Thermodynamics in Terms of a Sequence of $n$–chains Derived from a Martingale Decomposition of the Energy Process

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The role of the algebraic method has long been understood in shedding light on the topological structure of sets. However, when the set is a simplicial complex and host to a dynamical process, in particular the trajectory of a canonically distributed system in thermal equilibrium with a heat bath, the algebra re-enters. Via a theorem of Lévy and Dynkin, there is a correspondence between a system’s energy process at equilibrium and a sequence of $n$–chains on the state space.

FUNDAMENTALS AND REVIEW

Thermostatics

Let the set $\{\omega_1, \omega_2, \ldots, \omega_N\}$ be the state space for a random process $\{x_t : t \in [0, \infty)\}$. According to the results of [1], under the assumption that the “position” process $x_t$ is a trajectory of a canonically distributed subsystem in equilibrium with a heat bath at temperature $\theta$, there is a well defined energy process

$$h(x_t) = \theta \log \left( \frac{\Pi}{p(x_t)} \right)$$  \hspace{1cm} (1)

where,

$$\Pi = \left( p_1 p_2 \cdots p_N \right)^\dagger$$  \hspace{1cm} (2)

and for $k = 1, 2, \ldots, N$

$$p_k = p(x_t \in \omega_k).$$

Further [2], if the $N$–state process $x_t$ has a characteristic Carlson depth (in the finite state Markoff case this is simply the $L^1$ norm of the cycle between visits to a rare state) we have

$$\theta(\Delta t) = \frac{\text{const.}}{\|t\|_2 \sqrt{\left(\log[\Pi_{\Delta t_1}]\right)^2 + \left(\log[\Pi_{\Delta t_2}]\right)^2 + \cdots + \left(\log[\Pi_{\Delta t_{N-1}}]\right)^2 + 1}}$$  \hspace{1cm} (3)

where, $\Delta t_k$ is the characteristic time associated with the $k^{th}$ state during a cycle and

$$\Pi = \left( \Delta t_1 \Delta t_2 \cdots \Delta t_N \right)^\dagger.$$

For a simple example see [3]. Sample Isotherms as seen from the time domain are shown in figure [4].

Thermodynamics

With these microscopic quantities in hand, one is in a position to calculate the free energy and many other important quantities. The internal energy

$$U = p \cdot h$$

will be of particular importance in the next subsection.

It may happen that there are changes to the observed probabilities, changes in the length of the characteristic time scale or both. If it is as-
assumed that these changes are occurring in a subsystem that is in a state of continual equilibrium with a heat bath (or perhaps the observer shifts her attention from one subsystem to another all in established equilibrium with the same bath), the notions of work done, heat gained or lost by the system become applicable.

In equilibrium these changes are given by the product rule for differentiation (the First Law) as

$$\dot{U} = \mathbf{p} \cdot \dot{\mathbf{h}} + \mathbf{p} \cdot \dot{\mathbf{h}}$$  \hspace{1cm} (4)

In the nonstationary case equation (2) transforms in the obvious way from $\Pi$ into $\Pi(t)$. Similarly $h(x_t)$ becomes $h(x_t, t)$, etc. The calculation of the rates involve time derivatives of these quantities and are easily computed. The vectors appearing in the dot products on the RHS of equation (4) are typically high dimensional.

Fortunately, in the statistical mechanical context, the work rate admits a low dimensional description as well. Typically this is system dependent. Famous examples include pressure and volume changes or magnetization and changes in an applied field. The low-dimensional description of the heat rate is often system independent and is given in terms of temperature and entropy.

Frequently, as the microscopic dynamics often occur on state spaces with a topology these same macroscopic phenomena may also admit a second, low-dimensional interpretation in terms of their interplay with features of the state space. The purpose of this paper is to illustrate the twofold nature of the thermodynamics. The connection is accomplished via the subsystem’s trajectory through its path space and the path decomposition of Lévy and Dynkin.

Dynkin-Lévy Decomposition of the Path

This subsection focuses some elementary aspects of the martingale theory on applications to the energy process. In particular, the context is that of a canonically distributed subsystem’s trajectory through its state space. For readers unfamiliar with the martingale point of view an excellent reference for this section is [4].

Recall that according to the Lévy Formula, see for example [5], the martingale decomposition of a Markoff process is given by:

$$g(x_t) - g(x_0) - \int_0^t \sum_{k \neq x_s} q_{x_s k} (g(k) - g(x_s)) \, ds$$

here

$$q_{x_s k} = \lim_{s^+ \to s} \frac{P(x_{s+} = k | x_s)}{s^+ - s}$$

is the generator of the process.

