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LETTER TO THE EDITOR

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Subinay Dasgupta

Department of Physics, University of Calcutta, 92 APC Road, Calcutta 700 009, India

E-mail: `subinay@cubmb.ernet.in`

Abstract.   We present here a classical kinetic model that incorporates the process of aggregation and dissociation. The model is analysed by an accurate numerical procedure and it is found that the steady-state mass distribution has a peak at a mass numerically equal to the density. We also find that with increasing number of updates (t) a system of size N approaches the steady state as $\alpha t^{-\beta} \exp(-\gamma' t/N^3)$. Two close variants of the model are also analysed and compared.

The steady-state mass distribution for kinetic models that represent in some way the process of aggregation and dissociation has always been a matter of interest. While the study of the generalized Smoluchowski equation

$$\frac{\mathrm{d}c_k}{\mathrm{d}t} = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_j \sum_{j=1}^{\infty} K_{kj} c_j \tag{1}$$

and its many variants bears a long history [1–5], other models [6–8] that incorporate the process of aggregation, catalysis, etc, have also been considered. (Here, c_i is the concentration of the i-type polymers and K_{ij} is the collision kernel.) In most of these studies a power-law or exponential decay is observed† for high mass. Majumdar *et al* [3], in one of their models, have also found a peak at a high mass (after the tail of algebraic decay). Recently, it has been shown [9]‡ that one finds a peak in the mass distribution for the ground state of a quantum mechanical Hamiltonian, that describes hopping of bosons to nearest neighbouring sites. A mass distribution that is non-monotonic and has a peak has also been known to experimentalists for a long time, in connection with (e.g. [10]) the distribution of Au clusters on NaCl and Ag clusters on C.

In this Letter, we propose a classical kinetic model that incorporates the process of aggregation and dissociation and shows a mass distribution that has a peak at a mass numerically equal to the density and decays exponentially at a high mass. For density < 1, there is no peak and the distribution decays monotonically. We shall also study how the system approaches steady state as a function of time and analyse some close variants of this model.

The system under consideration is a linear lattice (of, say, N sites), identical particles are distributed over the lattice sites, and any site may contain any number of particles or none of them.

† The author of [5] does not mention this, but for his model I, the cluster size ν_k decays with k exponentially, while for his models II and III, ν_k decays first algebraically and then exponentially.
‡ The experimental plots in [9] correspond to $m^{2/3} P(m)$ vs $m^{1/3}$ in our notation. We have checked that figure 1 retains its nature when plotted in this way.

The rule of updating is as follows:

$\mathcal{C}$: Choose a site randomly, remove $2f$ fraction of its population and distribute it equally among its two nearest neighbours.

It is clear that f is the only parameter in this model and that the total number of particles M, and hence the density $\rho = M/N$, is conserved. The mass distribution function $P(m)$, $(m = 0, 1, 2, \ldots, M)$ is defined as the probability of getting exactly m particles at any site. Here the number of particles to be removed from a site itself depends on the number of particles at that site. This feature was also present in many models studied earlier [1–5].

We mention here that our model has some similarity with the class of models that involve stochastic transaction of money in economic systems [11].

Let us first write down the steady-state equation for our model under the approximation that the neighbouring masses are not correlated. The number of sites having mass m is reduced when such sites themselves are updated, or when non-vacant nearest neighbours of such sites are updated. This leads to a contribution $-[2 - P(0)]P(m)$ to $\mathrm{d}P(m)/\mathrm{d}t$, remembering that the probability of having a non-vacant site is $[1 - P(0)]$. Mass m at a site originates when a site having mass $m/(1 - 2f)$ is updated, so that a $2f$ fraction of the mass goes off, leaving the residual amount m. Mass m also originates when a site having mass m' $(m' = 0, 1, \ldots, m-1)$ has a neighbour with mass $(m - m')/f$ and that neighbour is updated. This leads to the steady-state equation

$$\frac{\mathrm{d}P(m)}{\mathrm{d}t} = -[2 - P(0)]P(m) + P\left(\frac{m}{1-2f}\right) + \sum_{m'=0}^{m-1} P(m')\, P\left(\frac{m-m'}{f}\right) = 0.$$

A complication arises if mass m is allowed to have integral values only $(0, 1, 2, \ldots)$, since $m/(1-2f)$ and $(m-m')/f$ may then have non-integral values and integer parts of these quantities have to be taken. To avoid such complication, one may allow m to have continuous values from 0 to M. (Incidentally, the summation in the last equation will then be replaced by integration.)

