Scale invariance in two-dimensional reaction-limited colloidal aggregation

1995 J. Phys.: Condens. Matter 7 L397

(http://iopscience.iop.org/0953-8984/7/30/002)

J. Phys.: Condens. Matter 7 (1995) L397–L403. Printed in the UK

LETTER TO THE EDITOR

Scale invariance in two-dimensional reaction-limited colloidal aggregation

J C Earnshaw and D J Robinson†

The Department of Pure and Applied Physics, The Queen's University of Belfast, Belfast BT7 1NN, UK

Received 31 May 1995, in final form 19 June 1995

Abstract. Experimental studies of reaction-limited cluster–cluster aggregation in dense colloidal monolayers at liquid surfaces demonstrate that the system evolves to a state lacking any characteristic length scale. In particular, the structure function $S(q, t)$ diverges in the limit $t \to \infty$ and $q \to 0$, suggestive of self-organized criticality. The self-organization is reflected in the cooperative nature of the divergence.

Recent interest in colloidal aggregation [1], largely driven by the concepts of fractal geometry, has concentrated upon the structure of individual clusters or the kinetics of growth. However, very recently unexpected intercluster correlations have been discovered for rather dense colloidal systems. In particular, it has been shown [2, 3] that in diffusion limited cluster–cluster aggregation (DLCA) the non-equilibrium system evolves to a stationary scaling state characterized by a single time-dependent length scale: the structure function [2, 3], the distribution of intercluster separation and various topological properties [4, 5] are stationary or scale to universal functions. However, no such state emerges in the dense limit of reaction-limited cluster–cluster aggregation (RLCA) [2, 3], but rather the system exhibits progressively increasing intercluster inhomogeneity as aggregation proceeds [3, 4]. This paper presents evidence suggesting that RLCA represents a case of *self-organized criticality*.

It has recently been proposed [6] that spatially extended dynamical dissipative systems may exhibit a phenomenon described as self-organized criticality (SOC): without external tuning of any parameters, a system evolves to a state characterized by the absence of any intrinsic scale of length or time, structures existing on all scales up to and including the size of the system. The predictions of SOC have attracted widespread interest. The structural signature of SOC is particularly significant because algebraically decaying temporal correlations may occur even in equilibrium systems [7]; however, generic scale invariance of length has been observed in few real physical systems. One of the few examples is the fracturing of various amorphous materials [8] (but see [9]).

Our studies of RLCA in two dimensions (2D) suggest that it provides an example of a system which evolves without external influence into a state manifestly lacking any characteristic length scale. The evolution can be followed in real time. The study of aggregation in 2D rather than 3D presents certain advantages: sedimentation is absent,

† Andor Technology, The Queen's University of Belfast, Belfast BT7 1NN, UK.

0953-8984/95/300397+07$19.50

visualization of structures is simpler, the high-density limit can be realized more easily and aggregates are less likely to mechanical instability.

Our experimental methods have been described elsewhere [10]. In brief, polystyrene latex spheres of ~ 1 μm diameter were spread on the surface of an aqueous subphase. Area fractions were rather high, typically $\approx 10\%$. Due to ionization of surface groups the particles are highly charged in water and interact via long-range forces. Adding salt ($CaCl_2$) to the subphase induced irreversible aggregation, which proceeded to completion over a period of hours. The clusters observed for salt concentrations <0.5 M were consistent with RLCA [10]. Due to some mobility of the colloidal monolayers, images grabbed at various times (measured from initiation of aggregation) represent quasirandomly selected samples. We present results from a typical experiment at 0.23 M $CaCl_2$; the conclusions are fully supported by other experiments.

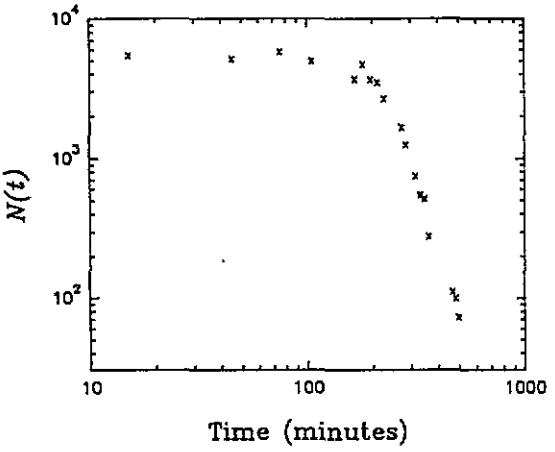

Figure 1. Total number of clusters versus time. Note the crossover from slow to rapid growth.

