Nonequilibrium Phase Transitions in Models of Aggregation, Adsorption, and Dissociation

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We study nonequilibrium phase transitions in a mass-aggregation model which allows for diffusion, aggregation on contact, dissociation, adsorption, and desorption of unit masses. We analyze two limits explicitly. In the first case mass is locally conserved, whereas in the second case local conservation is violated. In both cases the system undergoes a dynamical phase transition in all dimensions. In the first case, the steady state mass distribution decays exponentially for large mass in one phase, and develops an infinite aggregate in addition to a power-law mass decay in the other phase. In the second case, the transition is similar except that the infinite aggregate is missing. [S0031-9007(98)07462-6]

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The steady state of a system in thermal equilibrium is described by the Gibbs distribution. Phase transitions which occur in such equilibrium systems as one changes the external fields such as temperature or magnetic field are by now well understood. On the other hand, there is a wide variety of inherently *nonequilibrium* systems in nature whose steady states are not described by the Gibbs distribution, but are determined by the underlying microscopic dynamical processes and are often hard to determine. Examples include systems exhibiting self-organized criticality [1], several reaction-diffusion systems [2], fluctuating interfaces [3], and many others. As one changes the rates of the underlying dynamical processes, the steady states of such systems may undergo nonequilibrium phase transitions. As compared to their equilibrium counterparts, these nonequilibrium steady states and the transitions between them are much less understood due to the lack of a general framework. It is therefore important and necessary to study simple models amenable to analysis in order to understand the mechansims of such phase transitions.

Here we study the nonequilibrium phase transitions in an important class of systems which involve microscopic processes of diffusion and aggregation, dissociation, adsorption and desorption of masses. These processes are ubiquitous in nature, and arise in a variety of physical settings, for example, in the formation of colloidal suspensions [4] and polymer gels [5], on the one hand, and aerosols and clouds [6], on the other. They also enter in an important way in surface growth phenomena involving island formation [7]. In this Letter, we introduce a simple lattice model incorporating these microscopic processes and study the nonequilibrium steady states and the transitions between them both analytically within mean-field theory and numerically in one dimension.

Our lattice model, which evolves in continuous time, is defined as follows. For simplicity we define the model on a one-dimensional lattice with periodic boundary conditions although generalizations to higher dimensions are quite straightforward. Beginning with a state in which the masses are placed randomly, a site is chosen at random. Then one of the following events can occur.

(1) Adsorption: With rate q, a unit mass is adsorbed at site i; thus $m_i \to m_i + 1$.

(2) Desorption: With rate p, a unit mass desorbs from site i; thus $m_i \to m_i - 1$ provided $m_i \geq 1$.

(3) Chipping (single-particle dissociation): With rate w, a bit of the mass at the site "chips" off, i.e., provided $m_i \geq 1$, a single particle leaves site i and moves with equal probability to one of the neighboring sites $i - 1$ or $i + 1$; thus $m_i \to m_i - 1$ and $m_{i\pm1} \to m_{i\pm1} + 1$.

(4) Diffusion and aggregation: With rate 1, the mass m_i at site i moves either to site $i - 1$ or to site $i + 1$. If it moves to a site which already has some particles, then the total mass just adds up; thus $m_i \to 0$ and $m_{i\pm1} \to m_{i\pm1} + m_i$.

Note that we have assumed that both desorption and diffusion rates are independent of the mass. In a more realistic situation these rates would depend upon the mass. However, our aim here is not to study this model in full generality, but rather to identify the mechanism of a dynamical phase transition in the simplest possible scenario involving these microscopic processes. Indeed, we show below that even within this simplest scenario, novel dynamical phase transitions occur which are nontrivial yet amenable to analysis.

Though the model can be studied in the full parameter space of all four basic processes, for simplicity we restrict ourselves here to the following two limiting cases: (i) $p = 0$, $q = 0$, i.e., only chipping, diffusion, and aggregation moves are allowed. In this limit, mass is locally conserved by the moves, and we call this model the conserved-mass aggregation model (CMAM). (ii) $w = 0$, i.e., all moves except for chipping are allowed. In this case, adsorption and desorption lead to violation of local mass conservation. We call this the in-out model. In this Letter, we analyze the CMAM model in some detail and only outline the main results for the in-out model.

