Validity of path thermodynamics in reactive systems

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Path thermodynamic formulation of non-equilibrium reactive systems is considered. It is shown through simple practical examples that this approach can lead to results that contradict well established thermodynamic properties of such systems. Rigorous mathematical analysis confirming this fact is presented.

Stochastic thermodynamics was introduced in the early eighties in the framework of jump Markov processes, using the Gibbs-Shannon definition of entropy [1]. Path thermodynamics is a generalization of stochastic thermodynamics. It is based on the concept of "path entropy", an entropy associated with sample paths (trajectories) of a stochastic process. Nowadays the general belief is that path thermodynamics is the ultimate theoretical formalism for physico-chemical systems ranging from macroscopic to nanometer scale [2–5]. Yet, we show in this letter that many practical reactive systems cannot be described by path thermodynamics, in the sense that the predicted entropy production contradicts the corresponding well established thermodynamic result.

For instance, consider a perfectly homogeneous dilute reactive system, as can be produced experimentally in a "continuously stirred tank reactor" (CSTR). The CSTR is a particularly useful device that maintains a reactive system out of equilibrium by fixing the concentration of some reactants [6, 7]. In principle, by recording the step-by-step evolution of the system, a large number of sample paths can be collected for detailed analysis. In practice, such data are usually obtained by numerical simulation, using a well-established algorithm introduced some decades ago by Gillespie [8]. Suppose now that two of the reactions, say $R_1$ and $R_2$, are of the type $X \leftrightarrow Y$ and $X + Y \rightarrow 2Y$. Starting from an arbitrary state $(X, Y \neq 0)$, both reactions lead to the very same change, that is $(X, Y) \rightarrow (X - 1, Y + 1)$ (forward) or $(X, Y) \rightarrow (X + 1, Y - 1)$ (backward). Consequently, when analyzing the sample paths of this system, there is no criterion that allows us to differentiate $R_1$ from $R_2$. However, we know from the basic principles of irreversible thermodynamics that the
entropy production of reactive systems depends on the characteristics of each individual reaction (see, for example, Section 9.5 of ref. [9]). We thus conclude that in this case the entropy production based on path thermodynamics would necessarily be inconsistent with irreversible thermodynamics result [10]. Note that similar observation was reported by D. Sleznev et al. [11].

This example illustrates another well known shortcoming in the traditional (Gibbs-Shannon) stochastic modeling of physico-chemical systems when it comes to the description of their thermodynamic properties. As pointed out by Esposito and Van den Broeck [12, 13], the stochastic formulation of physico-chemical systems needs to be supplemented by explicit reference to the presence and properties of the thermal and/or particle reservoirs maintaining them out of equilibrium. Without this information, the stochastic formulation often leads to a "coarse grained" entropy production that contradicts the thermodynamic result [14]. However, for the class of reactive systems presented above, this goal cannot be achieved at the level of their sample paths but only at the level of master equation (or Fokker-Planck equation) where the contributions of elementary reactions are treated separately.

An unexpected consequence of this issue is that the sample paths of a class of one variable reactive systems behave, in a stationary non-equilibrium regime, like those of a system at thermodynamic equilibrium. For instance, let us consider again the example of a dilute reactive mixture in a CSTR that is now set up in order to maintain constant the concentration of all but one of the reactants, say $X$. Suppose that the reactions involving that component $X$ are of the type

$$A_j + jX \xrightleftharpoons[k_{ji}]{k_{ij}} B_j + (j+1)X, \quad j = 0, 1 \cdots N (1)$$

Unlike the previous example, here all of the reactions lead exactly to the same changes, that is, $X \rightarrow X + 1$ (forward) or $X \rightarrow X - 1$ (backward). As mentioned above, the sample paths of this system do not permit us to distinguish one reaction from another. They are thus equivalent to sample paths of a system with a single reversible reaction, symbolically represented as $X \rightleftharpoons X + 1$. This equivalence in turn implies that the corresponding sample paths are perfectly reversible in stationary regime, in the sense that any path joining an arbitrary state $S_1$ to another arbitrary state $S_2$ will occur with the same probability as the corresponding reverse path joining $S_2$ to $S_1$ (the mathematical proof will be presented below). But such time-reversal symmetry concerns only the thermodynamic equilibrium state where, on average, each forward reaction in (1) is exactly balanced by its reverse. We are thus faced with a paradox. On the one hand, in the stationary regime, the sample paths of this system, under given (time-independent) non-equilibrium constraints, possess time-reversal symmetry, which is the key signature of thermodynamic equilibrium states [15]. And,
on the other hand, the Gibbs-Shannon entropy production of the same system, under the very same non-equilibrium conditions, proves to be strictly positive, converging to the macroscopic thermodynamic result in the vanishing noise limit [1].

