Selection of the scaling solution in a cluster coalescence model

Daniel Kandel¹

Department of Physics of Complex Systems, Weizmann Institute of Science, Rehovot 76100, Israel

The scaling properties of the cluster size distribution of a system of diffusing clusters is studied in terms of a simple kinetic mean field model. It is shown that a one parameter family of mathematically valid scaling solutions exists. Despite this, the kinetics reaches a unique scaling solution independent of initial conditions. This selected scaling solution is marginally physical; i.e., it is the borderline solution between the unphysical and physical branches of the family of solutions.

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Phenomena of diffusion, aggregation and coalescence of clusters of particles occur in various scientific areas [2]. Of particular interest to us is the relevance of these phenomena to the physics of thin films. In recent years, material scientists have been able to observe [3] clusters of atoms or vacancies diffusing on thin film surfaces. The diffusion and coalescence of these clusters affect the morphology of the film, which in turn affects its electrical properties and the possibilities to use it in the fabrication of electronic devices.

In many systems, the time-dependent cluster-size distribution exhibits a scaling behavior, which has been the subject of several existing studies [4,5]. The theoretical studies start from a kinetic model of the diffusing clusters, and then determine the scaling exponents by making a scaling ansatz. Finally, the scaling function is found by solving the kinetic model numerically starting from some initial cluster size distribution.

The purpose of this work is to investigate the properties of the scaling function. In particular, the questions answered in this Letter are: Does the scaling function depend on initial conditions? Starting from a scaling ansatz, is there a unique solution for the scaling function? The answers to both questions turn out to be no. We show, on the one hand, that simulations of a cluster coalescence model starting from different initial cluster size distributions approach the same scaling function in the long time limit. On the other hand, solving the equation for the scaling function that results from a scaling ansatz, we obtain a one parameter family of scaling functions. This implies that out of all the solutions for the scaling function, one is *selected dynamically*. A selection criterion is proposed and verified numerically. The applicability of this selection criterion to other models, which exhibit a scaling behavior, will be studied in future work.

The simplest model that describes diffusion and coalescence of clusters is the model of Meakin [4], where Ddimensional spherical clusters diffuse in a d-dimensional space with diffusion constants, $\mathcal{D}(s)$, that depend on the cluster size, s (the number of particles in the cluster). When two clusters with s_1 and s_2 particles touch, they merge irreversibly and form a new spherical cluster of size $s = s_1 + s_2$. Thus, the cluster size distribution depends on time, and the average cluster size growth is limited only by the finite number of particles in the system. Following Meakin, we assume an algebraic decay of the cluster diffusion constant with size:

$$\mathcal{D}(s) \sim s^{-\zeta}$$
 . (1)

In the present work we use D = d = 2. This is the case of two-dimensional clusters diffusing on a twodimensional surface, appropriate for diffusion of islands (or voids) of atoms on the surface of a thin film, for example. In this case, it is possible to show that the cluster diffusion constant indeed decays algebraicly with cluster size. The different values of the exponent ζ correspond to various microscopic mechanisms responsible for island diffusion [6]. For example, $\zeta = 3/2$ when mass transport on the surface is dominated by diffusion of atoms along island boundaries. If, however, mass transport is dominated by exchange of atoms between islands and nearby terraces, one obtains $\zeta = 1$ or $\zeta = 1/2$. When this exchange process is fast compared with the diffusion of atoms on the terraces, $\zeta = 1$. The case $\zeta = 1/2$ is obtained in the opposite limit, when surface diffusion is fast compared with the exchange kinetics.

To analyze the scaling behavior of such a system, we adopt a mean field approximation due to Smoluchowski [7]. In this approach, the time-dependent density of clusters of size s, $\rho(s,t)$, is assumed to obey the following rate equation:

$$\frac{\partial \rho(s,t)}{\partial t} = \sum_{s'=1}^{s-1} \mathcal{D}(s')\rho(s',t)\rho(s-s',t) - \sum_{s'=1}^{\infty} \left[\mathcal{D}(s) + \mathcal{D}(s')\right]\rho(s,t)\rho(s',t) \quad .$$
(2)

The r.h.s. of this equation consists of a gain term due to the coalescence of clusters of sizes s' and s - s' into a cluster of size s, and a loss term due to the coalescence of clusters of size s with clusters of all sizes.

Simulations of various versions of this model have shown (see, e.g. [4]) that, in the long time limit, the density of clusters obeys the scaling relation

$$\rho(s,t) = t^{-\alpha} f\left(\frac{s}{\bar{s}(t)}\right) \quad , \qquad \bar{s}(t) \sim t^{\beta} \quad , \tag{3}$$

where $\bar{s}(t)$ is the time dependent average cluster size, and the exponents α and β depend on the form of the diffusion constant: $\alpha = 2/(\zeta + 1)$ and $\beta = 1/(\zeta + 1)$. These values of the exponents can be easily verified by substituting the scaling ansatz (3) in Eq. (2) (see below).

