Scaling theory for diffusion-limited cluster aggregation in a porous medium

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Abstract – A scaling theory is developed for diffusion-limited cluster aggregation in a porous medium, where the primary particles and clusters stick irreversibly to the walls of the pore space as well as to each other. Three scaling regimes are predicted, connected by smooth crossovers. The first regime is at low primary-particle concentrations where the primary particles stick individually to the walls. The second regime is at intermediate concentrations where clusters grow to a certain size, smaller than the pore size, then stick individually to the walls. The third regime is at high concentrations where the final state is a pore-space-filling network. The time to reach the final state is also calculated for all three cases.

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Diffusion-limited aggregation (DLA) and diffusion-limited cluster aggregation (DLCA) attracted much attention from the early 1980s following the discovery of scale-invariant (fractal) structures [1–3]. In DLA, primary particles undergo random walks before adhering irreversibly to a growing cluster [1]. In DLCA, both primary particles and growing clusters undergo random walks, adhering to each other when they come into contact [2]. Despite a couple of decades or so of intense study, there still remain interesting questions about these processes. On the one hand deep puzzles linger about the origins of the scale invariance and whether a simple fractal picture suffices [4], and on the other hand generalisations to more complicated situations have been considered, such as DLCA as a function of primary particle concentration [5] or in the presence of sedimentation [6] or flow [7,8].

In this letter I present a scaling analysis of DLCA as a function of the primary particle concentration for the case where the primary particles and clusters can adhere irreversibly to the walls of the porous medium as well as to each other. I consider the case where the primary particles are much smaller than the pores. My motivation is to gain a deeper understanding of the deposition of small particles into porous materials, with applications that range from deep-bed filtration [9], to the aggregation and deposition of colloidal asphaltene in reservoir rocks in oil recovery [10]. The results presented here are also hopefully intrinsically interesting, although the model still lacks certain features present in real systems such as flow. This will be discussed further at the end. Previously, DLA has been studied in confined geometries [11], but this is not really relevant to the present problem.

Let me start by summarising what is known about DLCA [12]. Firstly, as already mentioned, the clusters have a scale invariant structure such that the aggregation number \( N \) of a cluster of linear size \( R \) obeys

\[
N \sim \left( \frac{R}{R_0} \right)^{d_f},
\]

where \( R_0 \) is the primary particle size and \( d_f \) is the fractal dimension. This scaling law has been confirmed both in experiments on aggregating colloids and in computer simulations [3,13]. For the remainder of this letter my focus will be on the practically relevant case of \( d = 3 \) dimensions, where \( d_f \approx 1.75 \) [3,13].

A second line of enquiry into DLCA has been into the kinetics of the process [14–16]. A long time ago, Smoluchowski presented a mean-field theory to describe the evolution of the cluster size distribution [17]. When updated to take account of the fractal structure of the aggregates, Smoluchowski’s theory has turned out to be suprisingly accurate. One result of Smoluchowski’s theory is that the cluster size distribution remains bell-shaped [14,15]. In scaling terms this justifies the notion of a characteristic cluster size. Armed with this foreknowledge,
it is possible to use a simple scaling argument to determine how the characteristic cluster size grows with time [16]. In fact this is the key to the development, since the scaling argument generalises in a straightforward way to the problem of DLCA in a porous medium, by taking account of the depletion kinetics of clusters as they adhere to the walls.

The kinetic scaling argument for pure DLCA runs as follows. Let the \( n(t) \) be the cluster number density at time \( t \). Then, in mean field theory, \( \frac{dn}{dt} = -k_{\text{agg}}n \), where \( k_{\text{agg}} \) is the aggregation rate for the characteristic clusters. Again taking a mean field approach, this aggregation rate is given by the classic Smoluchowski diffusion-limited reaction rate \( k_{\text{agg}} \sim RDn \), where \( R \) is the characteristic cluster size and \( D \) is the corresponding diffusion coefficient. This result can be derived by considering the steady state diffusive flux to a sphere of radius \( \sim R \) from a concentration field of number density \( n \) at infinity. Now, the Stokes-Einstein relation implies \( D \sim (R_0/R) \times D_0 \), where \( D_0 \) is the primary particle diffusion coefficient. One concludes that \( \frac{dn}{dt} \sim -R_0D_0n^2 \). Integrating this gives \( n/t \sim -R_0D_0nt^2 \). 

Recognizing the depletion kinetics of clusters as they adhere to the walls much faster than they undergo aggregation. This is experimentally unattainable but this point will be discussed in more depth at the end.

Since \( \lambda^2/D \) is the time it takes for the cluster of size \( R \) to diffuse a distance of order the pore size, the rate at which such clusters are depleted by sticking to the walls is given in scaling terms by \( k_{\text{dep}} \sim D/\lambda^2 \). This assumes \( R \ll \lambda \), which will be verified \textit{a posteriori}. This rate should be compared to the aggregation rate from Smoluchowski’s theory above. Both are changing in time and to compare on a like-for-like basis the \( t \)-dependence should be explicitly extracted. One finds

\[
\tau_{\text{gel}} \sim R_0^2/D_0 \times \phi_0^{-3/(3-d_f)}. \tag{3}
\]

A point to note in idealised DLCA is that the final state of the system is always a gelled state. Experimentally other factors may intervene of course, such as sedimentation or creaming, or cluster rupture due to flow.

