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Statistical Dynamics with Sources and Sinks

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We describe the statistical dynamics of a neoclassical system of oscillators on a lattice, whose boundary points are maintained at prescribed temperatures.

Spohn and Lebowitz [1] have obtained a linear dynamical system as the limit of a conservative quantum system, and interpret it as describing a dissipative system in which some parts of the boundary are held at various temperatures. The Markov matrix of their model is a convex sum of others, each obeying the "condition of detailed balance" at the various temperatures. This idea was explored further by Hasagawa and Nakagomi [2,3]. It it likely however that this class of models is just a special case of a wide range of interesting models. We therefore look at this question again, using the versatile method of statistical dynamics [4]. We consider the computable case where the region in which the reactions occur is a finite lattice Λ. At each $x \in \Lambda$ is given the configuration space Ω_x, and the total configuration space, the sample space of the chemicals, is

$$\Omega_c = \prod_x \Omega_x. \tag{1}$$

The presence of a sample space indicates that we are using classical, rather than quantum, probability. We do not use classical particles, however; rather, the random variables are elements of the abelian algebra generated by the number densities of certain quantum fields on the lattice. It is because these commute with each other that we can use classical probability, and justifies the name "neoclassical". The use of random fields, the number densities, avoids the Gibbs paradox, which arises if the sample space of the whole space is not the product as in (1). This product structure fails in classical Hamiltonian theories of particles, which is why such theories are inconsistent with thermodynamics. See [5], p.205 and p.228 for a clear account.

Each Ω_x is itself a product: $\Omega_x = \prod_A \Omega_x(A)$. Here A labels a type of chemical (or ion, molecule, atom, excited state, nucleus, elementary particle....) The possible A are the same at each x. For the sample space $\Omega_x(A)$ we may take that of the Boson oscillator

$$\Omega_x(A) = \{0, 1, 2 \ldots\}$$

or we may take the Fermion space

$$\Omega_x(A) = \{0, 1\}.$$

We could even take the N-level atom $\{1,\ldots N\}$. If we choose the Fermion case, then a hidden repulsive force due to the Pauli principle is introduced. This is a painless way to deal with a hard core. The random variable $n_A(x)$ is just the value of the occupation number of the sample point at x in the space $\Omega_x(A)$. A sample point $\omega_c \in \Omega_c$ is of course just the specification of all these variables for all chemicals for all x.

We must specify the energy if we are going to be able to formulate the first law of thermodynamics. For a dilute gas a good choice is the energy of the free quantum fields, that is

$$H_c = \sum_{x,A} \hbar\omega_A n_A(x) \tag{2}$$

To enable mixing to take place in the finite lattice, we shall assume that all the angular velocities ω_A are rationally related. For simplicity, and to avoid confusion with the notation of ω as a sample point, we shall put all the angular velocities equal to 1.

A new feature of statistical dynamics is the heat-particle. We can choose one of the symbols, A say, to represent the shared kinetic energy (=heat) of the remaining chemicals at x. But it is perhaps more physical to introduce a Boson operator for each *bond* b of the lattice. Its excited states will then represent the phonon, or state of vibration of the electrostatic field attracting one molecule to its nearest neighbour. Thus we define the "phonon" or "photon" sample space $\Omega_\gamma = \prod_b \Omega_b(\gamma)$, and the "heat energy"

$$H_\gamma = \sum_b \hbar\omega_\gamma(b). \tag{3}$$

Here, $\omega_\gamma(b)$ is not the frequency (which is 1) but is the occupation number of the boson oscillator at the bond b when the sample point is ω_γ. The total sample space is then

$$\Omega = \Omega_c \times \Omega_\gamma \tag{4}$$

and the total energy of the system is then

$$H = H_c + H_\gamma. \tag{5}$$

This energy function divides the total sample space Ω into energy-shells: $\Omega = \cup_E \Omega_E$ where

$$\Omega_E = \{\omega : H(\omega) = E\}.$$

The dissipative dynamics is given by a bistochastic map T. This is initially defined as a linear map on the (abelian) algebra $\mathcal{A}$ of bounded random variables f on Ω. The space $\mathcal{A}$, regarded as a linear space, is in duality with the space of linear forms on $\mathcal{A}$. The positive normalised elements of this dual space are exactly the probability measures p on Ω. We denote by $\Sigma(\Omega)$ the space of probability measures on Ω, which we shall call the "state-space" for short. The duality relation between $\mathcal{A}$ and its dual coincides on $\Sigma(\Omega)$ with the expectation value

$$\langle p, f\rangle = \sum_{\omega\in\Omega} p(\omega)f(\omega). \tag{6}$$

Since our space Ω is discrete, probability measures on it are naturally identified as functions on Ω, and the formula (6) defines a scalar product on $\mathcal{A}$ making it into a real Hilbert space. For each linear map T on $\mathcal{A}$, denote by $T^\dagger$ the adjoint of T relative to this scalar product.

