From ageing to immortality: cluster growth in stirred colloidal solutions

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Our model describes cluster aggregation in a stirred colloidal solution. Interacting clusters compete for growth in this ‘winner-takes-all’ model; for finite assemblies, the largest cluster always wins, i.e. there is a uniform sediment. In mean-field, the model exhibits glassy dynamics, with two well-separated time scales, corresponding to individual and collective behaviour; the survival probability of a cluster eventually falls off according to a universal law $(\ln t)^{-1/2}$. In finite dimensions, the glassiness is enhanced: the dynamics manifests both ageing and metastability, where pattern formation is manifested in each metastable state by a fraction of immortal clusters.

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Systems that are far from equilibrium exhibit remarkable physics: some commonly known examples in the context of glassy systems are ageing and metastability. There are, however, much simpler consequences of nonequilibrium dynamics; in this Letter, we present a model of cluster growth which is inherently disequilibrating. Here, instead of available masses being equally distributed between competing clusters, the largest cluster always wins. Somewhat surprisingly, the two-step relaxation and ageing characteristic of glassy dynamics is manifested for infinite systems. Additionally, in finite dimensions, the system relaxes asymptotically to a metastable state in a complex energy landscape; in each such state, a fraction of immortal clusters from nontrivial spatial patterns.

In our model, $n$ pointlike, immobile clusters with time-dependent masses $m_i(t)$ for $i = 1, \ldots, n$, evolve according to the following equations:

$$\frac{dm_i}{dt} = \left(\alpha \frac{t}{t^{1/2}} \sum_j g_{ij} \frac{dm_j}{dt}\right) m_i - \frac{1}{m_i}. \quad (1)$$

These dynamical equations were originally written to model the kinetics of black hole growth in a radiation fluid. The present model is, however, of potential interest in many other situations; its dynamical behaviour in fact illustrates the rich-get-richer principle in economics, and its form bears some resemblance to Lotka-Volterra type predator-prey models in biology. In this Letter, we visualise Eqs. (1) as representing a simple model of aggregating clusters in a stirred colloidal system.

In our toy model, clusters grow by accreting mass from the fluid and from other clusters; they can also dissolve away if they are small, as the fluid is stirred. The gain term in (1) is the sum of the free rate for an isolated cluster, proportional to the parameter $\alpha > 1/2$, and of contributions from all other clusters via the fluid, with a coupling $g_{ij}$ between clusters $i$ and $j$; the loss term is taken to be inversely proportional to the cluster mass. The stirring of the fluid results, in this simple-minded picture, in the explicit time dependences in (1).

We first recall the one-cluster result. (For convenience, we work with reduced time $s = \ln \frac{t}{\alpha}$ to renormalise away the effect of initial time $t_0$), reduced masses $x_i = \frac{m_i}{t^{1/2}}$ and square masses $y_i = x_i^2 = \frac{m_i^2}{t}$. Large clusters, whose initial mass $y_0$ is greater than some threshold $y_*$, with $y_*(t_0) = \left(\frac{2t_0}{2e-1}\right)$, are survivors: they survive and keep on growing forever. Small clusters, whose initial mass is below this threshold dissolve and die out in a finite time. In a very dilute sediment, we would thus expect globules of matter to be suspended indefinitely, and to grow forever.

As the concentration of the solute is increased, interactions between the colloidal clusters become significant. We consider first two interacting clusters with interaction strength $g$. If their initial masses are exactly equal, this equality is maintained by symmetry forever. The reduced mass $x(s)$ of each mass then obeys:

$$x' = \frac{(2\alpha - 1)x^2 - 2gx^3}{2x(1+gx)}. \quad (2)$$

The fixed points of (2) are given by $(2\alpha - 1)x^2 - 2gx^3 = 0$; there is a critical value $g_c = \left(\frac{2(2\alpha - 1)}{2\alpha - 3}\right)^{1/2}$ which separates two kinds of behaviour. For large couplings $g > g_c$, there is no fixed point; physically this implies that the clusters feed on each other and disappear quickly. For small couplings $g < g_c$, there are two positive fixed points

$$y_*^{1/2} < x_1 (\text{unstable}) < (3y_*)^{1/2} < x_2 (\text{stable}). \quad (3)$$

Small clusters, such that their mass $x_0 < x_1$, are dynamically attracted by $x = 0$; thus lighter clusters dissolve away rapidly. Large clusters, such that their mass $x_0 > x_1$, are dynamically attracted by $x_2$: heavier clusters thus grow forever according to the law as $m(t) \approx x_2 t^{1/2}$. Here the interaction is small enough that symbiosis is achieved; the clusters feed on each other so as to increase, rather than deplete, mutual growth.
For two clusters with initially unequal masses, any small initial mass difference always diverges exponentially at early times: later stages of the dynamics cannot be described in closed form. The details of the transient behaviour can be found in [1]. However, the asymptotic behaviour is such that the largest cluster wins: survival of the biggest is therefore the single generic scenario for two clusters with unequal initial masses. The surviving large cluster may then either also disappear in a finite time, or survive and grow forever, depending on whether its mass at the time of the lighter cluster’s death is less or greater than the threshold $y_\star$. This generalises easily to any finite number $n \geq 2$ of colloidal clusters; in every case, our model predicts that there will at most be one large sediment formed [2].

