Asymptotic Results for the Random Sequential Addition of Unoriented Objects

G. Tarjus and P. Viot

Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris CEDEX 05, France

(Received 11 July 1991)

Asymptotic kinetics for random sequential addition of unoriented nonspherical objects is characterized by an algebraic time dependence. By studying 1D systems, we show that the exponents describing the random sequential addition of objects with and without proper area are not simply related: Whereas the asymptotic behavior for rectangles follows the expected $t^{-1/2}$ law, the long-time kinetics for infinitely thin line segments is governed by a nontrivial, irrational, exponent ($t^{\sqrt{2}-1}$) which results from a competition between creation and destruction of targets in the asymptotic regime.

PACS numbers: 68.10.Jy, 02.50.+s, 82.65.−i

Random sequential addition (RSA) is a model for irreversible adsorption of filling space that has attracted much recent attention [1]. Although conceptually simple (objects are placed sequentially and randomly, subject to the condition that they cannot overlap and that, once inserted, they cannot move), RSA models display a rich behavior, the study of which usually requires extensive computer simulations. In the last two years, the effort has been directed towards generalizing the basic model [2–6], in particular by considering the RSA of nonspherical objects added with random orientations [3–6].

An interesting feature of RSA models for objects with a nonzero proper area or volume is that the system reaches a jamming limit at a saturation density which is less than random close packing and that the asymptotic approach to this limit is usually described by an algebraic time dependence

$$\rho_\infty - \rho(t) \sim t^{-1/n}, \tag{1}$$

where ρ is the number density. Equation (1) is valid for objects added with random orientations and n is then equal to the number of degrees of freedom per object [3,6]. Although no definite proof of Eq. (1) has been given, analytical and numerical arguments have been presented that strongly support its validity [3–6]. Note that for isotropic objects, n is equal to the number of dimensions and Eq. (1) reduces to the usual Feder's law [7,8].

In recent studies on very elongated objects in two dimensions, it was also realized that the kinetics at intermediate times was similar to that of infinitely thin objects (line segments or "needles") [5]. For the latter, there is no jamming limit and the number density keeps increasing:

$$\rho(t) \sim t^{\alpha}. \tag{2}$$

Sherwood [4] recently suggested, by transposing the arguments used to derive Eq. (1), that the exponents in Eqs. (1) and (2) differ simply by their sign (e.g., in two dimensions where $n=3$, $\alpha=\frac{1}{3}$) and he claimed that the $t^{1/3}$ power law was numerically verified for needles in two dimensions. However, a subsequent simulation of the same system by Ziff and Vigil [5] showed that the exponent α is larger than $\frac{1}{3}$ and close to 0.38. No argument has yet been presented to explain this discrepancy, which is unfortunate since connecting the intermediate-time regime, described by Eq. (2), with the asymptotic regime, described by Eq. (1), is a key to a proper description of the RSA of very elongated objects.

To resolve the question, we have studied analytically and numerically the simplest relevant one-dimensional systems: the RSA of infinitely thin line segments (needles) and of rectangles, added with random orientations and no overlap, and such that their centers are placed randomly onto a line. We show that, *whereas the asymptotic approach to the jamming limit for rectangles is described, as expected, by Eq. (1) with $n=2$, the long-time kinetics for needles is governed by Eq. (2) with an irrational exponent, $\alpha=\sqrt{2}-1$, which is nontrivially related to the number of degrees of freedom.* This breakdown of Sherwood's prediction comes from the competition between creation and destruction of intervals that is present even in the asymptotic regime. To derive the exponent α, we show that in the long-time regime the RSA of needles is reducible to a simpler model describing an RSA of points onto a line subject to an additional linear condition. The analytical results are well supported by the computer simulation data which are very accurate for these one-dimensional problems.