Given the controversial nature of the issues illustrated by the above examples, we now concentrate on the strictly mathematical aspects of the problem. First, we prove that the necessary condition for the validity of path thermodynamics is that there exists one, and only one, elementary reaction associated with each possible composition change of the system. Second, we prove that the class of reactive systems illustrated by the scheme (1) have sample paths that are time-reversible in stationary regime, even though the system operates under non-equilibrium constraints.

Let $\tilde{X}(t)$ be a pure $N$-dimensional ($N < \infty$) jump Markov process, that is a continuous-time Markov process with countable state space $\mathcal{E} \in \mathbb{Z}^N$ which has all its sample paths constant, except for isolated jumps. A jump Markov process is entirely characterised by the so called transition probabilities per unit time, or transition rates, defined as [16, 17]

$$W(X | X') = \lim_{\Delta t \downarrow 0} \frac{1}{\Delta t} \left[ P(X, t + \Delta t | X', t) - P(X, t | X', t) \right]$$

where the limit is assumed to be uniform in time $t$. The function $P(X, t + \Delta t | X', t)$ represents the conditional probability to have $\tilde{X}(t+\Delta t) = X$, given that $\tilde{X}(t) = X'$. Noticing that $P(X, t | X', t) = \delta_{X_t.X}$, we deduce that $W(X | X') \geq 0, \forall X' \neq X$. And since the convergence in (2) is assumed to be uniform in time, we have $\sum_X W(X | X') = 0$. Finally, using the Markovianity of $\tilde{X}(t)$, it can be shown that the conditional probability distribution obeys the so-called Kolmogorov forward equation, or master equation [17],

$$\frac{d}{dt} P(X, t | X_0, t_0) = \sum_{X'} W(X | X') P(X', t | X_0, t_0)$$

for $t > t_0$, with $\lim_{t \downarrow t_0} P(X, t | X_0, t_0) = \delta_{X_0.X}$. We note that the definition (2) implies that

$$P(X, t + \Delta t | X', t) = W(X | X') \Delta t + o(\Delta t), \forall X \neq X'$$

Let us assume that from any state $S \in \mathcal{E}$, any other state $S' \in \mathcal{E}$ can be reached by a succession of jumps. This assumption excludes the existence of absorbing states as well as uni-directional processes, such as "pure birth" or "pure death" processes. If the state space $\mathcal{E}$ is finite, then this assumption also implies that there exists a unique stationary probability distribution $P_s(X)$ that is reached exponentially fast in time from any initial state $X_0 \in \mathcal{E}$. As far as physico-chemical systems are concerned, it is reasonable to assume that this property remains true even if $\mathcal{E}$ is not finite. Here, however, all we need is to assume that $\tilde{X}(t)$ remains bounded, almost surely, at least
over a finite time interval \([t_0, t_f]\). It can then be proved that the master equation (3) has a unique solution in this time interval \([18]\). We will show that this unicity theorem, due to Kolmogorov, effectively restricts the class of reactive systems that can be described by path thermodynamics.

Let us now concentrate on sample paths of \(\tilde{\mathbf{X}}(t)\). We consider a finite time interval \([t_0, t_f]\) that we divide into \(n\) sub-intervals, \(t_0 < \cdots < t_n \equiv t_f\), with \(n \gg 1\). We then introduce the (joint) probability distribution \(P(\mathbf{X})\), where \(\mathbf{X} \equiv \{X_0, t_0; X_1, t_1; \cdots; X_{n-1}, t_{n-1}; X_f, t_f\}\) represents a discretized sample path of \(\tilde{\mathbf{X}}(t)\) that starts from the state \(X_0\) at the initial time \(t_0\) and ends up at the state \(X_f\) at the final time \(t_f\). Before proceeding further, it is important to notice that, contrary to what is stated by some authors, a conditional probability of the type \(P(X_{i+1}, t_{i+1} | X_i, t_i)\) does not correspond to the probability of observing the jump \(X_i \rightarrow X_{i+1}\) at the given instant of time \(t_{i+1}\), the jump may actually occur at any instant of time in the interval \([t_i, t_{i+1}]\). Besides, from the strict mathematical point of view, the statement "observing a jump at a given instant of time" is simply of zero measure. Furthermore, it is worthwhile to recall a basic Kolmogorov theorem stating that stochastic processes (including those with continuous realisations) are completely characterized by their discretized sample paths, such as \(\mathbf{X}\), provided the associated probability distribution exists and remains invariant under the permutation of the pairs \((X_i, t_i)\) and \((X_j, t_j)\), \(\forall i, j \in [0, n]\) \([18]\).

