Sticky spheres, entropy barriers, and nonequilibrium phase transitions

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A sticky spheres model to describe slow dynamics of a nonequilibrium system is proposed. The dynamical slowing down is due to the presence of entropy barriers. An exact steady state analysis of the representative mean field equations, in the case when the clusters are chosen with the same *a priori* probability, demonstrates a nonequilibrium phase transition from an exponential cluster size distribution to a power law.

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I. INTRODUCTION

When a macroscopic system in equilibrium at high temperature is quenched rapidly to low temperature, either or both of the following can happen. The system may get thermally arrested in a metastable (local energy minimum) state much faster than it could equilibrate at that temperature and hence its subsequent dynamical evolution becomes slow, for details, see Ref. [1]. On the other hand, the system may still have thermal freedom to sample a large number of equal or almost equal energy states, upon a temperature quench, so that its dynamical evolution again becomes slow, for example, see Ref. [2]. In other words, the system would remain trapped for a long time due to the presence of *energy* and/or *entropy* barriers. As a result, the relaxation of the system to its equilibrium could become anomalously slow. It is often history dependent, usually referred to as ''aging,'' and could become progressively slower with time. Glasses [3], obtained by the rapid quenching of liquids, provide simple examples of aging systems which evolve slowly forever towards their putative equilibrium states; granular systems whose density compaction is logarithmically slow in response to mechanical tapping [4] and reaction-diffusion systems [5], provide other recent examples. Quite often one finds that these systems develop a certain degree of spatial disorder as well. Experimental evidence for such a scenario has recently been reported in the literature [6]. An interesting problem in this context is to see whether simple *local* dynamical rules could be devised so as to capture the essential features of the nonequilibrium slow dynamics. In particular, it would be of interest to devise dynamical rules that could lead to slow logarithmic growth of length scales often found in several systems. To this end, we propose in this paper a sticky sphere model to describe the slow dynamics of a nonequilibrium system.

The model consists of hard spheres placed randomly on a regular lattice. The energy of the system is defined in such a way that nearest neighbor contacts between the spheres are energetically favored, hence the name ''sticky'' spheres. An appropriate length scale for this system is the mean cluster size. We present numerical evidence to show that this quantity grows logarithmically with time at zero temperature. However, for nonzero temperatures, it saturates asymptotically to a stationary value. The model and the simulation details are discussed in Sec. II. A general mean field formulation of this model is presented in Sec. III. An exact steady state analysis of this mean field model for the special case when the clusters are chosen with the same *a priori* probability, described in Sec. IV, shows a phase transition from an exponential to a power law cluster size distribution. A brief summary of the results is presented in Sec. V.

II. MODEL

Consider a regular one dimensional lattice of size $M+N$, consisting of N sites unoccupied and M sites occupied by hard spheres of size equal to the lattice spacing. Therefore the spheres on nearest neighbor sites touch each other. We assume periodic boundary conditions.

Let us define the ''energy'' of the system, $E(t)$, at time t as the negative of the total number of nearest neighbor contacts:

$$E(t) = -\sum_{k=1}^{M} (k-1)c_k(t), \tag{1}$$

where $c_k(t)$ is the total number of k-mers (i.e., clusters consisting of k spheres touching each other at time t). We assume that the number of spheres in the system is conserved: $\Sigma_{k=1}^{M} k\, c_k(t) = M$. The lowest energy state of the system corresponds to having a single M-mer with energy, $E_0 = -(M-1)$, and may henceforth be called the ''ground state'' of the system. On the other hand, the highest possible energy realizable for the system depends on the values of both M and N.

For given M and N, we can always have a configuration of spheres with a maximum of $(M-N)$ nearest neighbor contacts, with $M > N$. This implies that the maximum energy the system can have is given by, $E_{max}(M,N) = -(M-N)$. However, when the system consists of only monomers, which can be realized when $M \leqslant N$, the energy is zero. Thus we have

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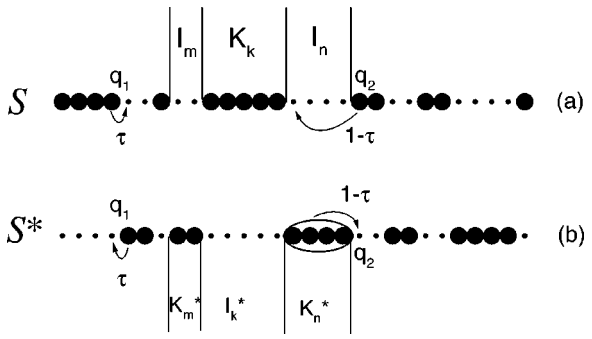