Here we show that the Smoluchowski equation together with the scaling ansatz are not sufficient to find the scaling function f, since they lead to a one parameter family of scaling functions. To show this, we start from the generalized scaling ansatz

$$\rho(s,t) = g(t)f\left(\frac{s}{\bar{s}(t)}\right) \quad . \tag{4}$$

We substitute this form of $\rho(s, t)$ into Eq. (2), and change variables from s and t to $u = s/\bar{s}(t)$ and t. We also replace summation over s by integration over u. This is justified, since in the long time limit $\bar{s}(t)$ is very large. Therefore, when s changes by one, the change in u is much smaller than one. These algebraic manipulations together with the functional form of the diffusion constant, $\mathcal{D}(s) = K/s^{\zeta}$, lead to the following equation:

$$\frac{g'(t)}{Kg(t)^2} \bar{s}^{\zeta-1} f(u) - \frac{\bar{s}}{Kg(t)} \frac{d\bar{s}}{dt} u f'(u)
= \int_0^u \frac{1}{u'^{\zeta}} f(u') f(u-u') du'
- \int_0^\infty \left(\frac{1}{u^{\zeta}} + \frac{1}{u'^{\zeta}}\right) f(u) f(u') du' ,$$
(5)

where g'(t) and f'(u) are the first derivatives of g(t) and f(u), respectively.

Now we take into account the conservation of the total number of particles in the clusters, Θ : $\sum_{s=1}^{\infty} s\rho(s,t) = \Theta$, where Θ does not depend on time. Using the scaling ansatz (4), we obtain a relation between g(t) and $\bar{s}(t)$:

$$g(t) = \frac{\Theta}{\int_0^\infty u f(u) du} \frac{1}{\bar{s}^2} \quad . \tag{6}$$

This result can now be combined with Eq. (5) to get the following equation for the scaling function f:

$$-\frac{1}{K\Theta}\bar{s}^{\zeta}\frac{d\bar{s}}{dt}\int_{0}^{\infty}u'f(u')du' \left[2f(u)+uf'(u)\right] \\ =\int_{0}^{u}\frac{1}{u'^{\zeta}}f(u')f(u-u')du' \qquad (7) \\ -\int_{0}^{\infty}\left(\frac{1}{u^{\zeta}}+\frac{1}{u'^{\zeta}}\right)f(u)f(u')du' \quad .$$

The r.h.s. of Eq. (7) depends on u, but not on t. Hence, the l.h.s. of the equation cannot depend on time, and we can rewrite Eq. (7) in the form

$$\mu\int_0^\infty u'f(u')du'\left[2f(u)+uf'(u)\right]=$$

$$-\int_{0}^{u} \frac{1}{u'^{\zeta}} f(u') f(u-u') du' +$$

$$\int_{0}^{\infty} \left(\frac{1}{u^{\zeta}} + \frac{1}{u'^{\zeta}}\right) f(u) f(u') du' ,$$
(8)

where $\mu \equiv \bar{s}^{\zeta} \frac{d\bar{s}}{dt} / K\Theta$ is a constant that does not depend on t or u. This immediately implies that $\bar{s} \sim t^{1/(\zeta+1)}$, and therefore $\beta = 1/(\zeta+1)$ as stated above. Since $g \sim \bar{s}^{-2}$, the value of the exponent α is also confirmed.



FIG. 1. Numerical solutions of the equation for the scaling function with $\zeta = 1/2$. The different curves represent solutions with various values of μ (the number near the curves): (a) $\mu \ge \mu_0$ and (b) $\mu \le \mu_0$.

In addition, we can now find the scaling function f(u) by solving Eq. (8) with the appropriate boundary condition. In this case, it is an integral condition that we derive from the definition of the average cluster size, $\bar{s} \equiv \sum_{s=1}^{\infty} s\rho(s,t) / \sum_{s=1}^{\infty} \rho(s,t)$. Using the scaling ansatz

(4) in this definition, we obtain the integral condition

$$\int_0^\infty f(u)du = \int_0^\infty u f(u)du \quad . \tag{9}$$

Before we actually solve for the scaling function f, it is important to note that one can multiply any solution of Eq. (8) by a constant to get a new solution that satisfies the same integral condition. To eliminate this trivial (and physically meaningless) freedom, we enforce another integral condition:

$$\int_0^\infty f(u)du = 1 \quad . \tag{10}$$

Interestingly, the constant μ is a free parameter in the problem of finding the scaling function as defined above. Our aim now is to show that there is a range of values of the constant μ , for which there are legitimate solutions of Eq. (8) that obey the integral conditions (9) and (10). They are all valid scaling functions for this system.