Of particular interest in the sequel is the case when $g(\cdot)$ is the energy function $h(x_t, t)$ and the temperature is held constant. Under these conditions the Dynkin-Lévy kernel becomes

$$\theta \sum_{k \neq x_s} q_{x_s k} (s) \left( \log \frac{\Pi(s^+)}{p(k, s^+)} - \log \frac{\Pi(s)}{p(x_s, s)} \right).$$

Note: it may also be that the generator is itself a function of time.

On the Choice of State Space

As the main purpose of this paper is to bring out the connection between the physical and and
algebraic descriptions of the subsystem’s trajectory it is worthwhile to choose a state space that is meaningful in either context.

Exchange rules in the context of urn models, \[\mathbb{E}, \mathbb{E}_1, \mathbb{E}_2,\] are frequently used as state spaces to study diffusion, spin flip dynamics, granular materials, phase transitions, etc. Further the resulting state spaces are often simplexes or simplicial complexes which have long been used as building blocks in the study of algebraic geometry and topology.

A particularly simple member of this family of exchange models is the Gordon-Newell queue \[\mathbb{G}.\] For an interpretation of that process in terms of its thermodynamics see \[\mathbb{G}.\] Figure 2 illustrates the algebraic topology associated with its dynamics. Despite the potential for an arbitrarily large number of non-degenerate (energy levels are distinct) microstates, both the thermodynamic and algebraic descriptions of the energy process are three dimensional. The connection will be more fully developed in the sequel.

![FIG. 2: A basic example of a 2-simplex derived from the state space for Gordon-Newell exchange. The 0-chain, 1-chain and 2-chain shown (color coded) are derived from the martingale decomposition of the local energy process.](image)

Elements of the Gordon-Newell Process

The state space of a Gordon-Newell process may be represented as a matrix. The dimension of the column space is the number of urns.

The rows represent the states accessible to the system and may be used as state labels.

For an instantiation based on \(M\) balls and \(m\) urns, the cardinality of the state space is simply the number of ways to put \(M\) balls (indistinguishable) in \(m\) urns. In equation (5) an example of the state space matrix and row labeling scheme are presented. The left hand side of equation (5) defines the list of state labels associated with a space based on three urns and three balls (a total of ten states). The right hand side of the equation lists the states themselves.

The dimension of the column space is equal to the number of urns.

In the sequel there will be essentially two types of vector dot products, those describing macrostructure and those describing microstructure. For clarity, dot products with respect to the low dimensional row space will be denoted with a circled circle notation, for example (see equation (5))

\[
\alpha(7) \odot \eta = 1\eta_1 + 2\eta_2 + 0\eta_3.
\]

Dot products in the column space and other high dimensional vectors will use the standard “\(\cdot\)” notation.

The labels \(\alpha(1), \alpha(4)\) and \(\alpha(10)\) are the 0-simplexes. These are the states with all the balls in one urn or, alternatively, the states with two urns empty. The states \(\alpha(2)\) and \(\alpha(3)\) belong to the same 1-simplex, namely the set of states with the first urn empty and the others non-empty. The label \(\alpha(6)\) state belongs to the interior of the region. That is, the set of states with no empty urns.

\[
\begin{align*}
\alpha(1) & = 0 & 0 & 3 \\
\alpha(2) & = 0 & 1 & 2 \\
\alpha(3) & = 0 & 2 & 1 \\
\alpha(4) & = 0 & 3 & 0 \\
\alpha(5) & = 1 & 0 & 2 \\
\alpha(6) & = 1 & 1 & 1 \\
\alpha(7) & = 1 & 2 & 0 \\
\alpha(8) & = 2 & 0 & 1 \\
\alpha(9) & = 2 & 1 & 0 \\
\alpha(10) & = 3 & 0 & 0
\end{align*}
\]

\[3 \text{ urns}\]
A basic version of the exchange rule consists of
an \( m \times m \) global routing table (a transition probability matrix for an embedded discrete process) and \( m \) -timescales that characterize (globally) the rate of activity of the individual urns.

Let \( P_{ij} \) denote the probability that the discrete process transitions a single ball from urn “i” to urn “j”. The stationary vector (eigenvalue 1) of the transition matrix will be denoted \( \{ \pi_1, \pi_2, \ldots, \pi_m \} \). The urn rates will be denoted \( \{ q_1, q_2, \ldots, q_m \} \).