Let us summarize our main results as follows: (i) In the CMAM, single particles are allowed to chip off from massive conglomerates. This move corresponds to the physical process of single functional units breaking off from larger clusters in the polymerization problem. It leads to a replenishment of the lower end of the mass spectrum, and competes with the tendency of the coalescence process to produce more massive aggregates. The result of this competition is that two types of steady states are possible, and there is a dynamical phase transition between the two. In one state, the steady state mass distribution $P(m)$ decays exponentially, while the other is more striking and interesting: $P(m)$ decays as a power law for large m but in addition develops a delta function peak at $m = \infty$. Physically this means that an infinite aggregate forms that subsumes a finite fraction of the total mass, and coexists with smaller finite clusters whose mass distribution has a power-law tail. In the language of sol-gel transitions, the infinite aggregate is like the gel while the smaller clusters form the sol. However, as opposed to the models of irreversible gelation where the sol disappears in the steady state, in our model the sol coexists with the gel even in the steady state. Interestingly, the mechanism of formation of the infinite aggregate in the steady state resembles Bose-Einstein condensation (BEC), though the condensate (the infinite aggregate here) forms in real space rather than momentum space as in conventional BEC. (ii) In the in-out model too we find a phase transition in the steady state as the adsorption (q) and desorption (p) rates are varied. In one phase (low values of q) $P(m)$ decays exponentially, whereas in the other phase (high q) it has a power-law tail. This power-law phase is similar to that of the Takayasu model [8] of particle injection and aggregation.

We first analyze the CMAM within the mean-field approximation, ignoring correlations in the occupancy of adjacent sites. Then we can directly write down equations for $P(m,t)$, the probability that any site has a mass m at time t:

$$\begin{aligned}\frac{dP(m,t)}{dt} &= -(1+w)[1+s(t)]P(m,t) \\ &\quad + wP(m+1,t) + ws(t)P(m-1,t) \\ &\quad + P*P; \qquad m \geq 1\,, \end{aligned} \tag{1}$$

$$\frac{dP(0,t)}{dt} = -(1+w)s(t)P(0,t) + wP(1,t) + s(t)\,. \tag{2}$$

Here $s(t) \equiv 1 - P(0,t)$ is the probability that a site is occupied by a mass, and $P*P = \sum_{m'=1}^{m} P(m',t)P(m-m',t)$ is a convolution term that describes the coalescence of two masses.

The above equations enumerate all possible ways in which the mass at a site might change. The first term in Eq. (1) is the "loss" term that accounts for the probability that a mass m might move as a whole or chip off to either of the neighboring sites, or a mass from the neighboring site might move or chip off to the site in consideration. The probability of occupation of the neighboring site, $s(t) = \sum_{m=1} P(m,t)$, multiplies $P(m,t)$ within the mean-field approximation where one neglects the spatial correlations in the occupation probabilities of neighboring sites. The remaining three terms in Eq. (1) are the "gain" terms enumerating the number of ways that a site with mass $m' \neq m$ can gain the deficit mass $m - m'$. The second equation Eq. (2) is a similar enumeration of the possibilities for loss and gain of empty sites. Evidently, the mean-field equations conserve the total mass.

To solve the equations, we compute the generating function, $Q(z,t) = \sum_{m=1}^{\infty} P(m,t)z^m$ from Eq. (1) and set $\partial Q/\partial t = 0$ in the steady state. We also need to use Eq. (2) to write $P(1,t)$ in terms of $s(t)$. This gives us a quadratic equation for Q in the steady state. Choosing the root that corresponds to $Q(z=0)=0$, we find

$$\begin{aligned} Q(z) &= \frac{w+2s+ws}{2} - \frac{w}{2z} - \frac{wsz}{2} \\ &\quad + ws\frac{(1-z)}{2z}\sqrt{(z-z_1)(z-z_2)}\,, \end{aligned} \tag{3}$$

where $z_{1,2} = (w + 2 \mp 2\sqrt{w+1})/ws$. The value of the occupation probability s is fixed by mass conservation which implies that $\sum mP(m) = M/L \equiv \rho$. Putting $\partial_z Q(z=1) = \rho$, the resulting relation between ρ and s is

$$2\rho = w(1-s) - ws\sqrt{(z_1-1)(z_2-1)}\,. \tag{4}$$

The steady state probability distribution $P(m)$ is the coefficient of z^m in $Q(z)$ and can be obtained from $Q(z)$ in Eq. (3) by evaluating the integral