We introduce first the simpler model. Connection with the RSA of needles will be made later. We consider the RSA of points onto a segment of line characterized by a length L and by an additional property which we call its weight and set equal to L. Two neighboring points on the segment define an interval: When a point is added anywhere within an interval, the interval is destroyed but, at the same time, two smaller intervals are created. At each step of the process, every interval is characterized by its length h and an additional variable, the weight w, which is introduced as follows. The points are dropped randomly, one at a time, onto the segment. However, to be accepted, the deposition of a point must satisfy an additional condition: A random number, η, is chosen between 0 and L (from a uniform distribution) and the deposition is definitely accepted only if η is smaller than the weight w of the interval in which the point has been dropped. In case of acceptance, a weight is assigned to the newly created intervals; it is set equal to η for the interval that is left of the accepted point and to $w-\eta$ for the other one. Denoting then $G(h,w,t)$ the distribution function for intervals of length h and weight w at time t, it is straightforward to derive the equation governing its time evolution:

$$\frac{\partial G(h,w,t)}{\partial t} = -hwG(h,w,t) + 2\int_h^L dh' \int_w^L dw' G(h',w',t) . \qquad (3)$$

The number density of points on the line at time t is related to $G(h,w,t)$ by

$$\rho(t) = \int_0^L dh \int_0^L dw\, G(h,w,t) . \qquad (4)$$

More generally, one can introduce the moments of the distribution function $G(h,w,t)$ as

$$M(\lambda,\mu,t) = \int_0^L dh \int_0^L dw\, h^\lambda w^\mu G(h,w,t) , \qquad (5)$$

where λ and μ are real numbers larger than -1. We are interested in the long-time behavior of $M(\lambda,\mu,t)$, especially of $\rho(t)=M(0,0,t)$, and we assume that this behavior is described by an algebraic time dependence, $M(\lambda,\mu,t) \sim a(\lambda,\mu)t^{b(\lambda,\mu)}$. By combining Eqs. (5) and (3), we derive the moment equation,

$$(d/dt)M(\lambda,\mu,t) = [2/(\lambda+1)(\mu+1)-1] \times M(\lambda+1,\mu+1,t) ,$$

and, by inserting the assumed time dependence, we obtain a set of finite-difference equations to be satisfied by the exponent $b(\lambda,\mu)$:

$$b(\lambda+1,\mu+1) = b(\lambda,\mu) - 1 , \qquad (6)$$

$$b\left(\lambda, \frac{2}{\lambda+1} - 1\right) = 0 . \qquad (7)$$

Equation (7) expresses the property that all moments $M(\lambda,\mu,t)$ characterized by the relation $(\lambda+1)(\mu+1)=2$ are independent of time: the fact that, in addition to the expected relations associated with the conservation of the total length ($\lambda=1$, $\mu=0$) and total weight ($\lambda=0, \mu=1$), there is an infinity of sum rules which results from the competition between creation and destruction of intervals.

Assuming now that $b(\lambda,\lambda)$ is a linear function of λ [a property which can be deduced from Eq. (3) by scaling arguments and which we have numerically verified] leads to a unique solution for the preceding set of equations:

$$b(\lambda,\mu) = \tfrac{1}{2}\{[(\lambda-\mu)^2+8]^{1/2} - (\lambda+\mu+2)\} . \qquad (8)$$

This simple two-variable model thus leads to a variety of nontrivial power-law exponents for the long-time kinetics; the number density, for instance, goes as

$$\rho(t) = M(0,0,t) \sim t^{\sqrt{2}-1} . \qquad (9)$$

The above predictions are independent of the choice of L and are very well supported by our computer simulation results: Our numerical value for the exponent $b(0,0)$ of Eq. (9) is 0.415 ± 0.005; other results are shown in Fig. 1.