To explore an infinite assembly of interacting colloidal clusters, we explore the mean-field behaviour of the model; each cluster is connected to every other by a weak interaction $g = \frac{g}{n}$. When $n \to \infty$ limit at fixed $\overline{g}$, the scaled thermodynamic limit, one obtains [3]:

$$y'(s) = \gamma(s)y(s) - 2$$

for the reduced square mass $y(s)$ of any of the clusters. Eq. (4) can be solved only formally, as it is self-consistent [3].

Things simplify considerably when the rescaled coupling $\overline{g}$ is small; remarkably, a glassy dynamics [4] with two-step relaxation is observed. In Stage I, the clusters behave as if they were isolated: this corresponds to individual behaviour. The survivors of this stage are clusters whose initial masses exceed the threshold $y_\star$, exactly as in the one-cluster case recalled above. In Stage II, all the survivors interact with each other; the dynamics is thus collective, and turns out to be slow [7]. All but the largest cluster eventually die out during this stage, thus in terms of experimental predictions [8], again predicting a uniform asymptotic sediment. This weakly interacting mean-field regime of our model of interacting colloidal systems [5] such as ageing; this originates in the presence of two well-separated time scales of fast and slow dynamics, whose ratio grows as $1/\overline{g}$ [6].

For an exponential distribution of initial masses, in the late times of Stage II, the survival probability decays as

$$S(t) \approx \frac{2\alpha - 1}{\overline{g}} \left( C \ln \frac{t}{t_0} \right)^{-1/2},$$

with

$$C = \pi$$

irrespective of $\alpha$, $\overline{g}$ and the parameters of the exponential distribution. Also, the mean mass of the surviving clusters grows as

$$\langle m \rangle_t \approx \left( C t \ln \frac{t}{t_0} \right)^{1/2}.$$  

The universality inherent in the scaling results [6-7] is unusual, because it includes the prefactor $C$, which is itself independent of the details of the initial distribution $P(y_0)$ of square masses. It can in fact be shown that $C$ only depends on the tail exponent of this distribution in the vicinity of its upper bound $y_{\max}$, i.e. whether the initial distribution of masses is bounded or not. The interested reader is referred to [7] for further details; here we simply point out that this striking universality is a major result of our present work. Also, the logarithmic behaviour seen is yet another signature [8] of glassy dynamics. Returning to the physical system, this predicts that in a very weakly interacting system of colloidal particles, there is a slow freezing in of fluid disorder [9], resulting in a uniform sediment at asymptotically long times.

Finally, we study a lattice version of the model (we choose the chain $(D = 1)$, the square lattice $(D = 2)$, and the cubic lattice $(D = 3)$) in order to probe the effect of fluctuations. Clusters now sit on the vertices $\mathbf{n}$ of a regular lattice, with nearest-neighbour interaction $g$. In the limit of weak coupling ($g \ll 1$), our dynamical equations are:

$$x'_n = \left( \frac{2\alpha - 1}{2} + g \sum_m \left( \frac{1}{x_m} - \alpha x_m \right) \right) x_n - \frac{1}{x_n}, \quad (8)$$

where $m$ runs over the $z = 2D$ nearest neighbours of site $\mathbf{n}$.

The dynamics generated by [8], again consists of two successive well-separated stages. Fast individual dynamics are exhibited in Stage I, where the mass of each cluster evolves as if it were isolated. As in the mean-field case, the survival probability $S(s)$ decays rather fast from $S(0) = 1$ to a plateau value $S_1$. The effects of going beyond mean field are only palpable in Stage II, where interactions become relevant and lead to a slow dynamics which is now very different from the mean-field scenario. The survival probability $S(s)$ in fact decays from its plateau value $S_1$ to a non-trivial limiting value $S_{\infty}$, reflective of metastability. The effect of fluctuations is already palpable: unlike the mean field result, this predicts that a finite number of clusters will survive. We elaborate on this below.