The aggregation kinetics show a crossover from slow to rapid growth (figure 1). In the slow regime the number of clusters is roughly constant, growth occurring via accretion of monomers, whereas in the rapid phase cluster–cluster aggregation leads to a rapid decrease in the number of clusters. While a typical micrograph contains some 3×10^4 particles, there are fewer clusters, so that some statistical fluctuations are evident in the results. Separate experiments are qualitatively but not quantitatively similar, so that it is not possible to average data to improve the statistics, as with computer simulations.

Representative micrographs are shown in figure 2. The inhomogeneity apparent in these images contrasts sharply with the comparatively ordered intercluster structure which develops in DLCA [3, 4]. In particular the cluster size distribution shows a power law decay from monomers up to a time-dependent cut-off [10]. In the later stages of aggregation the largest clusters were comparable in size with the micrograph itself: we refer to such clusters as 'spanning' ones.

We have computed the structure functions for the system as the square modulus of the 2D Fourier transform of the central 512×512 pixel portion of each micrograph:

$$S(q,t) \propto \left| \int \rho(r,t) e^{iq \cdot r} dr \right|^2 \tag{1}$$

where $\rho(r,t)$ is the local density. Figure 3 shows $S(q,t)$ obtained by azimuthally averaging the 2D functions. The functions are quite different from those observed for DLCA [3, 5].

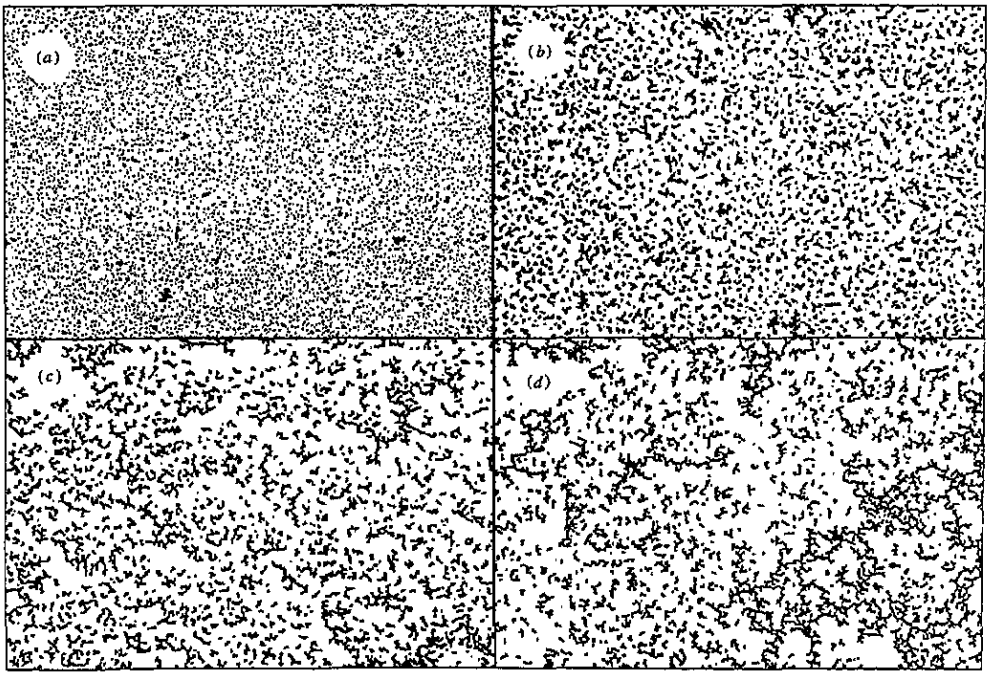

Figure 2. Four digitized images (730 × 486 μm^2) of the colloidal monolayer on a 0.23 M $CaCl_2$ substrate at (a) 75, (b) 270, (c) 315, (d) 330 min after initiation of aggregation. The polydispersity characteristic of RLCA is apparent.