We solved the equation for the scaling function numerically for $\zeta = 1/2$, using a method that will be outlined elsewhere [8], and a few examples of solutions are plotted in Fig. 1. We found that there is a special value of μ , which we denote by $\mu_0 \approx 1.232$, such that for $\mu \geq \mu_0$ the solutions are perfectly valid. Three examples of such solutions with $\mu = 1.232$, 1.9 and 2.5 are shown in Fig. 1(a). The solutions with $\mu < \mu_0$, on the other hand, are unphysical, since f(u) < 0 in these cases in a range of values of u. This can be seen in Fig. 1(b) in the cases $\mu = 0.6, 0.75$ and 1.0. In fact, for even smaller values of μ , the scaling function develops oscillations, and its limiting behavior at large values of u becomes ill-defined. We conclude that there is a one parameter family of valid and physical scaling functions which correspond to $\mu \geq \mu_0$.

Our question now is which of these scaling functions are actually reached by the physical system? This is of course a question about the kinetics of the system, and in order to answer it we should solve the kinetic Smoluchowski equation (2) starting from different initial cluster size distributions. This turns out to be a difficult task that consumes enormous amounts of computer time, since the amount of computer time required for every time step is proportional to the *square* of the number of possible values of cluster sizes.

To circumvent this difficulty, we used a much more efficient simulation method. Each simulation started with a set of $10^{6}-10^{7}$ clusters of various sizes picked according to the chosen initial cluster size distribution. At each time step a pair of clusters were picked at random. Let us denote their sizes by s_1 and s_2 . The two clusters were merged into a single cluster of size s_1+s_2 with probability $P(s_1, s_2)$ proportional to $\mathcal{D}(s_1) + \mathcal{D}(s_2)$. The clock was then advanced by $\delta t \sim 1/N(t)^2$, where N(t) is the total number of clusters in the system at time t. This process was repeated many times thus leading to an evolution of the cluster size distribution. It will be shown elsewhere [8] that the evolution of the *average* number of clusters of size s, induced by this kinetic model, follows the Smoluchowski equation. This procedure is much more efficient than a simple integration of Eq. (2), and the only price we have to pay is the statistical error induced by the stochastic nature of the model.



FIG. 2. (a) A log-log plot of island size distributions resulting from the simulations with $\zeta = 1/2$, at various stages of the evolution of the system. (b) The scaled island size distributions of (a) form a single curve to a very good accuracy.

The simulations were carried out for the case $\zeta = 1/2$ (results for other values of ζ will be presented elsewhere [8]), starting from several different initial cluster size distributions. For example, we started from clusters which were all of size 25, and also from a uniform distribution of clusters between the sizes 1 and 50. All the simulations we did exhibited a scaling behavior, and the scaling

function was independent of the initial distribution to the degree of accuracy of the results. In Fig. 2(a) we show the cluster size distributions, at different times, obtained from one of the simulations starting from a set of 10^6 clusters, all of size 1. We see from the figure that the most probable cluster size as well as the width of the distribution grow with time. Fig. 2(b) shows $t^{\alpha}\rho(s,t)$ as a function of the scaled cluster size $u = s/\bar{s}(t)$, with $\alpha = 4/3$ as deduced from the scaling analysis for $\zeta = 1/2$ (see above). Clearly, there is excellent data collapse and all the distributions fall on top of a single curve, which is the scaling function f(u) up to a multiplicative constant. Examination of the average cluster size as a function of time shows that $\bar{s}(t) \sim t^{\beta}$ with $\beta = 2/3$ as expected from the scaling analysis for $\zeta = 1/2$ (see above).



FIG. 3. The scaling function obtained from the simulations is shown as full circles. The solid line is the solution of the scaling function equation with $\mu = \mu_0 \approx 1.232$.

Our simulation results indicate that the scaling function is not sensitive to the initial cluster size distribution. This intriguing result implies that one scaling function (and a unique value of the parameter μ) is selected dynamically out of the one parameter family of possible physical scaling functions. Which one is it? What is the selected value of μ ? The solution to this puzzle can be inferred from Fig. 3, which shows the scaling function obtained from simulations (normalized so that $\int_0^{\infty} f(u) du = 1$) as full circles, and the scaling function for $\mu = \mu_0 \approx 1.232$ as a solid line. The resemblance of the two functions suggests that the kinetically selected scaling solution is the one at the border between the physical and unphysical branches of the family of solutions, i.e., the scaling function that corresponds to $\mu = \mu_0$.

One can argue that this selection principle is reasonable, since the initial cluster size distribution is cut off at some finite size. Assuming that the tail of the distribution develops gradually, the system will approach the physically legitimate distribution with the shortest tail. A close examination of the family of solutions leads to the conclusion that the scaling function with $\mu = \mu_0$ has the shortest tail, since it decays to zero faster than all the scaling functions with $\mu > \mu_0$.

A similar selection principle was proposed by Stavans et al. and Segel et al. [9] in relation with the selection of the steady state in the coarsening of cells in twodimensional soap froths, and by Maggs et al. [10] in connection with steady state length distributions of living polymers. This suggests that the selection principle proposed here may apply to a class of problems. In future work, we intend to investigate its applicability in various non-equilibrium systems that exhibit a scaling behavior.

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- [1] E-mail address: fekandel@weizmann.weizmann.ac.il.
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