Similarly we introduce the "reverse" joint probability distribution \(P^{(R)}(\tilde{\mathbf{X}})\), where \(\tilde{\mathbf{X}} \equiv \{X_f, t_0; X_{n-1}, t_1; \cdots; X_1, t_{n-1}; X_0, t_f\}\) represents the "reverse sample path" of \(\tilde{\mathbf{X}}(t)\) that starts from the final state \(X_f\) at the initial time \(t_0\) and ends up at the initial state \(X_0\) at the final time \(t_f\). Note that the superscript "\((R)\)" in \(P^{(R)}(\tilde{\mathbf{X}})\) indicates that we are dealing with the probability of the reverse path. In particular, the change of variables \(\mathbf{X} \rightarrow \tilde{\mathbf{X}}\) transforms \(P\) to \(P^{(R)}\), and vice versa.

Let us denote respectively by \(\Delta S\) and \(\Delta e S\) the entropy variation and the entropy flow along the sample path \(\mathbf{X}\) joining the initial state \(X_0\) to the final state \(X_f\). Similarly, we denote by \(\Delta_i S = \Delta S - \Delta e S\) the corresponding entropy production, also known as "path entropy production". The cornerstone of path thermodynamics is the relation

\[
\Delta_i S(\mathbf{X}) = k_B Z(\mathbf{X})
\]  

(5)

where \(k_B\) is the Boltzmann constant and the quantity \(Z(\mathbf{X})\) is defined as

\[
Z(\mathbf{X}) = \ln \frac{P(\mathbf{X})}{P^{(R)}(\tilde{\mathbf{X}})}
\]  

(6)

with the obvious assumption that \(\tilde{\mathbf{X}}\) is not of zero measure. This relation generalizes the traditional Gibbs-Shannon stochastic thermodynamics \([1]\) and, as such, it was at the origin of an impressive
resurgence of interest in this field [2, 4, 5]. The more so since \( Z(\mathbf X) \) obeys the (detailed) fluctuation theorem, in the sense that

\[
\frac{P(\zeta)}{P(-\zeta)} = \frac{P\{\zeta < Z \leq \zeta + d\zeta\}}{P\{-\zeta < Z \leq -\zeta + d\zeta\}} = \exp(\zeta) \tag{7}
\]

where \( P\{E\} \) denotes the probability for the event \( E \) to occur. It is important to notice that the validity of this result goes far beyond the simple case of jump Markov processes. It doesn’t rely on any physico-chemical property of the system, nor on the Markovian attribute of the underlying stochastic process, so long as the reverse process exists and remains bounded almost surely [10].

The relation (5) was established by several authors, using different approaches [19–23]. We shall not go through the mathematical demonstration of this relation, nor discuss the physical justification of the underlying concepts (see [3] and [4] for extensive reviews). The more so since this type of relation, with the associated fluctuation theorem, concerns a variety of systems subjected to a different type of non-equilibrium constraints, such as controlled time dependent driving external forces and/or reservoirs, nicely illustrated by Jarzynski using a Hamiltonian approach [24]. Instead, we will question the validity of (5) in reactive systems submitted to a given (time-independent) non-equilibrium constraint and modeled as a jump Markov process.

Since \( \hat X(t) \) is a Markov process, we can write

\[
P(X) = P(X_0, t_0) \times \prod_{i=1}^{n} P(X_i, t_i | X_{i-1}, t_{i-1})
\]

and

\[
P(R)(\hat X) = P(R)(X_f, t_0) \times \prod_{i=1}^{n} P(R)(X_{n-i}, t_i | X_{n-i+1}, t_{i-1})
\]

Inserting these relations into (6) and noticing that, by construction, \( P(R)(X_f, t_0) = P(X_f, t_f) \), we find

\[
Z(X) = \sum_{i=1}^{n} \ln \frac{P(X_i, t_i | X_{i-1}, t_{i-1})}{P(R)(X_{i-1}, t_{n-i+1} | X_{i}, t_{n-i})} + \ln \frac{P(X_0, t_0)}{P(X_f, t_f)} \tag{8}
\]

For \( n \gg 1 \), we can use the relation (4) to obtain the main result

\[
Z(X) = \sum_{i=1}^{n} \ln \frac{W(X_i | X_{i-1})}{W(X_{i-1} | X_i)} + \ln \frac{P(X_0, t_0)}{P(X_f, t_f)} \tag{9}
\]

This relation was first introduced by Lebowitz and Spohn [25] and later analyzed by Gaspard and Andrieux for the specific case of reactive processes [26]. Since then, combined with (5), it constitutes the starting point of practically all path thermodynamics formulations of reactive systems.

