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Deposition and evaporation of k-mers: Dynamics of a many-state system

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Abstract. When the dynamics of a system partitions the phase space of configurations into very many disjoint sectors, we are faced with an assignment problem: Given a configuration, how can we tell which sector it belongs to? We study this problem in connection with the dynamics of deposition and evaporation of k particles at a time, from a lattice substrate. For $k \geq 3$, the system shows complex behaviour: (a) The number of disjoint sectors in phase space grows exponentially with the size. (b) The asymptotic time dependence of the autocorrelation function shows slow decays, with power laws which depend on the sector. Both (a) and (b) are explained in terms of a nonlocal construct known as the irreducible string (IS), formed from a particle configuration by applying a deletion algorithm. The IS provides a label for sectors; the multiplicity of possible IS's accounts for (a), and let us determine sector numbers and sizes. The elements of the IS are conserved; thus their motion is responsible for the slow modes of the system, and accounts for (b) as well.

Keywords. Interacting stochastic systems; broken ergodicity; conservation laws.

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1. Many-state systems

It is well known that the number of microscopic configurations in a large statistical system grows exponentially with the volume. In a lattice system with N sites, the number of configurations $\Omega \sim \exp(\alpha N)$.

If the system is 'simple', it exists in a single macroscopic phase or state, in normal circumstances. Only at exceptional points in the phase diagram which require fine tuning of external parameters like the temperature and pressure, can it exist in one or two or a few more possible phases. The dynamical manifestation of this is that starting with any of the Ω possible configurations, the system will evolve to one or the other of the few steady states, each corresponding to a macroscopic phase.

By contrast, 'complex' systems have a large multitude of equivalent, or almost equivalent phases. The number of macroscopic states grows exponentially $\sim \exp(\gamma N)$. Physical examples of such systems are glasses, spin glasses and rubber. The phase space splits up into an exponentially large number of sectors, each of which consists of configurations which can be reached from each other by the dynamics. Inter-sector transitions do not occur, either because there exist strict conservation laws which forbid transitions, or because there are barriers between sectors, so that the time to go from one sector to another becomes infinite in the thermodynamic limit. Thus if we were to watch the evolution of the system starting from a configuration C_{initial}, we would find the system evolving into the steady state of the relevant sector. However, since this steady state is only one of a very large number of possibilities, we are faced with an assignment problem: Without explicitly evolving the system in time, how can one tell which of the many steady states will be reached from a given C_{initial}? How is one to label steady states?

In this paper, we discuss a model of k-mers, stochastically depositing on, and evaporating from, a one-dimensional lattice [1, 2]. For $k \geq 3$, this system has an exponentially large number of sectors and steady states, and is complex in the sense discussed above. We will show that for this system it is possible to find a sector-labelling scheme which relies on a novel sort of construct called the irreducible string [3]. This construction helps solve the assignment problem posed above. Moreover, we find that there is a nontrivial sector-dependence to the time-dependence of correlation functions: asymptotic decay laws show strong variations from one sector to another [4]. Once again, the irreducible string allows us to understand this sector-wise variation, in terms of the diffusive movement of its conserved but mobile elements.

2. Model of k-mer deposition and evaporation

Our model is a generalization of random sequential adsorption (RSA), a process considered by Flory [5]. In RSA, extended objects (made of k particles each) drop randomly onto a lattice substrate, provided that k adjacent sites on the lattice are empty. Of interest is the filling fraction as a function of time, and spatial correlation functions [6]. Over the past few years several extensions of RSA have been considered [7], including the effect of inter-particle interactions and monomer detachment.

We generalized the process by considering the effect of evaporation, in which k particles at a time may detach from adjacent sites of the substrate, and leave [1, 2]. An important aspect of the process is that it could be *any* k adjacent particles which leave — not necessarily the same k particles that fell in together. This property of reconstitution of k-mers is a crucial feature of the dynamics. Thus, in a small time dt, k adjacent empty sites become occupied simultaneously with probability ϵdt (deposition of a k-mer), while k adjacent occupied sites become empty with probability $\epsilon' dt$ (evaporation of a k-mer). Let us associate a pseudospin $S_i = \pm 1$ with site i, the value $+1$ corresponding to an occupied site and -1 corresponding to an empty site. Deposition corresponds to $|\downarrow\downarrow\downarrow\rangle \to |\uparrow\uparrow\uparrow\rangle$, while evaporation corresponds to the reverse transition.