FIG. 1. (a) Sticky sphere model: the dynamical moves available for a chosen particle; (b) its dual representation: the corresponding dynamical moves. $\tau \equiv e^{-\beta}$.

$$E_0 = -(M-1); \quad E_{max}(M,N) = \begin{cases} -(M-N) & \text{for } M > N \\ 0 & \text{for } M \leqslant N. \end{cases} \tag{2}$$

From Eq. (1), it follows that the energy per particle, $\epsilon(t) = -1 + [C(t)/M]$, where $C(t) = \Sigma_{k=1}^{M} c_k(t)$, is the average number of clusters at time t. Since $M/C(t)$ is just the mean cluster size, $\Lambda(t)$, we have $\epsilon(t) = -1 + [1/\Lambda(t)]$, or equivalently, $\Lambda(t) = 1/[1+\epsilon(t)]$. Thus we have a sticky sphere system in which nearest neighbor contacts are energetically favored.

We start from an initial ($t=0$) configuration of the sticky spheres placed on a one dimensional lattice segment in such a way that the system is in the highest possible energy state for given M and N. At any instant of time t, we choose a k-mer with a pre-assigned probability, p_k. Usually we take p_k as k/M, implying thereby that we choose a sphere at random with the *a priori* probability, $1/M$. If we have chosen a monomer ($k=1$), then it can hop either to its left or to its right with equal probability. On the other hand, if we have chosen a k-mer with $k>1$, then we choose one of its edge spheres (or equivalently, edge particles) at random with equal probability. We call it the ''active'' particle. We note that there is at least one empty site available for the active particle to hop. Consider the situation where we have chosen the left most sphere of the k-mer ($k>1$) as the active particle. This particle can hop to the left. Let there be an l-mer ($l \geqslant 1$) located to the left of the active particle such that there are n empty sites in between them. If $n=1$, we simply move the particle into the available empty site because it does not cost energy. At the end of this move, we have an $(l+1)$-mer and a $(k-1)$-mer separated by one empty site. If $n>1$, then we have two possibilities for the particle to hop, as illustrated in Fig. 1(a), and described below.

Hopping to the nearest neighbor empty site. If we move the active particle to the nearest empty site, then we would be creating a monomer in the system. This process would therefore cost one unit of energy. Hence, in order to take care of this energy cost, we move it to the nearest empty site with probability $e^{-\beta}$, where β is the inverse of the temperature. At the end of this move, we will have a monomer located in between an l-mer and a $(k-1)$-mer.

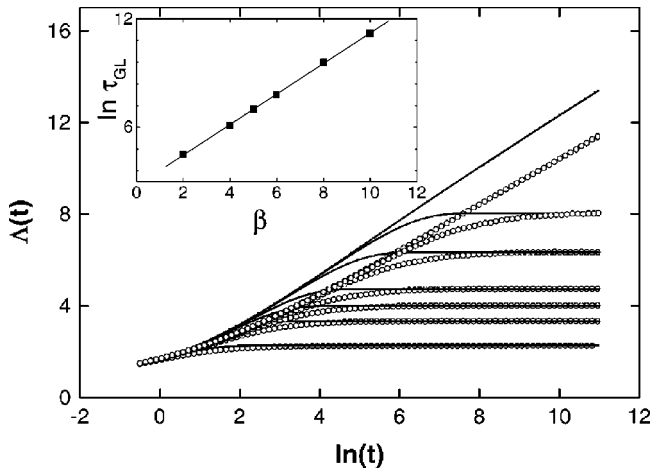

FIG. 2. Mean cluster size for $N=16\,384$. The time t is measured in units of $1/N$. Inverse of temperature $\beta = \infty$, 10, 8, 6, 5, 4, and 2, from top to bottom. Open circles represent simulation data obtained as 50 runs averages; continuous lines have been obtained from the Godrèche and Luck mean field formalism [4] of the Ritort model. Inset: Temperature dependence of τ_{GL}, the times beyond which simulation more or less agrees with GL.

Hopping to the farthest empty site. If the above move is not accepted, then we move the active particle to the farthest empty site so that it sticks to the right edge of the l-mer. The energy of the system (or equivalently, the number of nearest neighbor contacts in the system) does not change. At the end of this move, we will have an $(l+1)$-mer and a $(k-1)$-mer, with n empty sites in between them.