We say that T is stochastic if T maps the cone of non-negative random variables to itself, and $T1 = 1$, where 1 is the constant function 1. We say that T is bistochastic if T and $T^\dagger$ are both stochastic. It is easy to see that if T is stochastic, then $T^\dagger$ maps $\Sigma(\Omega)$ to itself; that is, $T^\dagger$ preserves the non-negativity of a probability p, and also conserves the total probability. In statistical dynamics we are interested in the dynamics of the states p rather than that of the observables. It is known that the set of bistochastic maps consists exactly of the maps that increase the Shannon entropy (or do not decrease it):

$$S(p) = -\sum_{\omega} p(\omega) \log p(\omega) \tag{7}$$

and $S(T^\dagger p) \geq S(p)$. Thus we can be sure to conform with the *second law of thermodynamics* by choosing T to be bistochastic. We incorporate the *first law of thermodynamics* by choosing a T so that T and $T^\dagger$ map each energy shell Ω_E into itself. One then shows that the mean energy is conserved by $T^\dagger$: $\langle T^\dagger p, H\rangle = \langle p, H\rangle$. It is easy to choose such energy-conserving T. We can select any symmetric Markov transition matrix on the energy shell, representing hopping from site to site (=diffusion) or reactions in which a point ω with certain occupation numbers at some site or bond makes a transition to a point $T\omega$ with a different number (=reaction). Here we act on the points of Ω by T by identifying a point with the random variable given by the Kronecker δ at the point. By emitting or absorbing heat-particles we can take account of the heat produced in exothermic reactions, and the cooling locally caused by endothermic reactions. There is no need to limit ourselves to symmetric Markov matrices, though this is usual in physics; for example to describe the dynamics of neural nets, a non-symmetric Markov chain seems more natural: there is no obvious relation between the probability that a neuron A will cause a neuron B to fire and the probability of the other way round. The choice of a bistochastic but not symmetric transition matrix would seem to be a good idea in this case.

It is important to note that in dissipative dynamics, information is lost but not energy; the energy is dissipated, that is, made more random, but the mean energy is conserved (if we include heat in the energy equation).

There is one further convenient idea in the theory, which is that of *local thermodynamic equilibrium.* The heat particle is supposed to represent thermalised energy, rather than a specific dynamic mode. The thermalising forces quite often act millions of times faster than the rest of the dynamics. We implement this idea by putting the heat-particles in a canonical state $p_\gamma(\beta(b))$ at some beta, possibly different for each bond. Thus we can describe a state in which the temperature is a function of position. Heat is not supposed to be correlated, so it is consistent to describe the state by a product state $p = p_c \otimes_b p_\gamma(\beta(b))$. We consider the case of discrete time. After a time step, the state has changed from p to $T^\dagger p$. This will not in general be a product state. But the thermalising forces will instantly replace it by the thermalised version. This is a map Q defined as follows. For any $p \in \Sigma(\Omega)$, let $\mathcal{M}_c p$ be the marginal probability of the chemicals, and let $\mathcal{M}_\gamma p$ be the marginal probability of the heat-particles. For any $p_\gamma \in \Sigma(\Omega_\gamma)$, let $Q_\gamma p_\gamma$ be the canonical state with the same mean energy as p_γ. This is known to have greater entropy than p_γ, unless they coincide. Then define the map Q by

$$Qp = \mathcal{M}_c p \otimes Q_\gamma \mathcal{M}_\gamma p. \tag{8}$$

The map Q decouples the chemicals from the heat, without destroying any correlations there may be among the chemicals. It also is entropy non-decreasing, and conserves the mean energy. We take our dynamics for an isolated system to be

$$p \to QT^\dagger p.$$

For this dynamics, which is non-linear, the Shannon entropy of the whole system, chemicals and heat, is a Lyapunov function, and under simple mixing conditions, such a system will converge to chemical equilibrium at a uniform temperature.

In [4] we proposed a further randomising map, which replaces the state of the chemicals, after each time-step, with a product state of grand canonical states, one for each x. The grand canonical state chosen at x is the one that has the same mean energy and particle number as the marginal state at x of the current state of the chemicals, that is, the state $T^\dagger p$ after the time step. This is known to have at least as much entropy as $T^\dagger p$, and obviously has the same mean energy. This map is the analogue of Boltzmann's Stosszahlansatz, and leads to a discrete for of the Boltzmann equation. This map simplifies the dynamics, which then reduces to a motion through the set of product grand canonical states. It does destroy any correlations between the chemicals that might be important in some reactions. We regard this extra randomisation as defining a different model, rather as being an approximation to the model proposed here, where only the heat-particle is randomised in this way.