3. Dimers

The case $k = 2$ corresponds to the deposition and evaporation of dimers. The action of the stochastic dynamics may be represented by an operator which acts in the 2^N-dimensional space of configurations. The spin notation leads to an unexpected identification: if $\epsilon = \epsilon'$, this operator can be mapped to the Hamiltonian of the spin-1/2 Heisenberg model, by making a spin rotation of one sublattice. (Here we have assumed that the lattice is bipartite, i.e., decomposable into two interpenetrating sublattices.) Exploiting the fact that the total spin operator commutes with the Heisenberg Hamiltonian as a consequence of spin rotational invariance (quite a non-obvious symmetry for the original stochastic process), it is possible to calculate in closed form the steady state autocorrelation function [1, 2]

$$C_i(t) = \langle S_i(0)S_i(t)\rangle - \langle S_i\rangle^2.$$

At long times, $C_i(t)$ varies as $t^{-d/2}$ where d is the dimension of the system. If $\epsilon \neq \epsilon'$, the corresponding spin operator has additional terms [2], corresponding to a staggered magnetic field and Dzyaloshniskii–Moriya cross-product interactions [8] of alternating sign. In this case, $C_i(t)$ cannot be evaluated in closed form, but can be shown to decay as $t^{-d/2}$ at large times. This answer is suggestive of a diffusion process at work, and this in turn would require a global conservation law, for all ϵ, ϵ'. In fact it is not hard to see that this is the conservation of $M_A - M_B$, where A and B label sublattices, and $M_A(M_B)$ is the total z-component of magnetization on sublattice $A(B)$. This is because the elementary processes of deposition and evaporation of two adjacent particles evidently increments or decrements the occupation of both sublattices equally.

4. Trimers: Phase-space decomposition

Now consider the case of trimers, $k = 3$ on a one-dimensional lattice of length L. (This case is typical of all higher k.) A major difference from the case of dimers is that the trimer deposition-evaporation model is a many-state system, with the number of sectors in phase space growing exponentially with the size of the system: as we will see below, the full phase space of 2^L configurations is partitioned into $\sim \mu^L$ sectors, where $\mu = 1.618...$ is the golden mean. A second important property of trimer dynamics is that the long-time decay of the steady state autocorrelation function $C_i(t)$ depends on the sector. This aspect is discussed in § 5.

4.1 *The irreducible string*

Both the existence of this large infinity of dynamically disconnected sectors and also the variety of asymptotic decay laws, from sector to sector, can be understood in terms of a novel, nonlocal construct, the irreducible string (IS). The IS is defined as follows [3]. Consider a spin configuration $C \equiv \{S_1, S_2, \ldots, S_L\}$ on a one-dimensional lattice with free boundary conditions. Starting (say) from the left, delete triplets of successive parallel spins, reducing the size of the spin-string by three by each such reduction. After completing a pass through the full string, re-start from the left and repeat the procedure, again and again. This 'deletion do loop' comes to a halt only when further reduction is impossible. The resulting irreducible string evidently has no parallel triplets of spins.

The irreducible string is a constant of the motion and uniquely labels each sector of phase space. The elementary step of deposition or evaporation changes three successive $\uparrow$ spins to three successive $\downarrow$ spins, or vice versa; evidently, the IS is invariant under this. Also, it is possible to prove that if two configurations have the same IS, they are necessarily reachable from each other by deposition-evaporation dynamics [9].

4.2 Sector decomposition

Given this labelling scheme for sectors in phase space, it is possible to prove the following facts about the number of sectors and their sizes [3, 9]:

(i) There are quite a few completely jammed configurations (1×1 sectors), for which the length of the IS is the length L of the lattice. The number of such sectors is $2F_L$, where F_L is the Lth Fibbonacci number, which approaches μ^L as $L \to \infty$.

(ii) The total number of sectors N_L obeys the recursion relation $N_L = N_{L-3} + 2F_L$, as each sector is either completely irreducible, or it is not. Consequently, $N_L \approx (1 + \mu)\mu^L$.

(iii) The size $D(L, I)$ of a sector is the number of configurations in it. Here I is the IS which labels it. It turns out that D depends on I only through its length $l(I)$. An explicit formula can be obtained for the generating function $g(I) \equiv \sum_{L=l}^{\infty} x^L D(L, I)$. It is then possible to find the asymptotic growth law for $D(I, L)$ for given I.

(v) The set of all fully reducible configurations $\{C\}_\phi$ constitute the sector labelled by the null irreducible string: $I \equiv \phi$. For this sector, $D_\phi \sim (27/4)^{L/3}$.

(vi) Consider picking a configuration C_{ran} totally at random from amongst the 2^L possible configurations — an important case, since most configurations are of this type. We may ask for the likely length l_{ran} of the corresponding IS. We find that $l_{\text{ran}} \approx L(1 - 3\mu^{-2}/2)$.