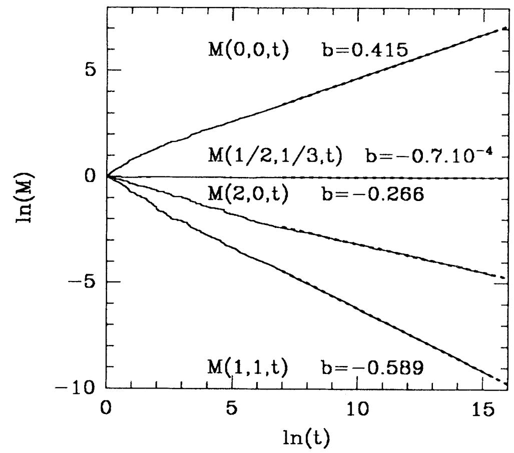

FIG. 1. Moments $M(\lambda,\mu,t)$ of the two-variable model [Eqs. (3)-(5)] as a function of time on a ln-ln plot. The moments are normalized such that $M(\lambda,\mu,t=1)=1$. The values of the exponent $b(\lambda,\mu)$ obtained from a least-squares fit (dashed lines) are displayed on the figure and are in excellent agreement with those predicted by Eq. (8): $b(0,0)=\sqrt{2}-1$, $b(\frac{1}{2},\frac{1}{3})=0$, $b(2,0)=\sqrt{3}-2$, $b(1,1)=\sqrt{2}-2$. The time t is defined by counting the cumulative number of attempts.

We now return to the RSA of unoriented line segments (needles) onto a line. The main reason to study one-dimensional systems is that one can usually derive the equations describing the kinetics of the process in a closed form. Even though the present RSA process involves two degrees of freedom per object (the position of the center on the line and an angle measuring the orientation of the needle relative to the line), one can still obtain an exact equation for the time evolution of $G(h,\theta,\theta',t)$, the distribution function for intervals of length h that are bounded by a needle of orientation θ (on the left-hand side) and a needle of orientation θ' (on the right-hand side):

$$\frac{\partial G(h,\theta,\theta',t)}{\partial t} = -\int_{0\,\{h \geq \delta(\theta,\theta'')+\delta(\theta'',\theta')\}}^{\pi} d\theta'' [h - \delta(\theta,\theta'') - \delta(\theta'',\theta')] G(h,\theta,\theta',t) + \int_0^\pi d\theta'' \left(\int_{h+\delta(\theta,\theta'')}^{L} dh' G(h',\theta'',\theta',t) + \int_{h+\delta(\theta'',\theta')}^{L} dh' G(h',\theta,\theta'',t) \right) , \qquad (10)$$

where $h \geq \delta(\theta,\theta')$ and $0 \leq \theta,\theta' \leq \pi$; L, the length of the segment of line, is much larger than the length of a needle (taken as unity), and

$$\delta(\theta,\theta') = \frac{|\sin(\theta-\theta')|}{2\max(\sin\theta,\sin\theta')} \tag{11}$$

is the shortest distance between the centers of two neighboring needles with orientations θ and θ' ($\theta=\pi/2$ corresponds to a situation in which the needle is perpendicular to the line). The number density of needles at time t is related to $G(h,\theta,\theta',t)$ by

$$\rho(t) = \int_0^\pi d\theta \int_0^\pi d\theta' \int_{\delta(\theta,\theta')}^L dh\, G(h,\theta,\theta',t)\,. \tag{12}$$

Connection to the simpler model presented earlier can be made by noting that for long enough times, and aside from a vanishingly small number of situations, the length, h, of any interval between needles and the difference, $\theta-\theta'$, between the orientations of any two neighboring needles decrease to zero: $h \to 0$ and $\theta-\theta' \to 0$ when $t \to +\infty$. In this long-time regime, the configuration formed by the needles on the line is made of a very large number of microdomains: Every microdomain contains a very large number of needles, all very close to each other and nearly parallel, and can be characterized by a mean orientation, θ_0. The exact equation, Eq. (10), can then be replaced by an approximate one that describes the process in each microdomain separately and is only valid asymptotically. After some manipulations, we find

$$\frac{\partial G(h,\delta,\theta_0,t)}{\partial t} = -\sin\theta_0(h^2-\delta^2)G(h,\delta,\theta_0,t) + 4\sin\theta_0 \int_h^{H_c} dh' \int_{|\delta-\delta'|\leq h'-h} d\delta'\, G(h',\delta',\theta_0,t), \quad t \to +\infty\,, \tag{13}$$

where H_c is an upper cutoff length, the value of which is irrelevant for determining the long-time kinetics, and $G(h,\delta,\theta_0,t)$ is the distribution function for intervals of length h between two needles characterized by a shortest distance of approach δ in a microdomain of mean orientation θ_0.

