PHYSICAL REVIEW
LETTERS

VOLUME 70 22 FEBRUARY 1993 NUMBER 8

Jamming and Kinetics of Deposition-Evaporation Systems and Associated Quantum Spin Models

Mustansir Barma,[a] M. D. Grynberg, and R. B. Stinchcombe
Department of Theoretical Physics, University of Oxford, 1 Keble Road, Oxford OX1 3NP, United Kingdom
(Received 8 October 1992)

A class of models of deposition and evaporation of dimers, trimers, ..., k-mers is studied analytically and by simulation. Correlation functions decay as power laws in time, related to broken symmetries in associated spin Hamiltonians. For $k \geq 3$, the number of jammed and evolving steady states increases exponentially with size. Finite size scaling studies support a phenomenological diffusive picture for dynamics and indicate universality over k in many subspaces.

PACS numbers: 05.50.+q, 02.50.–r, 75.10.Jm, 82.20.Mj

Stochastic models of lattice gas dynamics can provide valuable insight into nonequilibrium behavior and complex dynamics. In this Letter, we introduce a class of such models motivated by, and capturing some basic aspects of, simple deposition and evaporation processes involving k particles at a time. Despite their simplicity, the models exhibit unusually strong nonergodic behavior, a rich variety of partially and fully jammed steady states, and power law decays of dynamical correlation functions.

The models are studied analytically and numerically. They are equivalent to an interesting new class of quantum spin systems [1], whose simplest nontrivial member is the Heisenberg ferromagnet. These equivalences elucidate conservation laws and symmetries, and in some cases relate power laws in correlation functions to Goldstone modes. A phenomenological picture of the dynamics based on random walks of unjammed regions through jammed backgrounds is developed, and suggests that correlation functions have a diffusive tail. This is supported quantitatively by a Monte Carlo study of finite size scaling of the dynamical correlation function; a universal scaling function is shown to describe dynamics in several steady states for various k.

The basic process is the deposition and evaporation of k-mers on a d-dimensional lattice, where $k = 1, 2, 3, \ldots$ represents monomers, dimers, trimers, etc. Deposition of k-mers at rate ε and evaporation at rate ε' are attempted at random locations; a deposition attempt is successful if k successive sites are vacant, while evaporation requires k successive occupied sites. The rule for evaporation allows for reconstitution of k-mers. Our model includes as a special case ($\varepsilon'=0$) random sequential adsorption of k-mers on a lattice [2], and is related to lattice models of chemical reactions [3]. It differs from coordination models [4] and adsorption-desorption models considered earlier [5, 6] in that both deposition and evaporation involve k particles in our model—a crucial feature.

The case $d=1$ (linear k-mers on a chain) is typical and already exhibits very rich behavior. Consequently, we consider only this case in detail. The operator which describes the stochastic evolution of the system is $\exp(-Ht)$ where the "Hamiltonian" H is, for general k,

$$H = \sum_n (R_n - Q_n),$$
$$R_n \equiv \varepsilon \prod [\tfrac{1}{2}(1 - \sigma_l^z)] + \varepsilon' \prod [\tfrac{1}{2}(1 + \sigma_l^z)], \quad (1)$$
$$Q_n \equiv \varepsilon \prod \sigma_l^+ + \varepsilon' \prod \sigma_l^-,$$

where $\prod \equiv \prod_{l=n}^{n+k-1}$ and $\sigma_l^+ (\sigma_l^-)$ is a spin-$\frac{1}{2}$ raising (lowering) operator at site l. This form of Hamiltonian arises from having represented a particle (or vacancy) at site l by a pseudospin operator $\sigma_l^z = +1$ (or -1). The deposition (or evaporation) of a k-mer at k adjacent empty (or full) sites is equivalent to the flip of k

adjacent spins from down to up (or up to down), and this is given by the operator Q_n. Since this process only occurs with probability ε (or ε') ≤ 1, conservation of probability requires the appearance of a second operator R_n which does not change the up or down state of any spin. Since $\exp(-Ht)$ is a stochastic matrix [7], the eigenvalues E of H have a non-negative real part. The steady states are states with E=0 while positive energy eigenstates decay with lifetime $1/E$. States without k adjacent spins up (particles) or down (vacancies) are unchanged by Q_n and therefore also by R_n. These are the fully jammed states. Dynamics in a jammed environment is important for the long-time kinetics, and thus will be discussed later.