This model has two important features.

(i) The mean field equation is too complicated to tackle analytically or numerically, even when mass is taken as a continuous variable.

(ii) Computer simulation is faster as it takes fewer iterations to attain steady state. For example, the model of Majumdar *et al* [3] needs at least 10^8 iterations to attain steady state and 10^6 iteartions is misleading and insufficient (for $N = 1000$, $\rho = 10$), whereas for the present model 10^6 iterations (for $N = 1000$, $\rho = 10$) is sufficient.

Another crucial aspect of this model is that an accurate numerical calculation can be made for lattices of reasonable size. To do this, let us describe a particular configuration by the column vector $|\phi\rangle \equiv (m_1, m_2, \ldots, m_N)$ where m_i is the number of particles at the site i. Updating at the rth site is equivalent to operating a matrix $Q(r)$ on $|\phi\rangle$ where $Q(r)$ is an $N \times N$ unit matrix except for the following elements: $Q_{r,r}(r) = 1 - 2f$, $Q_{r\pm 1,r}(r) = f$. Successive updates correspond to operating successively $Q(r)$ on $|\phi\rangle$ with randomly chosen values of r. Thus t successive updates result in the state $T_t|\phi\rangle$ where T_t is the matrix given by

$$T_t = Q(r(t))\, Q(r(t-1))\, \ldots\, Q(r(1)). \tag{2}$$

Here $r(i)$ is the site selected in the ith update. To ensure the attainment of a steady state, one should verify that $T_t|\phi\rangle$ is independent of the random number generator and of $|\phi\rangle$. While the former criterion has to be checked by actually repeating the computation over several seeds of

the random number generator, we prove below that, in order to check the latter criterion, it is necessary and sufficient to check that the matrix T_t of equation (2) takes the form

$$
\begin{pmatrix}
x_1 & x_1 & x_1 & \cdots \\
x_2 & x_2 & x_2 & \cdots \\
\cdots & & & \\
x_N & x_N & x_N & \cdots
\end{pmatrix}.
\tag{3}
$$

Here the quantities x_i are random positive fractions with a distribution that is determined by our rule of update.

To prove the sufficiency of the condition, we note that this matrix operating on $|\phi\rangle$ gives $(Mx_1, Mx_2, \ldots, Mx_N)$, which is independent of the initial state $|\phi\rangle$. On the other hand, in order that $T_t|\phi\rangle$ becomes independent of $|\phi\rangle$, it is necessary that the following equality holds :

$$
T_t|1\rangle = T_t|2\rangle = \cdots = T_t|N\rangle
\tag{4}
$$

where $|r\rangle$ for $r = 1, 2, \ldots, N$ is the configuration when all the M particles are sitting at site r (i.e. $|1\rangle \equiv (M, 0, 0, \ldots)$, $|2\rangle \equiv (0, M, 0, \ldots)$, and so on). Now, any matrix operating on $|r\rangle$ gives the rth column of that matrix, so that equation (4) merely necessitates that all the columns of the matrix T_t should be identical, and this is precisely what is expressed in equation (3). To sum up, the algorithm will now be to calculate the matrix product (2) for so large a value of t that the product takes the form (3) and the average over the starting configuration is not needed separately. The structure of the matrix $Q(r)$ implies that multiplication of any matrix by $Q(r)$ does not alter the sum of elements in any column of that matrix, so that the constraint $\sum_i x_i = 1$ must hold good. After getting the mass present at every site in the steady state, viz. $(Mx_1, Mx_2, \ldots, Mx_N)$, one readily obtains the mass distribution function $P(m)$, which is obviously nothing but the frequency distribution of the quantities x_i.