Consider [8] for two neighbouring clusters $\mathbf{n}$ and $\mathbf{m}$ which have both survived Stage I. The contribution of cluster $\mathbf{m}$ to the large parenthesis in the right-hand side of [8] is proportional to $\alpha g x_m$. In the absence of coupling, we have $x_m \sim e^{(2\alpha - 1)s/2}$ [7]. The characteristic time scale of Stage II, that is the time at which interactions become significant, is reached when the product $g x_m$ becomes of order unity:

$$s_c \approx \frac{2}{2\alpha - 1} \ln \frac{1}{g}, \quad (9)$$

i.e. $t_c \sim t_0 g^{-2/(2\alpha - 1)}$. Thus, in this weak-coupling limit, the separation of time scales between fast individual and
slow collective dynamics is parametrically large. Figure 1 illustrates this two-step relaxation in the decay of the survival probability $S(s)$ in one dimension. Both stages of the dynamics appear clearly on the plot; different values of the interaction cause the system to age differently. In each case, a plateau is reached at $S(1) = 0.8$; however, the weaker the interaction, the longer the system takes to reach the asymptotic state, which occurs at a non-trivial limit survival probability $S(\infty) \approx 0.4134$. Since each curve corresponds to a decade shift in interaction strength $g$, it is shifted in terms of the onset time $s_o$ of slow dynamics by $2 \ln 10$ (thick bar), in excellent agreement with the estimate (9).

![Plot of the survival probability](image)

FIG. 1: Plot of the survival probability $S(s)$ on the chain with $S(1) = 0.8$. Left to right: Full line: $g = 10^{-3}$. Dashed line: $g = 10^{-4}$. Long-dashed line: $g = 10^{-5}$. Dash-dotted line: $g = 10^{-6}$. The thick bar has length $2 \ln 10 = 4.605$ (see text).

At the end of Stage II, the system is left in a non-trivial attractor, which consists of a pattern where each cluster is isolated: it is therefore a survivor and keeps growing forever. We call these attractors metastable states, since they form valleys in the existing random energy landscape; the particular metastable state chosen by the system (corresponding to a particular choice of pattern) is the one which can most easily be reached in this landscape (1, 8, 9). The number $N$ of these states generically grows exponentially with the system size (number of sites) $N$:

$$N \sim \exp(N\Sigma).$$

with $\Sigma$ the configurational entropy or complexity.

The limit survival probability $S(\infty)$ (Figure 1) is just the density of a typical attractor, i.e., the fraction of the initial clusters which survive forever. It obeys the inequalities

$$S(\infty) \leq S(1), \quad S(\infty) \leq 1/2.$$  

The first inequality expresses the fact that clusters generically disappear: the difference $1 - S(1)$ (resp. $S(1) - S(\infty)$) is the fraction of clusters which are dissolved out during Stage I (resp. Stage II). The second inequality is a consequence of the fact that each surviving cluster is isolated: the densest configuration for which this is the case is when either of the two sublattices is occupied, at which point the density is exactly 1/2. This value 1/2 of the highest density holds for the large family of so-called bipartite lattices, which includes the hypercubic lattices we have considered here (but does not, for example, include the triangular lattice).

For a given class of initial mass distributions, the limit survival probability $S(\infty)$ is a monotonically increasing function of the plateau value $S(1)$; the more the number of survivors after Stage I, the higher will evidently be the number of immortal clusters. For $S(\infty) = 0$, $S(1)$ is trivially 0; as the $S(1) \to 1$ limit is approached, the non-trivial maximum value $S(\infty)_{\max} < 1/2$ is reached. Additionally, when $S(1)$ is small, it can be shown that $S(\infty)$ is also small, and that it depends on $S(1)$ alone. This is shown below.

We define a supercluster as a set of $k \geq 1$ connected clusters which have survived Stage I, such that all their neighbours have disappeared during Stage I. The fate of superclusters depends on their size $k$ as follows.

$\star \quad k = 1$: If a supercluster consists of a single isolated cluster, it is a survivor, because its mass exceeds the survival threshold $y_s$. For $z = 2D$ and independently of initial mass distributions, a supercluster with $k = 1$ occurs with density $p_1 = S(1)(1 - S(1))^{2D}$. This corresponds to the survival of one cluster after, and the disappearance of its $2D$ neighbours during, Stage I.

$\star \quad k = 2$: If a supercluster consists of a pair of neighbouring clusters (represented as $\bullet$) both clusters evolve according to the dynamics described above: the smaller dies out, while the larger is a survivor. We are thus left with $\bullet \circ$ or $\bullet \bullet$ in the late stages of the dynamics. Such an event takes place with density $p_2 = S(1)^2(1 - S(1))^{2(2D - 1)}$.