We have simulated the above process for the case $M=N$ so that the dynamics will cover the full range of energy ($\epsilon = E/M$) from 0 to -1. The *a priori* probability, p_k, for choosing a k-mer is taken to be proportional to k in the simulation. We have presented in Fig. 2 the mean cluster size $\Lambda(t)$ as a function of $\ln(t)$ obtained by averaging the data over 50 independent runs for a system of size $N=16\,384$ and temperatures $\beta = 2, 4, 5, 6, 8, 10$, and ∞. We observe that $\Lambda(t)$ saturates asymptotically for temperatures $T>0$, whereas it continues to grow logarithmically at $T=0$.

We note that the logarithmically slow dynamics at zero temperature is purely due to entropy barriers because monomer creation is not possible at this temperature; the system evolves only by the process of hopping to the farthest neighbor empty site, which does not cost energy. In this sense, our model belongs to the same class of mean field models as that of Ritort [2]. In fact, we could anticipate this on heuristic grounds.

The system will necessarily have to be in the configurational state consisting of a monomer and an $(N-1)$-mer before it might be able to reach the ground state by choosing the monomer with probability $1/N$. This is a rare event because the larger cluster will always lose a particle with more probability. Precisely the same situation prevails [7] in the Ritort model as well. Hence we have also shown in Fig. 2 the growth of $\Lambda(t)$ obtained from Godrèche-Luck (GL) mean field formalism [8] of the Ritort model as continuous lines. We observe that our simulation data agree more or less

with those of the GL values for asymptotic times $t > \tau_{GL}$, where we have schematically shown the temperature dependence of τ_{GL} in the inset of Fig. 2. Clearly, $\tau_{GL} \to \infty$ as $\beta \to \infty$, and the simulation data fall on a line parellel to but below the GL line. The sticky sphere system therefore admits of a mean field description that incorporates the GL formalism at appropriate limits.

III. MEAN FIELD FORMULATION OF A ONE DIMENSIONAL STICKY SPHERE SYSTEM

The hopping of a single particle to its nearest/farthest neighbor empty site can be incorporated easily in a mean field description by considering the dual representation obtained by replacing particles by holes and holes by particles. k-mers ($k \geqslant 1$) of the sticky sphere system S [Fig. 1(a)] correspond to empty intervals of length k in its dual representation S^* [Fig. 1(b)], and vice versa. The energy of the system is still given by Eq. (1) except that $c_k(t)$ now stands for the number of successive empty sites of length k in S^*.

Consider a k-mer, K_k, in S having the empty intervals I_m and I_n to its left and right, respectively [Fig. 1(a)]. This corresponds to the empty interval I_k^* between an m-mer, K_m^*, and an n-mer, K_n^*, in S^*. Let P be the right most particle of K_k. The hopping of P to its right nearest neighbor site, Q, in S corresponds to the dissociation of the left most particle of K_n^* in S^*. On the other hand, hopping of P to the farthest neighbor site, R in S corresponds to the cluster K_n^* moving as a whole to the left by one lattice unit in S^*. Thus the nearest/farthest neighbor hopping of a particle in S corresponds to (single particle) dissociation/movement of a cluster in S^*.

In general, these processes may occur with probabilities q_1 and q_2, respectively. For convenience, we may rescale the time so as to have these events (namely, single-particle dissociation/movement of a cluster) occur with the rates unity and $\omega = q_2/q_1$, respectively. Spatial correlation in the system may be ignored by treating the k-mers ($k \geqslant 1$) in S^* as point masses occupying single lattice sites only. This leads to a simplified mean field description of the system in terms of a distribution of masses on N lattice sites. We study the stochastic evolution of the system in the thermodynamic limit, M, $N \to \infty$ with the mass density, $\rho \equiv M/N$, remaining finite.

Let $f_k(t)$ be the probability that a site will have mass k at time t. By definition, $\Sigma_{k=0}^{\infty} f_k(t) = 1$ and $\Sigma_{k=0}^{\infty} k f_k(t) = \rho$. Let p_k be the *a priori* probability for choosing a k cluster and, if chosen, let d_k be the *a priori* probability for moving it by one lattice unit. The evolution equation for $f_k(t)$ can now be written as

$$\frac{df_{k\geqslant 2}(t)}{dt} = \pi(t) f_{k-1}(t) - [\pi(t) + \lambda_\beta(t) p_k] f_k(t) + \lambda_\beta(t) p_{k+1} f_{k+1}(t) - \omega \Big\{ [p_k d_k + \Delta(t)] f_k(t) - \sum_{n=1}^{k} p_n d_n f_n(t) f_{k-n}(t) \Big\}, \quad (3)$$

where

$$\pi(t) \equiv \sum_{n=1}^{\infty} p_n f_n(t); \quad \Delta(t) \equiv \sum_{n=1}^{\infty} p_n d_n f_n(t);$$

$$\lambda_\beta(t) \equiv (1 - e^{-\beta}) s(t) + e^{-\beta}; \quad s(t) \equiv \sum_{n=1}^{\infty} f_n(t). \quad (4)$$

This equation consists of two parts, one corresponding to the single particle dissociation and the other to the cluster moving by a lattice unit as a whole. Each part has both the gain and the loss terms.