While a direct computer simulation of the present model is not difficult, it would be more accurate to follow the matrix method. For $N = 200$, $t = 5 \times 10^7$ was sufficient for attaining a steady state and the result is an asymmetric Gaussian-type mass distribution (figure 1). This distribution function has the following features.

  (i) The peak occurs at a mass value which is numerically equal to the density.
 (ii) The region $m < \rho$ is closely algebraic but the high-m region is nearly exponential.
(iii) The whole distribution is highly insensitive to the values of f and N for a given ρ.

We shall now investigate, how the system approaches steady state. The degree of approach may be measured by evaluating how far has the product (2) approached the structure (3). A good measure of this may be defined as

$$
d = \frac{1}{N}\sum_i d_i \qquad d_i = \frac{1}{N}\sum_j (T_t(i, j))^2 - \left(\frac{1}{N}\sum_j T_t(i, j)\right)^2.
$$

d_i is really the standard deviation of the elements of T_t in the ith row, and d is this quantity averaged over all the rows. d can also be interpreted differently. Suppose one performs t iterations starting first from the configuration $|1\rangle$, then from $|2\rangle$, and so on; the standard deviation of the mass at the ith site for different initial configurations is d_i, and d is the average of this quantity over all sites.

One must note that the decay of d with t may depend on N and but not on ρ, since the calculation of the matrix T_t does not involve M anywhere. It is found that with iterations, d first decays algebraically, then exponentially, and then becomes constant (figure 2). Leaving out the constant portion, the d vs t curve is therefore described for large t by the relation

$$
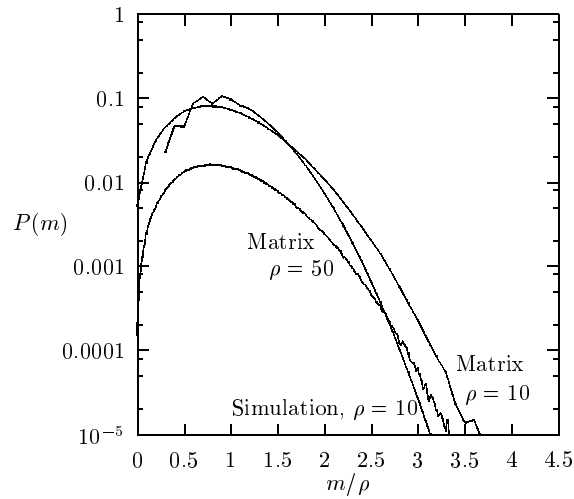d(t) = \alpha t^{-\beta} \exp(-\gamma t)
\tag{5}
$$

Figure 1. Mass distribution for the updating rule $\mathcal{C}$ for lattice size $N = 200$. For the matrix method, the average at the interval of 1000 iterations was taken between the 4×10^7-th and 5×10^7-th iterations. For simulation, the average at the interval of 1000 iterations was taken between the 10×10^7-th and 15×10^7-th iterations and this average was again averaged over 100 random number seeds.
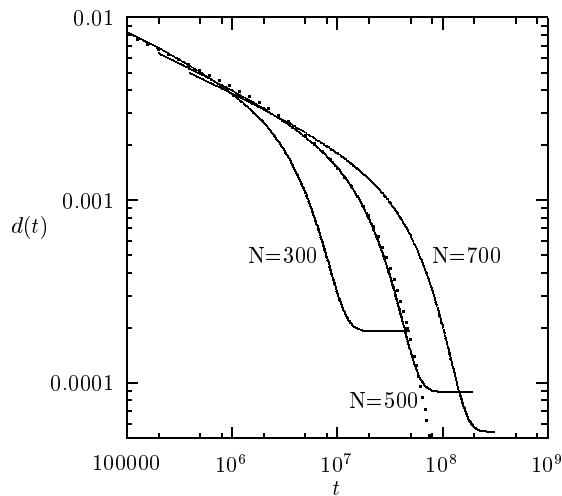