$\star \quad k \geq 3$: If three or more surviving clusters form a supercluster, they may a priori have more than one possible fate. Consider for instance a linear supercluster of three clusters ($\bullet \bullet \bullet$). If the middle one disappears first ($\bullet \circ \bullet$), the two end ones are isolated, and both will be survivors. If one of the end ones disappears first (e.g. $\bullet \bullet \circ$), the other two form an interacting pair, and only the larger of those two will survive forever (e.g. $\bullet \circ \circ$). The pattern of the survivors, and even their number, therefore cannot be predicted a priori.

The above enumeration implies $S(\infty) = p_1 + p_2/2 + \cdots$, where the dots stand for the unknown contribution of superclusters with $k \geq 3$. As $p_1 \sim S(1)$, $p_2 \sim S(1)^2$, and so on, we are left with the expansion

$$S(\infty) = S(1) - D S(1)^2 + \cdots$$
The dependence of $S_{(\infty)}$ on details of the initial mass distribution at fixed $S_{(1)}$ therefore only appears at order $S_{(1)}^3$. These results apply to the dilute limit, when few clusters survive stage I.

In the limit that there are many clusters which survive the fast dynamics of stage I, i.e. $S_{(1)} \to 1$, the limit survival probability, as mentioned above, reaches a non-trivial maximum value $S_{(\infty)}^{\text{max}} < 1/2$. This depends very weakly on the mass distribution; for instance, in one dimension one has $S_{(\infty)}^{\text{max}} \approx 0.441$ for an exponential distribution and $S_{(\infty)}^{\text{max}} \approx 0.446$ for a uniform distribution. We present below a way of visualising these dense distributions of immortal clusters.

If $(S_{(\infty)} = 1/2)$ on, say, a square lattice, (i.e. the highest density of immortal clusters is reached), there are only two possible ‘ground-state’ configurations of the system. These correspond to the full occupation of one of the two sublattices, with its counterpart being completely empty. In this limit, the two possible patterns of immortal clusters are each perfect checkerboards of one of two possible parities.

At every site $n$ with integer co-ordinates $(n_1, n_2, \ldots, n_D)$ we define the *survival index*

$$\sigma_n = \begin{cases} 1 & \text{if the cluster at site } n \text{ is a survivor} \\ 0 & \text{else} \end{cases}$$

and the *checkerboard index*

$$\phi_n = (-1)^{\sigma_n + n_1 + \cdots + n_D}.$$ (14)

The survival index depicts very simply the pattern of surviving clusters surrounded by empty sites: The checkerboard index, on the other hand, represents, for each site, the local choice of one of the two symmetry-related ‘ground states’, i.e., of one of the two sublattices. This is easiest to understand using a one-dimensional example: the two ground states are $++---\ldots$ or $+-+-\ldots$. All the $\phi_n$ are equal to $-1$ in the first pattern, and equal to $+1$ in the second pattern. The checkerboard index $\phi_n$ thus classifies each site according to the *parity* of the particular ground state selected locally at this site.

For generic initial conditions, i.e. a random distribution of initial masses, the immortal sites will evidently not form a perfect checkerboard. However, if the initial masses are large enough, the number of survivors of Stage I dynamics will be large, and the corresponding survival masses are large enough, the number of survivors of Stage I close to unity. In this limit, the asymptotic survival probability $S_{(\infty)}$ will be close to its ‘ideal’ value of $1/2$. The resulting pattern will now exhibit a *local* checkerboard structure, with frozen-in defects between patterns of different parities; the random structure of defects is of course entirely inherited from the (random) initial mass distribution, since the dynamics is fully deterministic. This is evident from Figure 2 which shows a map of the survival index and of the checkerboard index for the same attractor for a particular sample of the square lattice. The immortal (black) clusters in the left-hand part of the figure are surrounded by rivulets of voids, which are a consequence of initial conditions; in the right-hand figure, the deviation from a perfect checkerboard structure (all black or all white) is made clearer. The patterns make it clear that neighbouring sites must be fully anticorrelated because each immortal cluster is surrounded by voids. However, at least close to the limit $S_{(\infty)} = 1/2$, immortal sites are very likely to have next-nearest neighbours which are likewise immortal and massive. The detailed examination of survival and mass correlation functions made in a longer paper confirms these expectations.

To conclude, we have presented in this Letter a very simple ‘winner-takes-all’ model of cluster aggregation in stirred colloidal systems. Both mean-field and finite dimensional explorations of this model show a striking and a priori unexpected glassy phase; the system of interacting clusters shows *ageing* until it reaches its asymptotic state. The inclusion of fluctuations in the model via a finite-dimensional approach causes the replacement of the somewhat staid mean-field behaviour (which predicts a uniform sediment composed of one cluster at most) by something far more exciting: a random-energy landscape emerges, with many possible minima as its metastable states, and the system descends to the most accessible one. Each such metastable state is a complex pattern of isolated clusters, each of which, by virtue of its isolation, is *immortal*.

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