$$P(m) = \frac{1}{2\pi i}\int_{C_0} \frac{Q(z)}{z^{m+1}}\,dz \tag{5}$$

over the contour C_0 encircling the origin. The singularities of the integrand govern the asymptotic behavior of $P(m)$ for large m. Clearly the integrand has branch cuts at $z = z_{1,2}$. For fixed w, if one increases the density ρ, the occupation probability s also increases as evident from Eq. (4). As a result, both the roots $z_{1,2}$ start decreasing. As long as the lower root z_1 is greater than 1, Eq. (4) is well defined and the analysis of the contour integration around the branch cut $z = z_1$ yields for large m,

$$P(m) \sim e^{-m/m^*}/m^{3/2}, \tag{6}$$

where the characteristic mass, $m^* = 1/\ln(z_1)$ and diverges as $\sim(s_c - s)^{-1}$ as s approaches $s_c = (w + 2 - 2\sqrt{w+1})/w$. s_c is the critical value of s at which $z_1 = 1$. This exponentially decaying mass distribution is the signature of the "disordered" phase which occurs for $s < s_c$ or equivalently from Eq. (4) for $\rho < \rho_c = \sqrt{w+1} - 1$.

When $\rho = \rho_c$, we have $z_1 = 1$, and analysis of the contour around $z = z_1 = 1$ yields a power-law decay of $P(m)$,

$$P(m) \sim m^{-5/2}. \tag{7}$$

As ρ is increased further beyond ρ_c, s cannot increase any more because if it does so, the root z_1 would be less than 1 (while the other root z_2 is still bigger than 1) and Eq. (4) would be undefined. The only possibility is that s sticks to its critical value s_c or equivalently the lower root z_1 sticks to 1. Physically this implies that adding more particles does not change the occupation probability of sites. This can happen only if all the additional particles (as ρ is increased) aggregate on a vanishing fraction of sites, thus not contributing to the occupation of the others. Hence in this "infinite-aggregate" phase $P(m)$ has an infinite-mass aggregate, in addition to the power-law decay $m^{-5/2}$. Concomitantly Eq. (4) ceases to hold, and the relation now becomes

$$\rho = \frac{w}{2}(1 - s_c) + \rho_\infty, \tag{8}$$

where ρ_∞ is the fraction of the mass in the infinite aggregate. The mechanism of formation of the aggregate is reminiscent of Bose-Einstein condensation. In that case, for temperatures in which a macroscopic condensate exists, particles added to the system do not contribute to the occupation of the excited states; they only add to the condensate, as they do to the infinite aggregate here.

Thus the mean-field phase diagram (see inset of Fig. 1) of the system consists of two phases, "Exponential" and "Aggregate," which are separated by the phase boundary, $\rho_c = \sqrt{w + 1} - 1$. While this phase diagram remains qualitatively the same even in 1D, the exponents characterizing the power laws are different from their mean-field values (see Fig. 1).

We have studied this model using Monte Carlo simulations on a one-dimensional lattice. Although we present

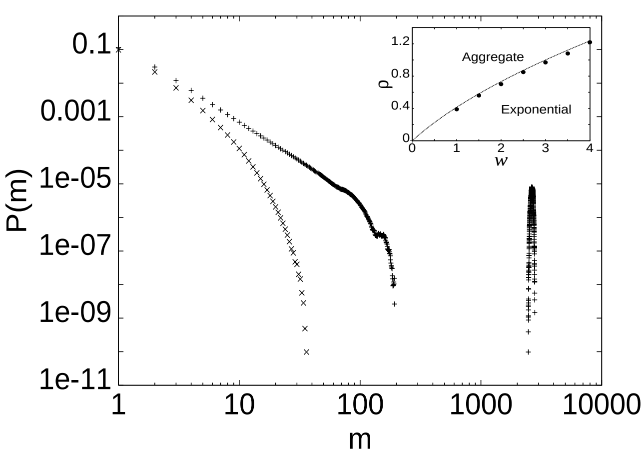

FIG. 1. Log-log plot of $P(m)$ vs m for the CMAM, for $\rho <, =, > \rho_c$ on a lattice with $L = 1000$. Inset: Phase diagram. The solid line and the points indicate the phase boundary within mean-field theory and 1D simulation, respectively.