Figure 2. Decay of the parameter d (which measures the degree of approach to steady state) with number of updates for $\mathcal{C}$. Results for the matrix method are shown with continuous lines; the broken line is $\alpha t^{-\beta} \exp(-\gamma'/N^3)$ for $N = 500$ with $\alpha = 0.18$, $\beta = 0.27$, $\gamma' = 5.5$.

where t is the number of updates from the beginning. The constant α is nothing but the intercept on the y-axis, and can be easily evaluated by producing the algebraic portion of the curve to $t = 1$. The constant β is the slope of the algebraic portion in a log–log plot. Knowing α and β, one can evaluate γ by fitting the exponential portion. The algebraically decaying portions for different N are found to overlap, while the exponential portion varies for different N. Hence,

the values of α and β are independent of N. One finds

$$\alpha = 0.18 \pm 0.01 \qquad \beta = 0.27 \pm 0.01$$

while γ scales with N as

$$\gamma = \gamma'/N^3 \tag{6}$$

with $\gamma' = 5.5 \pm 0.5$. Hence, in the limit $N \to \infty$, γ vanishes and the decay of d becomes purely algebraic. Also, the plot of $\log(d')$ vs t', where $d' = dt^\beta$ and $t' = t/N^3$, will be the straight line $\log(\alpha) - \gamma' t'$, independent of N. The collapse of data for the d' vs t' curve is shown in figure 3.
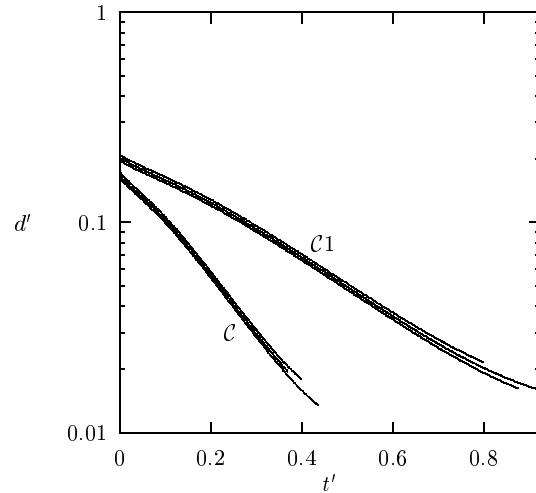

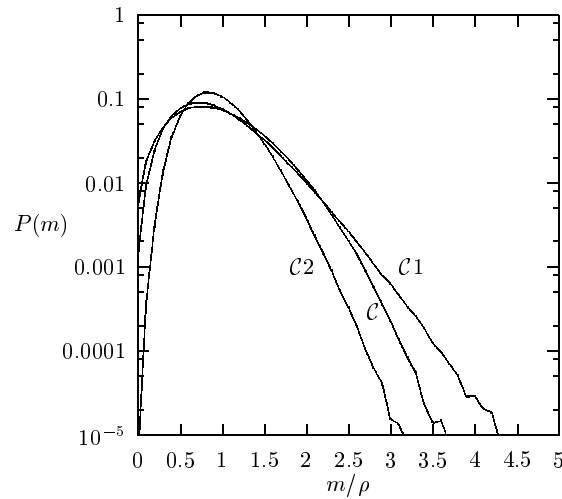**Figure 3.** Collapse of data for d' vs t'. Only $N = 500$, 600 and 700 are shown.

Figure 4. Mass distribution for different updating rules at density $\rho = 10$ and lattice size $N = 200$ from the matrix method. As in figure 1, the average at the interval of 1000 iterations was taken between the 4×10^7-th and 5×10^7-th iterations.

We shall now consider two other variants of the rule of updating:

$\mathcal{C}1$: Choose a site randomly (say i), remove f fraction of its population, choose randomly one nearest neighbour of i, add the removed mass to this neighbour.