A family of conservation laws holds, if, as will be assumed throughout, the number of sites L is a multiple of k. Divide the chain into k sublattices $\alpha = 1, 2, \ldots, k$ such that site $l \in \alpha$ if $l = k\gamma + \alpha$ where γ is an integer. An important symmetry property can be inferred from the observation that deposition or evaporation of k-mers changes the occupation of all k sublattices by the same amount. The quantities $M_{\alpha\beta} \equiv M_\alpha - M_\beta$, where $M_\alpha \equiv \sum_{l\in\alpha} \sigma_l^z$ is a measure of occupation of sublattice α, are therefore constants of the motion. Thus they commute with H. The quantities $M_{\alpha\beta}$ are the infinitesimal generators of rotations around the z axis of all spins on each of the k different sublattices by angles θ_α ($\alpha = 1, 2, \ldots, k$) provided that

$$\sum_{\alpha=1}^{k} \theta_\alpha = 0 . \tag{2}$$

The vanishing commutators $[M_{\alpha\beta}, H]$ imply that H is invariant under such rotation. This can be easily checked by noting that $\sigma_l^\pm \rightarrow \exp(\pm i\theta_l)\,\sigma_l^\pm$. This symmetry plays a crucial role in the following. For the random monomer case $k = 1$, there are no cooperative effects [6]. There is a unique steady state with average coverage (particle concentration) $\varepsilon/(\varepsilon + \varepsilon')$. Dynamical correlation functions decay exponentially.

For $k \geq 2$, cooperative effects strongly affect the number and nature of steady states and concomitant dynamics. Figure 1 shows Monte Carlo results for the particle number autocorrelation function $C(t) = \sum_l [\langle \sigma_l^z(0)\,\sigma_l^z(t)\rangle - \langle \sigma_l^z\rangle^2]/4L$ where the expectation value is taken in steady state. $C(t)$ and higher order space- and time-dependent correlation functions describe completely the full adsorption-desorption kinetics. Evidently $C(t)$ decays as a diffusive power law for the deposition-evaporation process for $k \geq 2$. This is at first sight surprising, since the process contains no explicit particle diffusion terms. Also shown in Fig. 1 is the effect of adding particle diffusion: the decay changes from power law to exponential. The spin Hamiltonian helps to explain these initially puzzling behaviors.

For the case k=2 (dimers), H involves nearest-neighbor spin-pair interactions. For the symmetric case $\varepsilon = \varepsilon'$, the

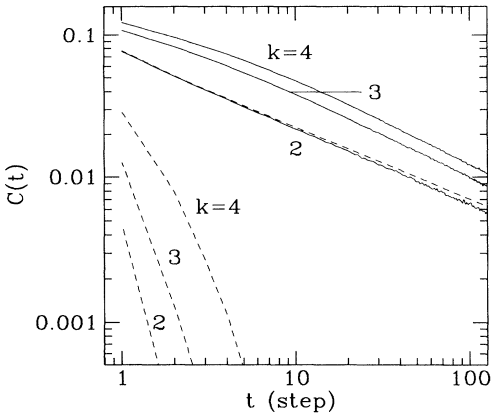

FIG. 1. The autocorrelation function for the deposition-evaporation process for $\varepsilon = \varepsilon'$, $L = 1.2 \times 10^5$, averaged over 100 histories (solid curves) shows power law decay ($\sim t^{-\frac{1}{2}}$) for $k = 2, 3, 4$. The dashed curve is an analytic determination for $k = 2$. Single particle diffusion changes the decay to exponential (dashed curves at the bottom left).

mapping $\sigma \rightarrow \hat{\sigma} \equiv (\hat{\sigma}^x, \hat{\sigma}^y, \hat{\sigma}^z) = (\sigma^x, -\sigma^y, -\sigma^z)$ on one sublattice takes H into the Heisenberg Hamiltonian

$$\hat{H} = \sum_l \frac{\varepsilon}{2}(1 - \hat{\sigma}_l \cdot \hat{\sigma}_{l+1}) . \tag{3}$$

Each of the $L + 1$ ground states of $\hat{H}$ corresponds to a steady state, and is labeled by distinct values of $\hat{M} = \sum_l \hat{\sigma}_l^z$. The calculation of the associated autocorrelation function $C(t)$ is straightforward but lengthy. It is carried out using selection rules based on the conservation of total spin, and is related to the dynamics of local active patches on an otherwise jammed background. The calculation shows that the asymptotic long-time adsorption-desorption kinetics is completely contained in this pair correlation function. Higher order (for example, dimer-dimer) correlation functions can be treated by generalizations of the method. The result [8] is $C(t) = (\frac{1}{4} - \hat{m}^2)\exp(-2\varepsilon t)\, I_0(2\varepsilon t)$, where $\hat{m} = \hat{M}/L$ and I_0 is the Bessel function of imaginary argument. Figure 1 shows that the Monte Carlo results agree well with this formula. In terms of the evaporation-deposition model, the full rotational symmetry of $\hat{H}$ arises from the conservation of probability, which implies equal coefficients of the transverse terms (describing transitions) and the longitudinal terms (corresponding to no change). Since the steady state breaks the rotational symmetry of $\hat{H}$, the Goldstone theorem implies the existence of low-lying bosons (spin waves) which are responsible for the asymptotic $t^{-\frac{1}{2}}$ decay of $C(t)$.