Any component of a stationary measure of the process may be given in terms of these parameters:

\[
\left( \frac{\pi_1}{q_1} \right)^{\alpha_1} \left( \frac{\pi_2}{q_2} \right)^{\alpha_2} \cdots \left( \frac{\pi_m}{q_m} \right)^{\alpha_m}
\]

where, \( \{ \alpha_1, \alpha_2, \ldots, \alpha_m \} \) are entries in that row of the state space matrix associated with the state label \( \alpha \).

A slightly more flexible version of the exchange rule allows the routing table and rates to vary locally from state to state. In addition, the parameters may be functions of time.

THE CONNECTION WITH THE HEAT RATE PROCESS

The Constant Temperature, Time Stationary Equilibrium

With the state energies and temperature given in terms of the canonically distributed subsystem’s statistics and timescales by equations (1) and (3), a stationary measure \( \mu(\cdot) \) of the exchange process may be expressed (componentwise) in a few ways

\[
\mu(\alpha) = \begin{cases} 
\left( \frac{\pi_1}{q_1} \right)^{\alpha_1} \left( \frac{\pi_2}{q_2} \right)^{\alpha_2} \cdots \left( \frac{\pi_m}{q_m} \right)^{\alpha_m} & 
\end{cases}
\]

Recall that the top expression on the RHS of equation (6) is the stationary measure in terms of the exchange rule parameters and was introduced in the last section. The middle expression follows using the substitution

\[
\eta_i = -\log(\frac{\pi_i}{q_i}).
\]

The bottom expression gives a stationary measure in terms of energy and temperature.

As is apparent from equation (3), the temperature may vary (via dilatation of the time scales) even though the state probabilities themselves are constant in time. When both the temperature and probabilities are constant in time

\[
h(x_t, t) = \begin{cases} 
h(x_t) \\
\theta \eta \oplus (\alpha(x_t) - \bar{\alpha}) 
\end{cases}
\]

where \( \bar{\alpha} \) is the arithmetic mean of the rows of the state space matrix. For the example given in equation (5) this vector is \( \{1, 1, 1\} \).

Dynkin-Lévy kernel for the energy process is given by

\[
\sum_{k \neq x_t} q_{x_t k} \theta h(\alpha(x_t)) - h(\alpha(k))
\]

In what follows the Dynkin-Lévy coefficient at a site “*” will be denoted \( \mathcal{d} L(\cdot) \).

Physical Significance of the Dynkin-Lévy Kernel for the Energy Process

Under the hypothesis of this subsection, constant temperature, time stationary equilibrium, the Dynkin-Lévy kernel takes the form given in equation (8). It may be shown that this corresponds to the heat process associated with the energy process \( h(x_t) \). For
\[ \langle dl(x_s) \rangle ds = \sum_{x_s} \sum_k p(x_s, s) P_{x_s,k}(s, s^+) \times [\alpha(k) - \alpha(x_s)] \otimes \eta \]
\[ = \sum_k p(k, s^+) [\alpha(k) - \alpha] \otimes \eta - \sum_{x_s} p(x_s, s) [\alpha(x_s) - \alpha] \otimes \eta \]
\[ = \sum_m (p(m, s^+) - p(m, s)) \times [\alpha(m) - \alpha] \otimes \eta . \]

So that,
\[ \langle dl(x_s) \rangle = \sum_m \dot{p}(m, s) h(m, s) . \quad (9) \]

This is of course the heat rate’s contribution to the “First Law”, equation (4).

**Algebraic Significance of the Dynkin-Lévy Kernel for the Energy Process**

Inspection of equation (8) shows that the Dynkin-Lévy coefficient at a site depends on the \( \alpha \) differences with the states to which the process may transition, weighted by the probability rate that the transition takes place during a small time \( s \to s^+ \).

Recall from the previous section that in the most basic version of the exchange rule there is one global matrix (site independent) that governs the transitions of the embedded discrete process and one set of inverse characteristic times that governs the rates of the urns.

A typical local neighborhood of an interior point “A” with state label \( \alpha(A) = \{a, b, c\} \) is shown in figure 3. The quantities relevant to the calculation of the Dynkin-Lévy coefficient at site “A” are listed in the table.

Notice that the table entries are invariant with respect to the actual location of site “A”. That is, the Dynkin-Lévy coefficients are constant on the interior of the simplex. A similar situation holds in the case “A” belongs to one of the boundaries.