At the very earliest times the present $S(q,t)$ appears almost flat for q from ~ 0.04 μm^{-1} to ~ 1 μm^{-1}. As time progresses a characteristic length scale seems to evolve, apparent in a rather broad peak in $S(q,t)$ (the breadth reflects the cluster size polydispersity of RLCA [11]). The peak persists for some time, but by the onset of rapid aggregation the dip at low q has filled in. Thereafter $S(q,t)$ at relatively low q simply increases until, for the final (top) three curves of figure 3, it follows a power law variation towards the lowest accessible values of q, with exponent close to the fractal dimension (d_f) expected for RLCA. The dashed line is *not* a fit to the data, but represents the fractal scaling expected for RLCA ($d_f = -1.55$). In this final phase, in which $S(q,t)$ appears quasistationary on the experimental time scales, the system evinces no characteristic length scale. This final scale-invariant state was found for all experiments in which RLCA occurred (i.e. <0.5 M $CaCl_2$), indicating that it is independent of the detailed interactions involved.

$S(q,t)$ reveals the *global* properties of the system, which comprises a heterogeneous collection of aggregates, covering a wide range of sizes, from monomers to rather large clusters. Analysis of the structure of the individual clusters confirms that they are fractal in nature, up to the largest length scales: figure 4 shows the scaling of the number of particles lying within a box of side l centred on the cluster centroid (the 'sandbox' method [10]) averaged over all clusters, including spanning ones, for the final three micrographs. The discontinuities at large l are apparently due to the rather poor cluster statistics in this regime. However, the data are all parallel to the linear variation shown: the number of particles within the box evidently scales as l^{d_f} for all l. While the fractal dimension, at 1.63 ± 0.01, is rather higher than expected for RLCA, it known that some internal restructuring of the aggregates occurs [10]. The clusters are thus separately fractal at all stages of aggregation,

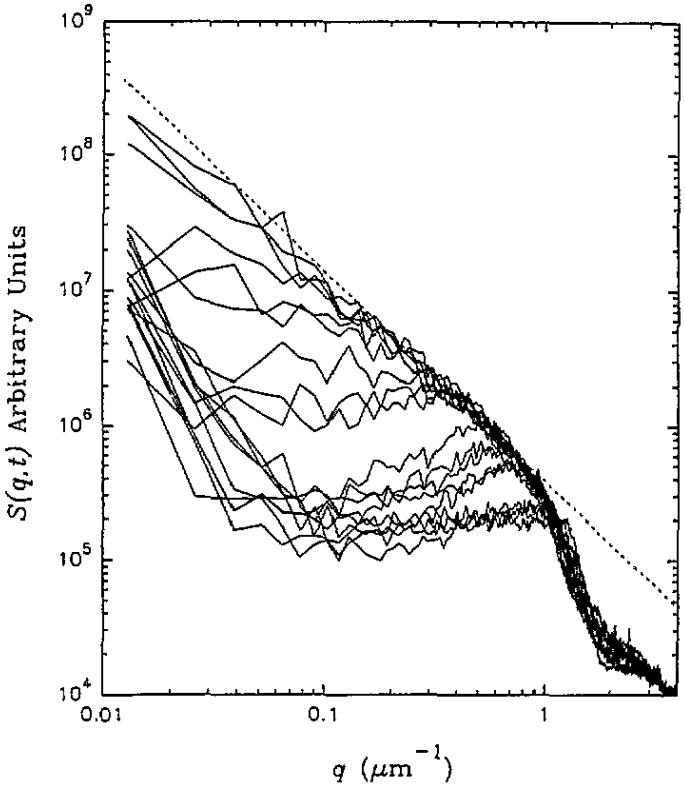

Figure 3. $S(q,t)$ for all micrographs, times running from 15 (bottom) to 495 min (top) after initiation of aggregation ($q = 0$ peak omitted). The dashed line has slope of $-d_f$ (=1.55).

but only in the later stages is their combined effect such as to cause the scaling of $S(q,t)$ to extend towards the lowest accessible q.