Explicit particle diffusion adds an exchange anisotropy term to $\hat{H}$ and destroys the rotation symmetry and associated conservation of $\hat{M}$. The resulting gap in the spin-wave spectrum leads to the exponential decay observed (Fig. 1) for this case.

For $\varepsilon \neq \varepsilon'$, the sublattice-transformed Hamiltonian $\hat{H}$ is non-Hermitian and not fully rotationally symmetric. Nevertheless, all $L+1$ steady states can be found explicitly. Further, $C(t)$ can be found in the sectors $\hat{M} = \pm(L/2 - 1)$ by solving a single-excitation problem. For arbitrary $\hat{M}$ the long-time behavior of $C(t)$ can be found [8] by studying the linear response of steady states to a driving field. The diffusion constant is $D = 2[\varepsilon\varepsilon'(1-m_A^2)(1-m_B^2)]^{\frac{1}{2}}[(1-m_A^2)+(1-m_B^2)]$ with m_A, m_B satisfying $m_A + m_B = 2\hat{M}/L$ and $(1+m_A)(1-m_B)\varepsilon = (1-m_A)(1+m_B)\varepsilon'$. The associated power law decay is consistent with the breaking of the continuous symmetry described above Eq. (2).

The possibility of an exact solution is hinted by the properties of the operator $R_n - Q_n$ in Eq. (1): for k=2, the operator satisfies two of the three requirements of a Temperley-Lieb algebra [9], while the third condition takes a generalized form, reducing to the standard one for $\varepsilon = \varepsilon'$.

The situation for $k \geq 3$ is more complex and interesting. The full phase space of 2^L microscopic configurations splits into a very large number $I(k,L)$ of invariant subspaces which are not connected to each other by the dynamics. $I(k,L)$ grows exponentially with L if $k \geq 3$, in contrast to $I(2,L) = L+1$. The exponential growth can be established as follows. Write $I(k,L) = I_1(k,L) + I^*(k,L)$, where $I_1(k,L)$ is the number of subspaces of size 1 (each corresponding to a completely jammed configuration) and $I^*(k,L)$ is the number of larger subspaces. $I_1(k,L)$ may be calculated using a recurrence relation, as each completely jammed configuration has no more than $k-1$ succesive parallel spins. With open boundary conditions, the result is $I_1(k,L) = 2F_k(L)$ where $F_k(L)$ are generalized Fibonacci numbers defined by $F_k(L) = \sum_{j=1}^{k-1} F_k(L-j)$ with $F_k(0) = 1$, $F_k(L) = 0$ for $-(k-2) \leq L < 0$. Asymptotically, $I_1(k,L) \sim \lambda^L$ where λ is the largest eigenvalue of $\lambda^k = 2\lambda^{k-1} - 1$.

Further, the number I^* of nontrivial invariant subspaces also grows exponentially with L. Evidence for this comes from studies of the form of H in the Ising (site-occupation) basis $|\{\sigma_l^z\}\rangle$, on finite rings with lengths in the range $3 \leq L \leq 18$. We find $I^* \sim \mu^L$ with $\mu > 1.4$ for $k=3$ and $\mu > 1.6$ for $k=4$. This exponential proliferation of subspaces with nontrivial evolution, indicating strongly broken ergodicity, is quite unusual in systems without quenched disorder. Each subspace Λ has a unique [7] steady state $|\Lambda,0\rangle$, which, in the symmetric case ($\varepsilon = \varepsilon'$), is an equal-weight linear combination of all configurations $|\{\sigma_l^z\}\rangle \in \Lambda$.