Let us consider a reactive system that includes at least two elementary reactions leading to the very same composition change \( C_\alpha \rightarrow C_\beta \), like for example \((X, Y) \rightarrow (X-1, Y+1)\). The corresponding conditional probability \( P(C_\beta, t + \Delta t | C_\alpha, t) \) includes necessarily all the elementary processes giving rise to the jump \( C_\alpha \rightarrow C_\beta \). In fact, associating a specific conditional probability to each of these elementary processes contradicts the Kolmogorov unicity theorem [cf. the discussion beneath
eq. (4)]. This mathematical evidence is precisely the core of the problem. Actually, the relation (9) is just a replica of the relation (8) where \( P(X_i, t_i \mid X_{i-1}, t_{i-1}) \) is replaced by \( W(X_i \mid X_{i-1}) \Delta t_i \). Therefore each \( W(X_i \mid X_{i-1}) \) in (9) is necessarily the sum of all the transition rates associated with elementary reactions giving rise to the jump \( X_{i-1} \rightarrow X_i \). And, evidently, the same argument holds for the matching backward reactions \( X_i \rightarrow X_{i-1} \). This is not a restriction at the level of the master equation formulation (3) where the contribution of elementary processes are separated from each others, precisely because they appear as a sum. The situation is different for the function \( Z(X) \) since it is defined as the sum of the logarithm of transition rates, the argument of each logarithm function being the sum of all transition rates leading to the same jump. Given that the entropy production of reactive systems depends on the characteristics of each individual reaction [9], the relation (5) implies automatically that stochastic thermodynamics remains limited to systems where there exists one, and only one, elementary process associated to each possible jump. This result completes the demonstration of our first statement.

Consider now the paradoxical issue illustrated by the reactive system (1) and let us assume that the associated stochastic process \( \hat{X}(t) \) possesses a stationary regime, i.e., the corresponding stationary probability distribution \( P_s(X) \) exists. Denoting the transition rates of this system by \( \lambda_j(X) \equiv W_j(X+1 \mid X) \) and \( \mu_j(X) \equiv W_{-j}(X-1 \mid X), \ j \in [1, N] \), and inserting these expressions into the master equation (3), we can easily verify that the latter satisfies the principle of detailed balance at the stationary state, i.e.

\[
\mu(X) P_s(X) = \lambda(X - 1) P_s(X - 1)
\]

where \( \lambda(X) = \sum_j \lambda_j(X) \) and \( \mu(X) = \sum_j \mu_j(X) \). This relation proves our second statement since we have a theorem that states that if a Markov process obeys detailed balance, then its sample paths are time reversible at the stationary regime (see, for example, Section 6.3 of [16] for details). However, for the sake of completeness, we give here a slightly simpler proof.

We observe that, by definition, the sequence of states visited by \( \hat{X}(t) \) along the sample path \( X \) is arbitrary, with the exceptions that \( \{ \hat{X}(t_0) = X_0; \hat{X}(t_f) = X_f \} \). Being in a state \( X_i \) at time \( t_i \), the process may well remain there during \( \Delta t_i = t_{i+1} - t_i \), so that \( X_{i+1} = X_i \). For the reactive system (1), there exist only two other possibilities: either \( X_{i+1} = X_i + 1 (i \neq n) \), in which case \( W(X_{i+1} \mid X_i) = \lambda(X_i) \), or \( X_{i+1} = X_i - 1 (i \neq 0) \) and thus \( W(X_{i+1} \mid X_i) = \mu(X_i) \). In both cases, we can easily check that (10) can be written as

\[
W(X_i \mid X_{i-1}) P_s(X_{i-1}) = W(X_{i-1} \mid X_i) P_s(X_i)
\]
Consequently, the relation (9) reduces to

\[ Z(X) = \ln \frac{P_s(X_f)}{P_s(X_0)} + \ln \frac{P(X_0, t_0)}{P(X_f, t_f)} \]  

which vanishes at the stationary regime, implying in turn that \( P_s(X) = P_s^{(R)}(\tilde{X}) \). This result completes the demonstration of our second statement.

Obviously, the core of the problem lies in the fact that the specificities of elementary reactions cannot be deduced from the sample paths of the corresponding reactive system. One possible way out of this issue is to supplement the stochastic formulation with a sort of "counting parameter", which is used to identify the actual elementary process responsible for each transition. This strategy was proposed by Gaspard et al. for the stochastic formulation of reactive systems [27], as well as for the so-called "quantum dots" problem [28], and conclusive results were obtained in both cases. However it is important to keep in mind that this procedure changes profoundly the statistical nature of the problem because the system is provided with some information that it does not actually possesses. Determining thermodynamic properties of a system under this modified condition is, at minimum, a problematic endeavor that requires evidently more profound investigations.

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