An interesting intermediate case, suitable for mesoscopic systems, is suggested by the idea of "quadratic temperature", introduced in [6,7]. Suppose that the fluctuations of a local observable, such as the energy or density, is directly observable in that it is not vanishingly small (as it is in macroscpic systems) and that the time-step is so short that after the linear action of the Markov matrix $T^\dagger$ the fluctuations are unchanged in the time interval. But suppose too that the local thermalising forces completely randomise the other aspects of the instantaneous state in the time step. According to Ingarden, this means that after the time step, the state should be that which maximises the entropy subject to the linear constraints of the conservation laws *and* the quadratic constraints given by the specification of the variances of the local observables. Then the dynamics in one time-step is a map on the set of generalised temperature states as defined in [6]. As the time step becomes smaller, we may wish to include more and more detail of the state; as we use temperatures of higher order we approach the full detail of the state, eventually reaching the formalism suggested here.

To describe a system with permanent oscillations, called a "heat mill" we need a driven system. In this, heat or chemical sources or sinks are introduced. A simple way to do this is, for example for sources of heat, is to fix some of the temperatures at certain bonds, termed the boundary of Λ, and after our map, $p \longrightarrow QT^\dagger p$, to restore those bonds to their original state. This is a mathematical model of the process by which a source or sink maintains a point at a fixed beta. This map will upset the conservation of energy, because it models heat flows into or out of the system, and may decrease instead of increase the entropy. In this way we may get a system without a Lyapunov function, in which convergence to equilibrium might not happen. It is a completely computable model, at least if the chemicals are Fermions, with a finite state-space and discrete time. The infinite state space of the heat-particle is summarised at each time by one parameter, $\beta(b)$, for each bond.

In a similar way, we can drive the system by a source (or sink) of a chemical, by maintaining the marginal distribution of the chemical at the site of the source to be a grand canonical state of a given chemical potential. In this way we may construct a "chemical mill".

Example
We give a model inspired by the theory of the transition state. At each site $x \in \Lambda$ we choose the sample space $\{0, A, B, \ldots, C, D\}$. Here, 0 means that the site is empty, and $A, \ldots D$ are

the possible ions that can reside at x. Only one ion can sit at x at each time, so the model describes hard particles. At the bonds of Λ we put the Boson space $\{0,1,2,\ldots\}$, and at some points x, called the boundary of Λ, we maintain the state at some specified chemical potential for some of the chemicals. Some of the bonds are kept at fixed temperatures. The tendency of the ions to bond to form molecules is achieved by specifying the energy, which is a function of the configuration. We take it to be a sum of terms, each associated with one of the bonds. Thus

$$H = H_c + H_\gamma = \sum_{b\in bonds} \{H_c(b) + H_\gamma(b)\}. \tag{9}$$

The term $H_c(b)$ is a function of the sample point, but depends only on the state at the ends of b. If the configuration at these ends is, say, A, B, where these ions combine with binding energy $E_{A,B} < 0$, we include this negative term in the energy $H(b)$. If A and B do not bind, but need an activation energy of $E_{A,B} > 0$ in order to react, we add this positive term. This gives a model repelling particles. For example, the Ising model has only one sort of chemical, and has a binding energy $-J$ on every bond. We will assume that all binding energies and activation energies are integral multiples of the photon energy, which sits on the bonds. The dynamics will be given by a stochastic matrix $T^\dagger$ which conserves energy. It will be local; this means that transitions occur only by the transfer of an ion from one end of a bond to the other, and the difference in the energies of the two configurations is taken or given to the heat particles sitting on the bond. Free diffusion occurs when an isolated particle moves to the other end of a bond, which also has no occupied neighbours. This is described by the usual first-order finite-difference operator. But if a particle is next to an attracting particle, it must reduce the number of heat particles on a bond if it breaks away. In order to move from an isolated point to become the neighbour of a repelling particle, the appropriate number of heat-particles must be borrowed from the bond (and must be present on the bond). To describe the reaction

$$A + B \rightleftharpoons C + D \tag{10}$$

we introduce a transition matrix giving probability $\mu \leq 1$ to the transition from the configuration with A, B at the ends of the bond to the configuration with C, D at the ends. The choice $\mu = 1$ gives the case, often assumed in the theory of the transition state, when the A, B configuration, called the "transition state" moves with probability 1 to the final state C, D. The final Markov matrix $T^\dagger$ is a weighted convex sum of all the contributions from all the bonds and all the processes. This includes a non-zero probability that the repelling particles A, B will drift apart by diffusion, without reacting, if the neighbouring spaces are free. Thus the model does not, in the end, give probability 1 for the transition state to react. We notice, too, that if the neighbouring sites are occupied, then the probability of drifting apart is reduced, and the reaction rate is therefore increased. This effect has been noticed in some other models. Finally, the dynamics is given, in one time-step, by the action of $T^\dagger$, followed by the thermalising of all the bonds at their local temperatures, and then the restoration of the state at the boundary to its fixed chemical potentials.

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