5. Trimers: Dynamics

We have seen that the DE process partitions phase space into an exponentially large number of sectors. A strong variation in the behaviour of $C_i(t)$, from one sector to another, is found in Monte Carlo studies [4]. For instance, in the sector with IS $= (\uparrow\uparrow\downarrow)^{fL}$ [i.e. the string $\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\cdots$ formed by repeating $\uparrow\uparrow\downarrow$ fL times] with $f < 1/3$, we find $C_i(t) \sim 1/t^{1/2}$. In the sector with IS $= (\uparrow\downarrow)^{fL}$ with $f < 1/2$, we find $C_i(t) \sim \exp(-bt^{1/2})$. If we start with a totally random initial configuration, we find that $C_i(t) \sim 1/t^{1/4}$. In the sector where the IS is a periodic string $(\uparrow\uparrow\downarrow\downarrow\uparrow\downarrow)^{fL}$ with $f < 1/6$, the autocorrelation function $C_i(t)$ depends on which sublattice site i lies (in a 3-sublattice decomposition of the lattice). $C_i(t) \sim 1/t^{1/2}$ for i on two sublattices, while $C_i(t) \sim \exp(-bt^{1/2})$ for i on the third sublattice.

An explanation of dynamical diversity can be found in terms of the IS: besides being a label on sectors, it has a dynamical meaning as discussed below. The point is that elements of the IS are themselves a subset of the full configuration of spins — namely, those that are left undeleted at the end of repeated application of the triplet reduction procedure (the 'deletion do loop' referred to above). Under time evolution, the configuration evolves, and as a result, the IS elements move on the lattice, though keeping their relative ordering intact (as the IS is a constant of the motion). In other words, the elements of the IS behave like a set of hard-core random walkers with spin (HCRWS), random-walking through the background of reducible spins. The diffusive motion of the HCRWS constitute the slow modes of the original model. We thus expect the HCRWS dynamics to account for the long-time properties of the deposition-evaporation system [4].

If we ignore the reducible background fluctuations (which occur rapidly, and contribute very little to the long-time behaviour), quite a lot can be said about HCRWS dynamics, as a good deal is known already about the diffusion of particles on a lattice, with mutual hard-core interactions (the exclusion process) [10]. The arrangement of spins on the particles in no way affects the particle dynamics, but is of course crucial in determining the spin autocorrelation function, which is what we need. The latter involves a convolution over the spin pattern (which in turn identifies a particular sector of the deposition-evaporation model), and the conditional probability in the exclusion process that particle m is at a particular site at $t = 0$, and particle $m + \Delta m$ is at the same site at time t.

The HCRWS model explains the variety of long-time behaviours found in different sectors in which the density of walkers l/L is finite, as detailed in the first paragraph of this section. However, in the null-IS sector, consisting of the set of all fully reducible configurations$\{C\}_{\phi}$, the dynamics is different, as it is the reducibility fluctuations which matter (these were the fast modes in the other sectors, and could be ignored there as a result). Numerical data from Monte Carlo simulations [4], and exact diagonalization of the transfer matrix for finite size systems [11] suggests that in this case fluctuations are slowly decaying and sub-diffusive in nature. The estimated value of the dynamical exponent $z \approx 2.5$ is quite different from the value for the Kardar–Parisi–Zhang type of stochastic growth models [12] which in one dimension are known to have $z = 3/2$.

6. Conclusion

Models of k-mer deposition and evaporation provide examples of many-state systems about which we can say quite a lot. Central to the understanding of both the phase space decomposition into exponentially many sectors, and also the diversity of asymptotic dynamical behaviour, is the irreducible string. The IS provides a compact and convenient means of labelling disjoint sectors, and thus provides a solution to the 'assignment problem' posed in the Introduction. Besides, the elements of the IS have a dynamical meaning: their diffusive movement through the lattice (with an implied hard core constraint between different elements) constitute the slow modes of the system; this allows for a characterization of the asymptotic decay laws of the autocorrelation function, and an understanding of their sector-wise variation.

Although we have not discussed it in this paper, the IS in fact encapsulates an infinite number of conservation laws. The way to construct conserved quantities (all of which are mutually commuting functions of $\{\sigma_1^z, \sigma_2^z \cdots \sigma_L^z\}$) is discussed in [3]. It is entirely possible that there is yet another family of conservation laws, which involve transverse components of the spin, σ_i^+ and σ_i^-. If they do exist, these transverse conservation laws would provide direct connections between the properties of different sectors. For dimers, where the decomposition of phase space is not nearly as severe, we know that transverse conservation laws do exist — they correspond to the conservation of total spin in that case. The elucidation of analogous conservation laws in many-state systems remains a challenging open problem.

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