results here for a relatively small size lattice, $L = 1024$, we have checked our results for larger sizes as well. We confirmed that all the qualitative predictions of the mean-field theory remain true, by calculating $P(m)$ numerically in the steady state. Figure 1 displays two numerically obtained plots of $P(m)$. The existence of both the "Exponential" (denoted by $\times$) for $\rho < \rho_c$ and the "Aggregate" phase (denoted by $+$) for $\rho > \rho_c$ is confirmed. In particular, the second curve shows clear evidence of a power-law behavior of the distribution, which is cut off by finite-size effects, and for an "infinite" aggregate beyond. We confirmed that the mass M_{agg} in this aggregate grows linearly with the size, and that the spread δM_{agg} grows sublinearly, implying that the ratio $\delta M_{\mathrm{agg}}/M_{\mathrm{agg}}$ approaches zero in the thermodynamic limit. The exponent τ_{CMAM} which characterizes the finite-mass fragment power-law decay for $\rho > \rho_c$ is numerically found to be 2.33 ± 0.02 and remains the same at the critical point $\rho = \rho_c$.

We note that in conserved-aggregation models studied earlier within mean-field theory [9,10], the steady state mass distribution also changed from an exponential distribution to a power law as the density was increased beyond a critical value. However, the existence of the striking infinite aggregate in the steady state for $\rho > \rho_c$ was not identified earlier.

We next study the steady state phase diagram of the in-out model in the q-p plane. In this model, mass is not locally conserved. The mass per site $M(t)$ evidently obeys the exact equation

$$\frac{dM}{dt} = q - ps(t), \tag{9}$$

where $s(t)$ is the fraction of sites occupied by a mass $m_i \geq 1$. In the steady state, let the mean value of $s(t)$ be s. If q/p is low, s adjusts to make $q - ps$ vanish, and the mean mass reaches a time-independent value M. This defines the finite-mass phase. As we will see below, as q/p increases beyond a critical value, s never catches up with q/p and reaches a steady state value which is less than q/p; in this phase, M increases linearly in time while $P(m,t) \sim m^{-\tau_T} f(mt^{-x})$ which in the long time limit converges to a time-independent form, decaying as a power law with exponent τ_T, even though the moments of this distribution diverge as time increases to infinity. We call this the growing-mass or the Takayasu phase. In fact, for $p = 0$ the in-out model reduces exactly to the Takayasu model (TM) of injection and aggregation of masses [8] which has found widespread applications ranging from river models [11] to granular systems [12]. Indeed, what we find here is that the growing mass phase of the TM at $p = 0$ persists up to a nonzero critical value $p_c(q)$ for a given q, while for $p > p_c(q)$ the mass stops growing and $P(m)$ decays exponentially for large m in the steady state.

The mean-field analysis of the in-out model is similar to that of the CMAM model though a little bit trickier.

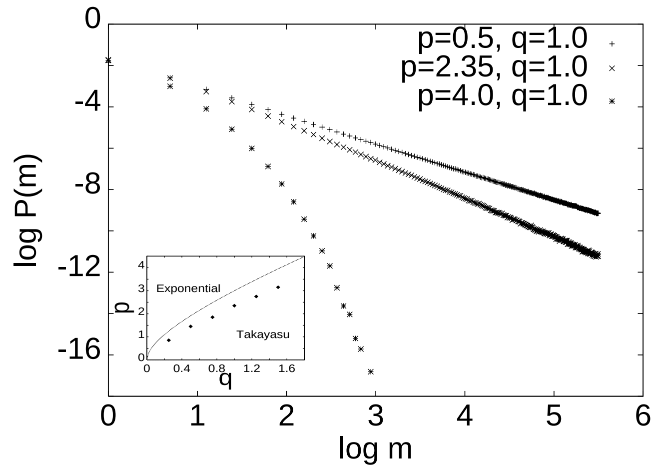

FIG. 2. Log-log plot of $P(m)$ vs m for the in-out model, for $p <, =, > p_c$, corresponding to the "Exponential," critical, and "Takayasu" phases. Inset: Phase diagram. The solid line and the points indicate the phase boundary within mean-field theory and 1D simulation, respectively.