It is also possible to form steady states involving linear combinations of the form $|\psi\rangle = \sum_\Lambda c_\Lambda |\Lambda,0\rangle$. For instance, several exact steady states follow from rewriting H as

$$H = \sum_n R_n \left(1 - \prod \xi_l\right), \tag{4}$$

where $\xi_l \equiv \alpha\sigma_l^+ + (1/\alpha)\sigma_l^-$ with $\alpha = (\varepsilon/\varepsilon')^{1/k}$. Product eigenstates of ξ_l with eigenvalues $m_l = \pm 1$ such that $m_l = m_\alpha$ for l on sublattice α, with $\prod_{\alpha=1}^k m_\alpha = 1$, are steady states which involve all the states $|\Lambda,0\rangle$ in linear combinations. From these new steady states, many more can be generated by applying the rotations specified by (2) since those operations do not change H. All these states do not share the rotation invariance of the Hamiltonian. This broken symmetry requires the existence of Goldstone modes, which are responsible for the asymptotic slow kinetics of the deposition-evaporation system. Indeed, distorted versions of those rotations [rotations by θ_l of the form $A_\alpha \exp(iql)$ for $l \in \alpha$] generate the Goldstone modes and also provide their energies.

In the Ising basis, steady states $|\Lambda,0\rangle$ corresponding to different subspaces Λ differ from each other in several respects. The majority of subspaces have nonzero values of the conserved quantities $M_\alpha - M_\beta$, etc. implying broken translational invariance in the steady state, i.e., $\rho_l \equiv \langle\Lambda,0|\frac{1}{2}(1+\sigma_l^z)|\Lambda,0\rangle$ depends on site l.

Turning to the dynamics, it is useful to introduce the notion of local jamming—the inability to deposit or evaporate owing to the absence of k successive parallel spins. Steady state dynamics entails a succession of stochastic transitions between states $|\{\sigma_l^z\}\rangle$ in Λ. The mean rate of such transitions $J(\Lambda) = \langle\Lambda,0|\sum_n R_n|\Lambda,0\rangle/L$ gives a quantitative measure of the lack of jamming in that steady state. For nonevolving states, we have $J(\Lambda) = 0$ (maximal jamming). A study of finite systems shows that for $k \geq 3$ even the least jammed steady state (that reached from an initially empty lattice) has fairly low J ($\simeq 0.36\varepsilon$ for $k=3$, $\varepsilon = \varepsilon'$) indicating quite a large degree of jamming.

We studied dynamics in a jammed environment by writing and solving evolution equations for a localized deviation (e.g., a patch of $k+1$ parallel spins) in an otherwise completely jammed background. Unlike mixed states such as those described under Eq. (4), the completely jammed states do not break the continuous symmetry of H expressed in Eq. (2) so in their case no power law decay can be inferred from the Goldstone theorem. Nevertheless, the deposition-evaporation kinetics induces a random walk of descendants of the parallel-spin patch on the lattice. The precise stepping rule and the associated diffusion constant depend on the details of the jammed background. A power law decay $\propto (Dt)^{-\frac{1}{2}}$ of the spin autocorrelation function $C_n(t)$ follows.

When there is a finite low density of unjammed patches in a jammed background, there are collisions between patches (Fig. 2). A plausible hypothesis is that at long times the only effect of collisions is to modify the diffusion constant. This would imply a diffusive tail ($\sim t^{-\frac{1}{2}}$) in $C(t)$, even away from the single-walker limit. This hypothesis has been tested by studying the autocorrelation function $C(L,t)$ in finite systems of size L. On general grounds we expect $C(L,t)$ to conform with finite size scaling in the limit $t \to \infty$, $L \to \infty$, t/L^z constant,

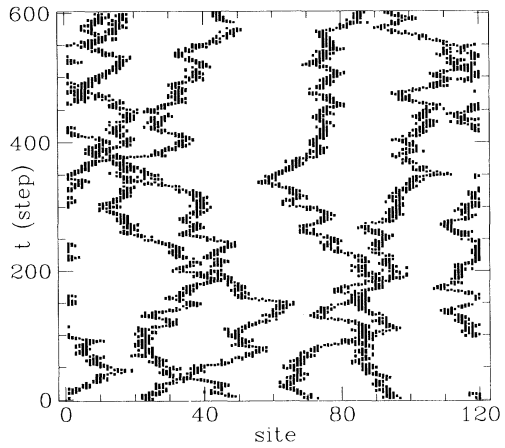

FIG. 2. A particular history of unjammed regions through a jammed background (here taken to be antiferromagnetic), showing characteristic random walk behavior; only updated spins are shown.