$\mathcal{C}2$: Access the sites sequentially, at a site i remove f fraction of its population, choose randomly one nearest neighbour of i, add the removed mass to this neighbour.

The rules $\mathcal{C}1$ and $\mathcal{C}2$ give nearly the same type of steady-state mass distribution as rule $\mathcal{C}$ (see figure 4); only $\mathcal{C}1$ has the region $m > \rho$ rather closely exponential. The temporal behaviour of $\mathcal{C}1$ and $\mathcal{C}2$ was also found to be similar to that of $\mathcal{C}$; thus, they follow equations (5) and (6), have the same value of β (namely, 0.27). Only the value of α differs slightly (0.20 for $\mathcal{C}1$ and 0.22 for $\mathcal{C}2$) while the value of γ' differs more (2.9 for $\mathcal{C}1$ and 3.2 for $\mathcal{C}2$). The collapse of data in the d' vs t' plot hence gives two new straight lines, one of which is shown in figure 3.

Note added. Recently, Majumdar *et al* [12] have studied a model (see their section VII) which is a variant of our models $\mathcal{C}$ and $\mathcal{C}1$. In their model, an f fraction of mass breaks off from site $(i - 1)$ and unites with the mass at site i, and the fraction f is distributed uniformly in the interval [0,1]. The *exact* mass distribution function has a peak at mass = density, decays exponentially at high mass, and is thus analogous to the distribution function of our model. We should mention that the width of the interface in another model [3] of Majumdar *et al* scales [12] with time in a way similar to that described by equations (5) and (6) above. However, the definition of width for their model is unrelated to the definition of $d(t)$ here.

References

[1] Privman V (ed) 1997 *Nonequilibrium Statistical Mechanics in One Dimension* (Cambridge: Cambridge University Press)
[2] Vigil R D, Ziff R M and Lu B 1988 *Phys. Rev.* B **38** 942
[3] Krapivsky P L and Redner S 1996 *Phys. Rev.* E **54** 3553
    Majumdar S N, Krishnamurthy S and Barma M 1998 *Phys. Rev. Lett.* **81** 3691
[4] White W H 1982 *J. Colloid Interf. Sci.* **87** 204
    Hendriks E M and Ziff R M 1985 *J. Colloid Interf. Sci.* **105** 247
[5] Ziff R M 1980 *J. Stat. Phys.* **23** 241
[6] Ziff R M, Gulari E and Barshad Y 1986 *Phys. Rev. Lett.* **56** 2553
    Grinstein G, Lai Z -W and Browne D A 1989 *Phys. Rev.* A **40** 4820
[7] Takayasu H, Nishikawa I, and Tasaki H 1988 *Phys. Rev.* A **37** 3110
[8] Takayasu H 1989 *Phys. Rev. Lett.* **63** 2563
[9] Dasgupta S 2000 *Phys. Rev.* E at press
[10] Lewis B and Anderson J C 1978 *Nucleation and Growth of Thin Films* (New York: Academic) pp 356–365, 387
[11] Ispolatov S, Krapivsky P L and Redner S 1998 *Eur. Phys. J.* B **2** 267
    (Ispolatov S, Krapivsky P L and Redner S 1997 *Preprint* cond-mat/9708018)
    Dragulescu A and Yakovenko V M 2000 *Preprint* cond-mat/0001432
    Chakraborti A and Chakrabarti B K 2000 *Preprint* cond-mat/0004256
    Melzak Z A 1976 *Mathematical Ideas, Modeling and Applications (Companion to Concrete Mathematics II)* (New York: Wiley)
    Mantegna R N and Stanley H E 2000 *An Introduction to Econophysics* (Cambridge: Cambridge University Press)
[12] Majumdar S N, Krishnamurthy S and Barma M 2000 *J. Stat. Phys.* at press
    (Majumdar S N, Krishnamurthy S and Barma M 1999 *Preprint* cond-mat/9908443)