In the case of single particle dissociation, there are two gain terms. The first one corresponds to the event of a dissociated particle sticking to a $(k-1)$ cluster. The second one corresponds to a particle dissociating from a $(k+1)$ cluster, taking care to account for the energy cost $e^{-\beta}$ involved in the event of its becoming a monomer. Similarly, the first of the loss terms corresponds to a dissociated particle sticking to a k cluster. The second one corresponds to a particle dissociating from a k cluster, taking care to account for the energy cost $e^{-\beta}$ in the event of its becoming a monomer. The probability of choosing a k cluster, $p_k (k \geqslant 1)$, has been introduced appropriately.

In the case of a cluster moving by one lattice unit as a whole, the gain term corresponds to an n cluster ($1 \leqslant n \leqslant k$) coming to stick to a $(k-n)$ cluster. The event of a k cluster moving out as well as that of a cluster coming in to stick to a k cluster constitutes the loss terms. The probability of moving a cluster, $p_n d_n (n \geqslant 1)$, has been introduced appropriately.

Similarly, the master equations satisfied by the fractions, $f_0(t)$ and $f_1(t)$, can be written as follows:

$$\frac{df_1(t)}{dt} = \mu_\beta(t) f_0(t) - [\pi(t) + p_1] f_1(t) + \lambda_\beta(t) p_2 f_2(t) - \omega \{ [p_1 d_1 + \Delta(t)] f_1(t) - p_1 d_1 f_1(t) f_0(t) \}, \quad (5)$$

$$\frac{df_0(t)}{dt} = -\mu_\beta(t) f_0(t) + p_1 f_1(t) + \omega s(t) \Delta(t), \quad (6)$$

where $\mu_\beta(t) \equiv p_1 (1 - e^{-\beta}) f_1(t) + \pi(t) e^{-\beta}$. In this model, the parameters ω and d's are all assumed to be temperature independent.

The mean field equations, obtained by ignoring the spatial extensions of k-mers ($k \geqslant 1$) in S^*, provide the simplest representation of the nearest/farthest neighbor single particle hopping of a sticky sphere system S. Yet, we cannot assume *a priori* that they describe the asymptotic dynamical behavior of S, because the probability p_k of choosing a k-mer actually stands for the probability of choosing the empty interval bounded on one side by the k-mer of interest. It is also important to note that the presence or absence of the aggregation term, $F_k \equiv \Sigma_{n=1}^{k} p_n d_n f_n f_{k-n}$, in Eq. (3) corresponds to the specific monomer dynamics implemented in S, viz., whether they jump to their farthest or to their nearest neighbor sites, respectively. However, in the case when the

clusters are chosen with equal *a priori* probability, empty intervals are also chosen with the same *a priori* probability (say, $p_k=1$); hence the mean field equations could provide an adequate description of *S*. Moreover, it turns out that an exact steady state analysis of these equations can be carried out in this case.

IV. STEADY STATE ANALYSIS

Here, we consider the case $p_j=d_j=1$, for which an exact steady state analysis can be carried out. It is clear from Eqs. (3)–(6) that the generating function, $Q_\beta(z,t)\equiv\Sigma_{k=1}^{\infty}z^k f_k(t)$, satisfies the following equation:

$$\frac{\partial Q_\beta(z,t)}{\partial t}=Q_\beta^2(z)-\left[a(z)+\frac{b}{z}\right]Q_\beta+c(z), \tag{7}$$

where

$$a(z)=2s+\frac{s}{\omega}+\frac{\lambda_\beta}{\omega}-\frac{sz}{\omega},$$

$$b(z)=-\frac{\lambda_\beta}{\omega},$$

$$c(z)=\lambda_\beta(z-1)\left[\frac{\mu_\beta(1-s)}{\omega}-s^2\right]+zs^2. \tag{8}$$