The ultimate state of the system thus lacks any characteristic length scale. No fine tuning of any parameter is required to achieve this, but rather the system spontaneously evolves to this scale-invariant state. Now, the spatial signature of SOC is power law divergence of

$$\lim_{q\to 0}\lim_{t\to\infty} S(q,t) \tag{2}$$

where some care may be required in the order in which the limits are taken. We thus consider the temporal evolution of $S(q,t)$ for various q values in the region of power law scaling (figure 5). For $t \leqslant 300$ min $S(q,t)$ is relatively unchanging for all q, reflecting the initial period of slow growth. Thereafter $S(q,t)$ rises to a q-dependent saturation value, albeit subject to fluctuations (cf. figure 3). It thus has a well defined $t \to \infty$ limit. Figure 6 shows that the average of $S(q,t)$ in this saturation limit diverges as a power law in q down to almost the lowest accessible q value (already apparent in figure 3). Departures from scale invariance at low q are inevitable for any finite sample of a system (such as the present video images); it is these low q effects which reduce the exponent of the fit of figure 6 slightly compared to the value of 1.55 expected for RLCA. Real time observations during the final stages clearly revealed clusters and voids larger than the video field of view, suggesting the existence of longer-range correlations.

RLCA thus exhibits divergence of the $t \to \infty$, $q \to 0$ limit of $S(q,t)$. The way this

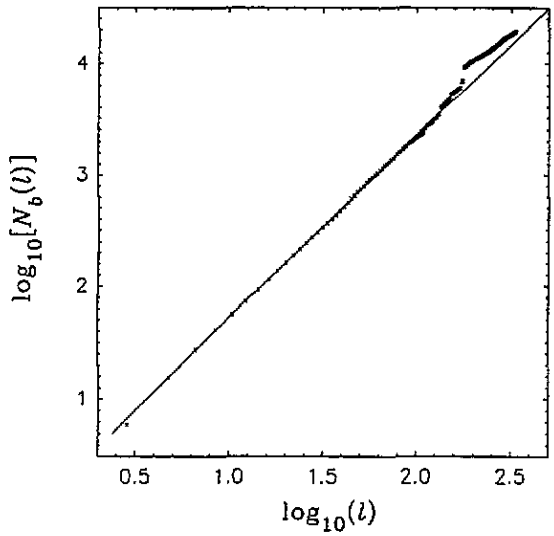

Figure 4. The fractal scaling, determined by the sandbox method, of all clusters, including spanning ones, for the final three micrographs. $N_b(l)$ is the number of particles within a cluster lying inside a box of side l centred near the cluster centroid (see [10]). The line is a fit for $\log(l) \leqslant 2.1$, and has slope 1.63 ± 0.01.

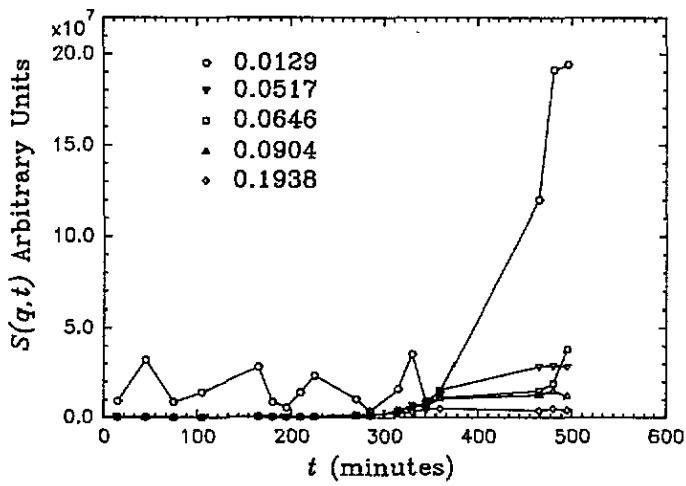

Figure 5. The evolution of $S(q, t)$ as $t \to \infty$ for selected values of q (indicated in the legend).

final state develops is instructive. We thus reconsider the temporal divergence of $S(q, t)$. As shown in figure 7, this divergence appears, within the fluctuations of the data, to follow a power law in t, indicated by the solid line in the figure. (An exponential divergence would describe the data almost as well.) Moreover, for all q below a threshold value ($\sim 0.2\ \mu m^{-1}$) the power law divergence collapses to a unique straight line, occurring later for lower q. The initiation of the divergence appears to move progressively from about 195 min to 360 min as q is reduced from $0.1938\ \mu m^{-1}$ to $0.0129\ \mu m^{-1}$, the lowest accessible value.