**TABLE I**: A break down of the summands that comprise a Dynkin-Lévy coefficient: possible transition states, \( \alpha \)--index differences and corresponding small time probabilities of transition. See figure 3.

| \( k \) | \( \alpha(k) - \alpha(A) \) | \( D_{A,k}(s, s^+) \) |
|-------|-----------------|----------------|
| A     | 0, 0, 0          | 1 - (            |
| B     | 1, 0, -1         | \( q_3 P_{11} \) ds |
| C     | 0, 1, -1         | \( q_3 P_{12} \) ds |
| D     | -1, 1, 0         | \( q_1 P_{13} \) ds |
| E     | -1, 0, 1         | \( q_1 P_{23} \) ds |
| F     | 0, -1, 1         | \( q_3 P_{21} \) ds |
| G     | 1, -1, 0         | \( q_3 P_{21} \) ds |

**FIG. 3**: Typical Neighborhood of an Interior Point in the State Space

Consider the 1—simplex of states that have the first urn empty and the other two urns non-empty (for a picture see the orange 1-boundary in figure 2). The typical neighborhood and table for this boundary are obtained from those shown above for the interior points by simply deleting points “D” and “E”. The same table and figure result for all points on this face. In this way a real valued coefficient is associated with each 1—simplex in the complex. The set of these coefficients specifies a particular 1—chain.

The reader should be able to convince herself that under the conditions of the basic exchange rule: one global (site independent) transition matrix and one global set of characteristic times for the urns, the Dynkin-Lévy coefficients for the energy process specify \( n \)—chains in higher dimensions as well.
THE CONNECTION WITH THE WORK RATE PROCESS

It may happen, see equation (3) or figure 1, that the probabilities vary in time but the system remains on a constant temperature surface. In this situation the quantities \( \pi, q, \) and \( \eta \) from equation (6) become functions of time. The Dynkin-Lévy kernel of the energy process takes the form (see the appendix, equation (18))

\[
\text{dl}(x_t) = - \sum_{k \neq x_t} q_{x_t,k}(s) \times (h(\alpha(x_t), s) - h(\alpha(k), s)) \\
= \theta \hat{\eta}(s) \odot (\alpha(x_t) - \bar{\alpha}) \\
+ \theta \sum_{k \neq x_t} q_{x_t,k}(s) \times \eta(s) \odot (\alpha(k) - \alpha(x_t))
\]

(10)

Comparison of (10) with equation (8) reveals an additional term

\[
\theta \hat{\eta}(s) \odot (\alpha(x_t) - \bar{\alpha}) .
\]

This site dependent term is clearly the local work rate at \( x_t \). For (see equation (4))

\[
\theta \sum_{x_t \in \Omega} p(x_t) [\hat{\eta}(s) \odot (\alpha(x_t) - \bar{\alpha})] \\
= \theta \sum_{m} p(m) [\hat{\eta}(s) \odot (\alpha(m) - \bar{\alpha})] \\
= p \cdot \hat{h} .
\]

(11)

SUMMARY

Under the same conditions, in the case of constant temperature but time varying dynamics, it is shown that, due to the presence of a site dependent (local) work rate term, the correspondence with the chain groups is lost. Thus, the connection has been made between transitions from one thermal equilibrium to another and from one sequence of p-chains on the state space to another.

APPENDIX A: DERIVATION OF THE DYNKIN-LÉVY KERNEL FOR THE ENERGY PROCESS

Let \( h(x_t, t) \) denote the energy of the state \( x_t \) at the time \( t \). That is, the Hamiltonian for the system may have an explicit time dependence. The collection of all system trajectories (the position processes \( \{x_t, t \in [0, \infty)\} \)) will be denoted \( \Omega \). Let \( P \) denote the probability on path space the describes the trajectories of the position process.

The energy difference between the an “initial” state \( x_{t_0} \) at time \( t_0 \) and a “final” state \( x_{t_m} \) at time \( t_m \), may be decomposed into a telescoping sum:

\[
\delta h |_{t_0}^{t_m} = h(x_{t_m}, t_m) - h(x_{t_0}, t_0) \\
= [h(x_{t_m}, t_m) - h(x_{t_{m-1}}, t_{m-1})] \\
+ [h(x_{t_{m-1}}, t_{m-1}) - h(x_{t_{m-2}}, t_{m-2})] \\
+ \ldots \\
+ [h(x_{t_1}, t_1) - h(x_{t_0}, t_0)] .
\]

(12)

As is customary, let \( \mathcal{F}_t \) be the \( \sigma \)-algebra generated by paths in \( \Omega \) up to time \( t \). For simplicity, it is supposed that \( \mathcal{F}_0 \) contains the information about the explicit time dependence of the Hamiltonian.