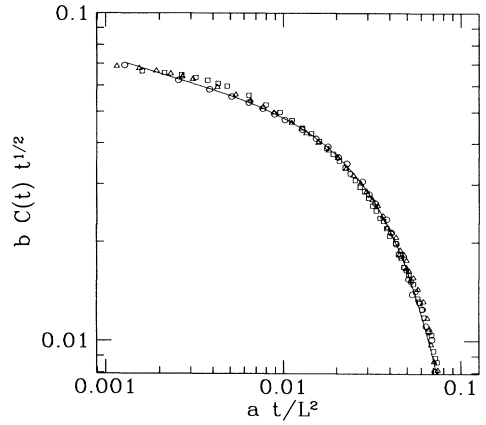

FIG. 3. Evidence for universality of k-mer kinetics from finite size scaling, for steady states reached from an initially empty lattice. Data (averaged over 10^6 histories) for k=2, L=28 (circles), k=3, L=54 (triangles), k=4, L=52 (squares) are shown; a and b are metric factors referred to in the text. The solid curve is the theoretical prediction for the scaling function.

i.e.,

$$bC(L,t) \simeq t^{-\theta} Y(at/L^z) , \tag{5}$$

where θ and z are critical exponents and Y is a universal scaling function. a and b are system-dependent (nonuniversal) metric factors. If the "diffusion hypothesis" is valid, (5) should hold irrespective of the value of k. Figure 3 shows the collapse of numerical data for k=2, 3, and 4 in the least jammed subspace, on setting $\theta = \frac{1}{2}$ and $z = 2$ as implied by the diffusion hypothesis. The solid curve is an analytical determination of the scaling function (possible because the problem is exactly solvable for k=2). Explicitly, we have $Y(y) = \frac{1}{4} y^{\frac{1}{2}} \sum_{n\neq 0} \exp\left(-4\pi n^2 y\right)$. The good agreement between k=2, 3, and 4 lends support to the diffusive picture, even in the subspace with the least jamming, where collisions are most frequent. Similar numerical studies reveal that while the diffusive picture continues to hold in other subspaces (including translationally noninvariant ones), it may fail in yet others, where $z < 2$ is suggested.

Generalizations of the deposition-evaporation models to include particle diffusion (already mentioned), k-mer diffusion, and nearest-neighbor cooperative effects are clearly of interest. Other interesting extensions to mixed k-mer, k'-mer cases and to higher dimensions are under consideration. For example, dimers with $\varepsilon = \varepsilon'$ on the square lattice share many of the properties detailed above for the case k=2, $\varepsilon = \varepsilon'$, $d = 1$, because sublattice mapping to the Heisenberg model is again possible. While the general k-mer problem in higher dimensions remains quite open, it will be shown elsewhere that the quantum spin analogy is very useful in such special cases as: linear k-mers on the square lattice, mixed k-mer k'-mer cases with k, k' both integer multiples of a common integer, or addition of particle diffusion or particle deposition or evaporation to the dimer case.

It is a pleasure to acknowledge fruitful discussions with Professor V. Privman. We also thank Professor J. W. Evans for sending us a copy of his review before publication. The support of the SERC under Grants No. GR/G02741 and No. GR/G02727 is acknowledged.

[a] On sabbatical leave from Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400005, India.

[1] For references to known results in this area see, e.g., M. Fowler, in *Nonlinearity in Condensed Matter*, edited by A.R. Bishop *et al.*, Springer Series in Solid State Sciences Vol. 69 (Springer, Berlin, 1987); I. Affleck, J. Phys. Condens. Matter **1**, 3047 (1989).

[2] P.J. Flory, J. Am. Chem. Soc. **61**, 1518 (1939); for recent reviews, see, e.g., M.C. Bartelt and V. Privman, Int. J. Mod. Phys. B **5**, 2883 (1991); and J.W. Evans (unpublished).

[3] R.M. Ziff, E. Gulari, and Y. Barshad, Phys. Rev. Lett. **56**, 2553 (1988); D. Ben-Avraham and J. Kohler, J. Stat. Phys. **65**, 839 (1991).

[4] J. Toner and G.Y. Onoda, Phys. Rev. Lett. **69**, 1481 (1992).

[5] A.H. Bretag, B.R. Davis, and D.I.B. Kerr, J. Membr. Biol. **16**, 363 (1974); A.H. Bretag, C.A. Hurst, and D.I.B. Kerr, J. Chem. Biol. **73**, 367 (1978); R. Dickman and R. Burschka, Phys. Lett. A **127**, 132 (1988).

[6] J.W. Evans and C.A. Hurst, Phys. Rev. A **40**, 3461 (1989).

[7] N.G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).

[8] R.B. Stinchcombe, M.D. Grynberg, and M. Barma (to be published).

[9] H.N.V. Temperley and E.H. Lieb, Proc. R. Soc. London A **322**, 251 (1971); R.J. Baxter, *Exactly Solved Models in Statistical Mechanics* (Academic, London, 1982).