The framework has now been set for the generalisation to DLCA in a porous medium. In this more complex situation, the basic idea is that there is a competition between the rate at which primary particles and clusters find each other, and the rate at which they are depleted by becoming stuck to the walls. I consider the case where the porous medium has a unimodal pore size distribution with a characteristic pore size \( \lambda \gg R_0 \). This would be the case, for example, for a porous medium formed from a random bead packing with bead diameter \( \sim \lambda \). In fig. 1 the pore space is represented schematically by a slit of width \( \lambda \) and of course the theory encompasses DLCA in such a slit geometry as a special case. The generalisation from a single characteristic pore size \( \lambda \) to multiple length scales or fractal pores spaces should not be too difficult.

I also take the starting point to be an initially random dispersion of primary particles at a number density \( n_0 \) (volume fraction \( \phi_0 \sim n_0 R_0^3 \ll 1 \)). It might be objected that an initially random dispersion in a porous medium is experimentally unattainable but this point will be discussed in more depth at the end.

\[
k_{\text{agg}} \sim \frac{k_0}{1 + k_0t}, \quad k_{\text{dep}} \sim \frac{D_0}{\lambda^2(1 + k_0t)^{1/d_f}}. \tag{4}
\]

Two situations should be considered, depending on the initial values of the rates for primary particles. Firstly, if \( k_{\text{agg}} \ll k_{\text{dep}} \) at \( t = 0 \), then the primary particles diffuse to the walls much faster than they undergo aggregation. This condition implies \( k_0 \ll D_0/\lambda^2 \) or

\[
\phi_0 \ll (R_0/\lambda)^2. \tag{5}
\]
Fig. 2: Intermediate regime of fig. 1: double-logarithmic plot showing how the cluster-cluster aggregation rate falls faster than the cluster-wall depletion rate as a function of time. Where the two rates cross over, clusters become attached to the walls, halting the aggregation process. The time at this cross over point should be less than the gelation time, otherwise wall cluster deposition is pre-empted by gelation. In $d = 3$ dimensions, $1/d_f \approx 0.57$.

In this limit aggregation is irrelevant and the final state is one where primary particles are stuck to the walls. Moreover, since there are $n_0$ particles per unit volume spread over the walls at a surface area per unit volume $\sim 1/\lambda$, the area fraction covered by particles is $R_0^2/n_0 \lambda \sim \phi_0 \lambda / R_0$. But, using eq. (5), $\phi_0 \lambda / R_0 \ll R_0 / \lambda \ll 1$. In other words the primary particles are very sparsely distributed over the walls. Finally the time to reach the final state is $\tau_{ppd} \sim \lambda^2 / D_0$ where $D_0$ is the primary particle diffusion coefficient. This can be written as

$$\tau_{ppd} \sim R_0^2 / D_0 \times (\lambda / R_0)^2.$$  (6)

This is independent of the primary particle concentration of course.

Now consider the case where $k_{agg} \gg k_{dep}$ at $t = 0$. In this situation, the primary particles start to aggregate before they see the walls. Equation (4) shows that $k_{agg}$ falls faster than $k_{dep}$ as time progresses since $d_f > 1$. Eventually the wall depletion rate must overtake the aggregation rate. This is strongly suggestive of a crossover, in other words one expects aggregation to proceed as in standard DLCA until $k_{agg} \sim k_{dep}$, at which point the clusters are removed by sticking to the walls. This is illustrated in fig. 2. Making this ansatz in eq. (4), and rearranging, shows that this point is reached on a time scale

$$\tau_{clid} \sim R_0^2 / D_0 \times (\lambda / R_0)^2 (\lambda / R_0)^2 / (d_f - 1).$$  (7)

Once the clusters are stuck to the walls, no further changes occur, so this is also the time to reach the final state of the system. The argument assumes $k_0 \tau_{clid} \gg 1$ but one can easily show that this is true. In fact, one can show that there is a smooth crossover between the regime of primary-particle deposition and the present cluster deposition regime, since $\tau_{clid} \rightarrow \tau_{ppd}$ and the aggregation number of the characteristic clusters $N \rightarrow 1$, as $\phi_0 \rightarrow (R_0 / \lambda)^2$ from above.

The time to reach the final state in eq. (7) is an increasing function of $\phi_0$ and at some point it must surpass the gelation time in eq. (3) which is a decreasing function of $\phi_0$. If this happens, the system will form a pore-space-filling network before it reaches the state where clusters become attached to the walls. To avoid this fate requires that $\tau_{clid} \ll \tau_{gel}$, which after some rearrangement implies $\phi_0 \ll (R_0 / \lambda)^{-d_f}$. Thus the cluster deposition regime occurs only in an intermediate range of volume fractions,

$$(R_0 / \lambda)^2 \ll \phi_0 \ll (R_0 / \lambda)^{-d_f}.$$  (8)

Note that this intermediate regime exists since $R_0 \ll \lambda$, and $d_f > 1$ is required for connected clusters.