Also, as is customary, let \( E(s|\mathcal{F}_t) \) denote the projection operator (conditional expectation) that projects its argument onto the set of square integrable functions on the measurable space \( (\Omega, \mathcal{F}_t) \) using the measure \( P \). The accumulated difference between the actual trajectory and its projections may be approximated as follows
\[ h_{\downarrow t_0} = \left[ h(x_{t_m}, t_m) - h(x_{t_{m-1}}, t_{m-1}) \right] \]

\[ - E(h(x_{t_m}, t_m) - h(x_{t_{m-1}}, t_{m-1}) | \mathcal{F}_{t_{m-1}}) + \left[ h(x_{t_{m-1}}, t_{m-1}) \right] \]

\[ - E(\ h(x_{t_{m-1}}, t_{m-1}) - h(x_{t_{m-2}}, t_{m-2}) | \mathcal{F}_{t_{m-2}}) + \cdots + h(x_{t_1}, t_1) - h(x_{t_0}, t_0) \]

\[ E(h(x_{t_{m+1}}, t_{m+1}) - h(x_{t_m}, t_m) | \mathcal{F}_{t_m}) \]

\[ = \left[ h(x_{t_m}, t_{m+1}) - h(x_{t_m}, t_m) \right] \]

\[ \times (1 - O(t_{m+1} - t_m)) \]

\[ + \sum_{k \neq x_{t_m}} \left[ h(k, t_{m+1}) - h(x_{t_m}, t_m) \right] \]

\[ \times P_{x_{t_m}, k(t_{m-1}, t_m)} \] (13)

more precisely:

\[ E(h(x_{t_{m+1}}, t_{m+1}) - h(x_{t_m}, t_m) | \mathcal{F}_{t_m}) \]

\[ = \frac{h(x_{t_m}, t_{m+1}) - h(x_{t_m}, t_m)}{t_{m+1} - t_m} (t_{m+1} - t_m) \]

\[ + \sum_{k \neq x_{t_m}} \left[ h(k, t_{m+1}) - h(x_{t_m}, t_m) \right] \]

\[ \times Q_{x_{t_m}, k(t_m)} (t_{m+1} - t_m) . \] (14)

Assuming that

\[ h(k, s^+) - h(k, s) \]

is small, for example \( h \) as a differentiable function of time, this is

\[ E(h(x_{t_{m+1}}, t_{m+1}) - h(x_{t_m}, t_m) | \mathcal{F}_{t_m}) \]

\[ = \frac{h(x_{t_m}, t_{m+1}) - h(x_{t_m}, t_m)}{t_{m+1} - t_m} (t_{m+1} - t_m) \]

\[ + \sum_k [h(k, t_m) - h(x_{t_m}, t_m)] \]

\[ \times Q_{x_{t_m}, k(t_m)} (t_{m+1} - t_m) \] (16)

Under these conditions the accumulated affects over the the time interval \([0, t]\) are

\[ \int_0^t \left( \frac{\partial h(x_s, s)}{\partial s} + \sum_k [h(k, s) - h(x_s, s)] \right) ds \] (17)

At constant \( \theta \), in terms of the exponents from equation (7)

\[ \theta \int_0^t \hat{\eta}(s) \odot [\alpha(x_s) - \bar{\alpha}] \]

\[ + \sum_k \eta(s) \odot [\alpha(k) - \alpha(x_s)] \]

\[ \times Q_{x_s, k(s)} ds \] (18)

At constant \( \theta \), in terms of fancier exponents resulting from the application of time varying microforces (local exchange rules and timescales)

\[ \theta \int_0^t ds \left( \hat{\eta}(s) \odot [\alpha(x_s) - \bar{\alpha}] \right. \]

\[ + \hat{\delta}(x_s, s) \odot \alpha(x_s) - \delta(\cdot, s) \odot \alpha(\cdot) \]

\[ + \sum_k Q_{x_s, k(s)} \left[ \eta(s) \odot [\alpha(k) - \alpha(x_s)] \right. \]

\[ + \hat{\delta}(k, s) \odot \alpha(k) - \delta(x_s, s) \odot \alpha(x_s) \right) \] (19)
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