s theory in phase space, i.e. in the framework of MNET, 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 obtaining the kinetic equation for the one-particle distribution function which coincides with the Boltzmann kinetic equation. Hence, this last result constitutes a test of our theory. Hence, we have shown a method based on the MNET for deriving kinetic equations.

We also stress that in our mesoscopic approach, the master matrix introduces a relaxation time scale which shows that our theory is valid when there is a broad separation between the hydrodynamic and microscopic scales. This separation of time scales allows the rate of change of the distribution vector due to the main stream flow velocity in phase space balance the irreversible change in order to achieve a stationary distribution at long time. This is precisely what happens in the context of the phenomena described by the kinetic equations.

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