In order to study the steady state behavior of the system, we set $\partial Q_\beta(z,t)/\partial t=0$ and choose the root of the resulting quadratic equation so that $Q_\beta(z=0)=0$ is ensured:

$$2Q_\beta(z)=\left[a(z)+\frac{b}{z}\right]-\sqrt{\left[a(z)+\frac{b}{z}\right]^2-4c(z)}. \tag{9}$$

Simplifying the algebra, we can show that

$$\left[a(z)+\frac{b}{z}\right]^2-4c(z)=\left\{\frac{s(z-1)}{\omega z}\right\}^2(z-z_1)(z-z_2), \tag{10}$$

where the roots $z_{1,2}$ are given by

$$z_{1,2}=\left(\frac{\tau}{s}+1-\tau\right)[1+2\omega\mp2\sqrt{\omega^2+\omega}];\quad \tau\equiv e^{-\beta}. \tag{11}$$

Hence we have the generating function

$$Q_\beta(z)=\frac{2\omega s+s+\lambda_\beta}{2\omega}-\frac{\lambda_\beta}{2\omega z}-\frac{sz}{2\omega}+\frac{s(1-z)}{2\omega z}\sqrt{(z-z_1)(z-z_2)}. \tag{12}$$

The value of *s* is fixed by the conservation of particle density ρ:

$$\rho=\left\{\frac{\partial Q_\beta(z)}{\partial z}\right\}_{z=1}=\frac{1}{2\omega}[\lambda_\beta-s(1+\sqrt{(1-z_1)(1-z_2)})]. \tag{13}$$

For a given ω, it is clear that the value of z_1, being always less than z_2, should not be less than unity for ρ to be real. As ρ increases, the steady state value for the number of clusters, *s*, increases, thereby reducing the values of $z_{1,2}$. Hence we have the condition

$$s\leqslant\frac{\tau P_1(\omega)}{1-(1-\tau)P_1(\omega)};\quad P_1(\omega)\equiv1+2\omega-2\omega\sqrt{1+\frac{1}{\omega}}. \tag{14}$$

The equality sign defines the critical value s_c at which the root $z=1$, and hence the critical density

$$\rho_c=\frac{\tau\rho_c^0}{\tau+2\omega(1-\tau)\rho_c^0};\quad \rho_c^0\equiv\sqrt{1+\frac{1}{\omega}}-1. \tag{15}$$

The number of clusters will not increase beyond s_c for $\rho>\rho_c$. It is of interest to consider the question of how this inequality influences the cluster size distribution. To this end, we consider the following contour integral:

$$f_k=\oint\frac{Q_\beta(z)}{z^{k+1}}dz. \tag{16}$$

The contour is chosen suitably so that only the portion of the contour above and below the branch cut $z=z_1$ contributes to the integral. The number of *k*-mers, f_k, has the asymptotic exponential form, $(1/z_1)^k$ for $\rho<\rho_c$ whereas it has a power law form, $k^{-5/2}$ for $\rho=\rho_c$; as the density is increased beyond ρ_c, in addition to the power law decay, the distribution develops a delta function peak corresponding to an ''infinite'' aggregate.

However, at zero temperature, $z_1<1$ for all nonzero values of ω; therefore the above steady state analysis breaks down. In fact, the condition expressed by Eq. (14) can be rewritten as

$$\tau\geqslant\tau_c;\quad \tau_c\equiv\frac{s[1-P_1(\omega)]}{(1-s)P_1(\omega)}. \tag{17}$$

For a given ω, the value of τ_c increases as we increase the particle density, until it becomes equal to the given temperature; beyond this, the steady state analysis breaks down. In other words, the steady state phase transition from the ''exponential'' regime to the ''aggregating'' regime is observable only in a limited range of temperature decided by ω and ρ. The infinite temperature version of a related model has been discussed by Majumdar, Krishnamurthy, and Barma [9].

V. SUMMARY

In this paper, we have presented a generic sticky sphere model for describing the nonequilibrium behavior of a system fast quenched to a low temperature. The evolution of the

system is based on a *local* dynamical rule—the nearest/farthest neighbor hopping of a randomly chosen particle. The mean cluster size, defining a length scale for the system, asymptotically saturates to a stationary value at nonzero temperatures, whereas it grows logarithmically with time at zero temperature. We have presented a general mean field formulation of this model and solved it exactly for the case when the clusters are chosen and moved with the same *a priori* probability. We have shown that the steady state cluster size distribution undergoes a phase transition (in appropriate temperature range) from an exponential form to a power law with an additional delta function peak corresponding to an infinite cluster.

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