Conversely, for

$$(R_0 / \lambda)^{-d_f} \ll \phi_0,$$  (9)

the final state is a pore-space–filling network or gel. The time to reach the final state in this situation is just the gelation time given by eq. (3).

At the crossover between cluster deposition and gelation, one has $\tau_{clid} \sim \tau_{gel} \sim R_0^2 / D_0 \times (\lambda / R_0)^3$. This is found by setting $\phi_0 \sim (R_0 / \lambda)^{3-d_f}$ in either of eqs. (3) or (7).

It is worth commenting on the properties of the clusters in cluster deposition regime of eq. (8). After some algebra one finds that the terminal characteristic cluster size, in units of the pore size, obeys $R / \lambda \sim \phi^{1/2}$, where $\phi \sim nR^d$ is the effective cluster volume fraction. This shows that the clusters only grow to span the pores as one approaches the crossover to the gelation threshold where $\phi \rightarrow 1$. This, incidentally, is also the promised a posteriori justification for $R \ll \lambda$ mentioned above. It also eliminates a possible fate of the aggregating system: at no point does the characteristic cluster size grow large enough to span the pores ($R \sim \lambda$), without getting ($\phi \ll 1$). Finally, by analogy to the primary particle deposition case, the effective area fraction covered by clusters in the cluster deposition regime is $R^2 n \lambda$. But one has $R^2 n \lambda \sim R^2 n (\lambda / R) \sim \phi / \phi^{1/2} \sim \phi^{1/2}$. This means that clusters deposit individually $(R^2 n \lambda \ll 1)$ in the cluster deposition regime ($\phi \ll 1$), and only start to touch each other as one approaches the gelation threshold ($\phi \rightarrow 1$). This also means that in the cluster-deposition regime it is safe to neglect effects such as hindered diffusion arising from cluster-cluster interactions.

With these considerations it has now been demonstrated that the crossovers between all the regimes are continuous. At this point the analysis is complete. There are three predicted scaling regimes: a primary particle deposition regime at the lowest primary particle concentration, a cluster deposition regime at intermediate concentrations, and a pore-space–filling network or gelation regime at the highest concentrations. This is shown schematically in fig. 1.

In terms of the primary particle volume fraction, these regimes are given by eqs. (5), (8) and (9), respectively.
Likewise the time taken to reach the final state in each of the regimes is given by eqs. (6), (7) and (3), respectively. A regime of pore-spanning clusters does not occur.

Figure 1 shows perhaps a surprising prediction, namely that the time to reach the final state increases with concentration in the intermediate cluster deposition regime, reaching a maximum at the gelation threshold. Naively one might have expected \( \tau_{ppd} \) to be an upper bound for the time to reach the final state. After all, non-aggregating particles would stick to the walls on a time scale \( \sim \tau_{ppd} \) independent of the concentration. However, in the cluster deposition regime for an aggregating system, \( \tau_{ppd} \) is initially much longer than the aggregation time. What happens then is that most of the primary particles form aggregates rather than finding the walls. The diffusion coefficient of an aggregate is smaller than that of a primary particle, hence the time to reach the final state (i.e. the time to diffuse to the walls) must exceed \( \tau_{ppd} \).

The present letter is a self-contained presentation of a scaling theory for DLCA in a porous medium. Although the predictions seem reasonable, and internally consistent, the approach is based at least in part on the ansatz, illustrated in fig. 2, that there is a crossover between cluster-cluster aggregation and cluster-wall depletion. For future work it is obviously prudent to test this. An obvious way is to use computer simulations. For these, it is probably sufficient to consider DLCA in a slit of width \( \lambda \), as indicated schematically in fig. 1. Experimental tests could also be attempted although they are harder to make since a proper comparison should ideally start from randomly dispersed neutral buoyant primary particles which are colloidal unstable. Usually, colloidal instability is induced by adding salt, or by some other mixing process, and in a porous material it seems inevitable that this would involve flow fields. However, ingenious methods have been devised for the \textit{in situ} destabilisation of colloidal suspensions, for example using the enzyme-catalysed hydrolysis of urea to increase the ionic strength [18]. Another possible way might be to shine UV light on colloids which have been stabilised by photo-destructible surfactants [19], although so far as I know this latter method has not been experimentally tested.

Some other directions for future work are as follows. Firstly it would be interesting to include the effects of a reduced sticking probability, both for particle-particle collisions, and for particle-wall collisions. One might anticipate a variety of cross-overs, based on our understanding of how reaction-limited cluster aggregation (RLCA) crosses over to DLCA [15]. Secondly for realistic applications it may be important to include the effects of flow fields and gravitational settling or creaming. One can anticipate that these could influence the behaviour in two distinct ways. Firstly, a different scaling regime may be entered for clusters being formed at Peclet numbers that are larger than unity [6]. Secondly, if the induced internal stresses are sufficiently large, they would have the effect of rupturing clusters and therefore limiting growth [8].

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