We defer the details for a future publication [13] and only outline the results here. We find that the critical line $p_c(q) = q + 2\sqrt{q}$ separates two phases in the q-p plane. For $p > p_c$, $P(m) \sim m^{-3/2} \exp(-m/m^*)$ for large m. For $p = p_c$, $P(m) \sim m^{-5/2}$, and for $p < p_c$, $P(m) \sim m^{-3/2}$ for large m. For a fixed q, the steady state occupation density $s(p, q)$ develops an interesting cusp as p crosses $p_c(q)$. For example, at $q = 1$, where $p_c = 3$, $s(p) = 1/p$ for $p > 3$ as follows simply from Eq. (9), but for $p < 3$, the determination of $s(p)$ is nontrivial [13] and is given by the positive root of the cubic equation, $16ps^3 + (8p^2 + 4p - 25)s^2 + (p^3 - 11p^2 - 43p - 25)s - p^3 + 2p^2 + 17p + 25 = 0$.

The qualitative predictions of mean-field theory—the existence of a power-law (Takayasu) phase [$P(m) \sim m^{-\tau_T}$] and a phase with exponential mass distribution, with a different critical behavior at the transition [$P(m) \sim m^{-\tau_c}$]—are found to hold in 1D as well. The Takayasu exponent τ_T is known exactly to be $4/3$ in 1D and $3/2$ within mean-field theory [8]. Figure 2 shows the results of numerical simulations in 1D for the phase diagram and the decay of the mass distribution in the two phases and at the transition point. The values obtained, $\tau_T = 4/3$ and $\tau_c \simeq 1.833$, are quite different from their mean-field values, $\tau_T = 3/2$ and $\tau_c = 5/2$, reflecting the effects of correlations between masses at different sites.

We may reinterpret the configuration of masses in the in-out model as an interface profile on regarding m_i as a local height variable. While the model may have some unphysical features in the context of an interface due to the columns of masses moving as a whole, the analogy helps, however, to understand physically the nature of the transition in the in-out model. In the interface language this corresponds to a wetting transition; the key factor responsible for the occurrence of the smooth phase is a substrate, implicit in the constraint $m_i \geq 0$ in the in-out model. The wet phase is identified with a growing mass phase, which has a rough profile, with exact roughness exponent $\chi_T = 5/2$ [13] in 1D. Since $\chi_T > 1$, the interface in the wet phase is not self-affine. Recently a nonequilibrium wetting transition was also observed in an interface model [14] where the interface in the wet phase is self-affine due to surface tension effects which are absent in our model. Interestingly, however, in our model the substrate is able to induce a self-affine interface at the critical point with roughness exponent $\chi = 1/3$ within mean-field theory and $\chi \approx 0.7$ in 1D [13], despite the anomalously large roughness of the wet phase.

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[1] P. Bak, C. Tang, and K. Wiesenfeld, Phys. Rev. Lett. **59**, 381 (1987).
[2] R. M. Ziff, E. Gulari, and Y. Barshad, Phys. Rev. Lett. **56**, 2553 (1986); G. Grinstein, Z.-W. Lai, and D. A. Browne, Phys. Rev. A **40**, 4820 (1989).
[3] M. Kardar, G. Parisi, and Y.-C. Zhang, Phys. Rev. Lett. **56**, 889 (1986).
[4] W. H. White, J. Colloid Interface Sci. **87**, 204 (1982).
[5] R. M. Ziff, J. Stat. Phys. **23**, 241 (1980).
[6] S. K. Friedlander, *Smoke, Dust and Haze* (Wiley Interscience, New York, 1977).
[7] B. Lewis and J. C. Anderson, *Nucleation and Growth of Thin Films* (Academic, New York, 1978).
[8] H. Takayasu, Phys. Rev. Lett. **63**, 2563 (1989); H. Takayasu, I. Nishikawa, and H. Tasaki, Phys. Rev. A **37**, 3110 (1988); M. Takayasu and H. Takayasu, in *Nonequilibrium Statistical Mechanics in One Dimension,* edited by V. Privman (Cambridge University Press, Cambridge, 1997).
[9] R. D. Vigil, R. M. Ziff, and B. Lu, Phys. Rev. B **38**, 942 (1988).
[10] P. L. Krapivsky and S. Redner, Phys. Rev. E **54**, 3553 (1996).
[11] A. E. Scheidegger, Int. Assoc. Sci. Hydrol. Bull. **12**, 15 (1967).
[12] C.-h. Liu *et al.,* Science **269**, 513 (1995); S. N. Coppersmith *et al.,* Phys. Rev. E **53**, 4673 (1996).
[13] S. Krishnamurthy, S. N. Majumdar, and M. Barma (to be published).
[14] H. Hinrichsen, R. Livi, D. Mukamel, and A. Politi, Phys. Rev. Lett. **79**, 2710 (1997).