The original equation, Eq. (10), can be interpreted as describing an RSA of points with a nonlinear condition, expressed by means of Eq. (11). Equation (13) represents then a linearized version of Eq. (10), in which the number of relevant degrees of freedom is reduced to two: h and δ.

By using the change of variables

$$(h,\delta) \to (x=(\sin\theta_0)^{1/2}(h-\delta),\ y=(\sin\theta_0)^{1/2}(h+\delta))$$

and introducing $g(x,y,t)$ as the interval distribution function averaged over all microdomains, we can rewrite Eq. (13) as

$$\frac{\partial g(x,y,t)}{\partial t} = -xyg(x,y,t) + 2\int_x^{H_c'} dx' \int_y^{H_c'} dy'\, g(x',y',t)\,, \tag{14}$$

where H_c' is an (irrelevant) upper cutoff length: $0 \leq x,y \leq H_c'$. The above equation is exactly similar to Eq. (3) and the full relation to the previously studied model is established by means of the following asymptotic expression for the number density of needles:

$$\rho(t) \sim \int_0^{H_c'} dx \int_0^{H_c'} dy\, g(x,y,t), \quad t \to +\infty\,. \tag{15}$$

We can now apply the results derived earlier and we conclude that the long-time behavior of the number density of needles $\rho(t)$ has an algebraic dependence characterized by a nontrivial exponent equal to $\sqrt{2}-1$: *This is the first irrational exponent ever found for the kinetics of an RSA process.* As shown in Fig. 2, the analytical result is in very good agreement with our computer simulation data.

Finally, we discuss the RSA of unoriented rectangles (having a large but finite aspect ratio) whose center is restricted to fall onto a line. The fact that the objects have now a nonzero thickness introduces a fundamental difference in the long-time kinetics of the filling process: The system reaches a jamming limit and the approach to this limit can be described *as an irreversible process of destruction of targets with no competing creation process* [3,6,8]; a target is defined as a small interval between two

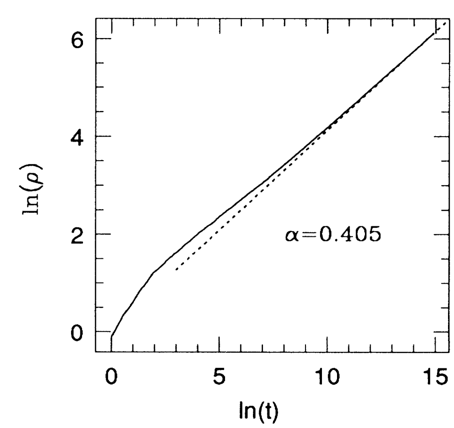

FIG. 2. Number density of needles on the line as a function of reduced time (ln-ln plot). Note that, as for the two-dimensional system [5,10], the curve approaches asymptotically a straight line *with a positive curvature.* The exponent obtained from a least-squares fit over the 27000 last needle insertions is then slightly less than predicted: $\alpha=0.405$. The time t and the density ρ are defined in reduced units by counting the cumulative number of attempts and the number of needles, respectively, and by multiplying by the needle length.

rectangles which allows the insertion of one and only one additional rectangle. For elongated rectangles and times long enough ($t > t_c$), the configuration formed by the rectangles on the line is made of small domains characterized by a mean orientation, θ_0, and the rate equation governing the filling of the targets in each domain can be expressed as

$$\frac{\partial G(h+2\epsilon(\sin\theta_0)^{-1},\delta,\theta_0,t)}{\partial t} = -\sin\theta_0(h^2-\delta^2)G(h+2\epsilon(\sin\theta_0)^{-1},\delta,\theta_0,t), \quad h \geq \delta, \quad t \geq t_c \,, \tag{16}$$

where ϵ is the width of a rectangle (the length is taken as unity), $h+\epsilon(\sin\theta_0)^{-1}$ is the length of the empty interval between the two rectangles defining the target, δ is the shortest distance of approach characterizing the orientations of these two rectangles, and G is the target distribution function. The difference between the number density of rectangles at the jamming limit and that at time t ($t \geq t_c$) is given by a sum over all targets which remain empty:

$$\rho(\infty)-\rho(t) \sim 4\int_0^{H_c} dh \int_0^h d\delta \int d\theta_0 G(h+2\epsilon(\sin\theta_0)^{-1},\delta,\theta_0,t_c)\exp[-\sin\theta_0(h^2-\delta^2)(t-t_c)] \,. \tag{17}$$

Equations (16) and (17) can be compared with Eqs. (13)-(15). As for the RSA of needles, only two variables, h and δ, which are correlated and both decrease to zero with increasing time, are relevant to determine the long-time kinetics. However, the absence of any creation process for the targets introduces a major simplification.

The additional ingredient which is needed to derive the asymptotic form of Eq. (17) is the assumption that in every domain at time t_c the total number of targets characterized by a length h approaches a limit which is different from zero when $h \rightarrow 0$. By using this latter assumption and introducing a new variable λ such that $\delta = h\sin\lambda$, we then obtain easily the expected $t^{-1/2}$ law for the asymptotic behavior of $\rho(\infty)-\rho(t)$ (the validity of this result, and of the above assumption, has been numerically verified for rectangles with an aspect ratio equal to 10 [9]). This lends support to the conclusion that the nontrivial nature of the exponent for infinitely thin needles is not a peculiar feature of the one-dimensional system, rather, it results from the competition between creation and destruction of targets that is present *even in the asymptotic regime;* a similar result is thus expected for needles in two dimensions [10].

It is a pleasure to thank J. Talbot for stimulating discussions. Laboratoire de Physique Théorique des Liquides is Unité de Recherche Associée No. 765 au CNRS.

[1] P. Schaaf and J. Talbot, Phys. Rev. Lett. **62**, 175 (1989); A. Baram and D. Kutasov, J. Phys. A **22**, L251 (1989); J. W. Evans, Phys. Rev. Lett. **62**, 2642 (1989); M. C. Bartelt, Phys. Rev. A **43**, 3149 (1991); R. Dickman, J. S. Wang, and I. Jensen, J. Chem. Phys. **94**, 8252 (1991).

[2] P. Nielaba, V. Privman, and J. S. Wang, J. Phys. A **23**, L1182 (1990); G. Tarjus, P. Schaaf, and J. Talbot, J. Chem. Phys. **93**, 8352 (1990); J. W. Evans and M. S. Miesch, Phys. Rev. Lett. **66**, 833 (1991); P. Schaaf, A. Johner, and J. Talbot, Phys. Rev. Lett. **66**, 1603 (1991).

[3] J. Talbot, G. Tarjus, and P. Schaaf, Phys. Rev. A **40**, 4808 (1989).

[4] J. D. Sherwood, J. Phys. A **23**, 2827 (1990).

[5] R. M. Ziff and R. D. Vigil, J. Phys. A **23**, 5103 (1990); R. D. Vigil and R. M. Ziff, J. Chem. Phys. **93**, 8270 (1990).

[6] P. Viot and G. Tarjus, Europhys. Lett. **13**, 295 (1990).

[7] J. Feder, J. Theor. Biol. **87**, 237 (1980).

[8] Y. Pomeau, J. Phys. A **13**, L193 (1980); R. H. Swendsen, Phys. Rev. A **24**, 504 (1981).

[9] We have used the procedures described in Ref. [6]. More details will be given in a forthcoming publication.

[10] Recent extended simulations for 2D needles seem to support this conclusion: The exponent α is about 0.40 and is thus consistent with the value found for the 1D system [R. M. Ziff (private communication)].