We regard the superimposition of the temporal divergence of $S(q, t)$ as the most significant feature of the present results. It demonstrates the cooperative nature of the

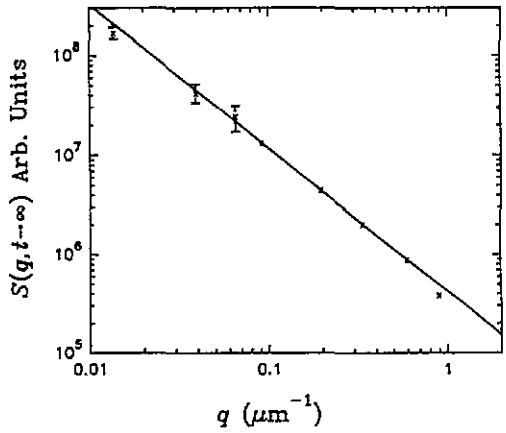

Figure 6. The $q \to 0$ divergence of $S(q, t \to \infty)$. The linear fit has a slope of -1.45.

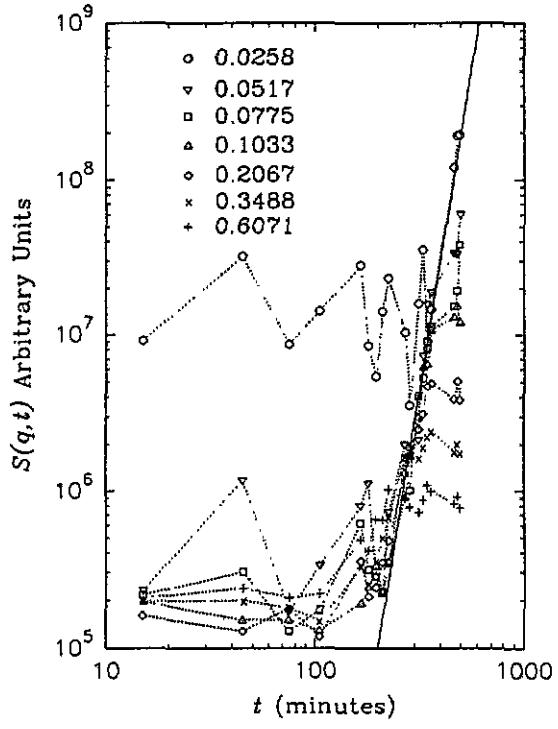

Figure 7. A log–log plot of the evolution of $S(q, t)$ for selected q (indicated in the legend). The solid line is discussed in the text.

approach to the scale-invariant state. The high-q divergence is an essential prerequisite for the low-q divergence to occur. This could arise from the trivial requirement that smaller clusters must exist before large-scale clusters can form. However, this is also true for DLCA, in which the aggregation never leads to generic scale invariance as seen for RLCA. The present divergence thus appears to go beyond this, requiring self-organization of the clusters into a state in which individual degrees of freedom interact to maintain generic

scale invariance [6].

The present results are intrinsic to RLCA and do not arise from experimental artifacts. Such long-range influences as convection in the subphase or unscreened forces propagating through the air [12] are also present at higher salt concentrations, where aggregation leads to a state dominated by a single length scale [3].

Certain earlier studies have found evidence that colloidal aggregation can lead to a state lacking any characteristic scale of length: in an earlier 2D study (apparently involving RLCA) the existence of 'giant' clusters exhibiting long-range spatial correlations and separate areas of smaller isolated clusters were demonstrated [13], while in 3D RLCA $S(q, t)$ is found to evolve with time to a power law divergence as $q \to 0$ [14]. The present results extend this previous work by demonstrating the fractal nature of the individual clusters up to the largest size and the cooperative nature of the approach to the scale invariant state.

In summary, RLCA involves the evolution of the 2D colloidal system to a state in which fractal structures on all length scales coexist and in which $S(q, t)$ diverges as $q \to 0$. The divergence of $S(q, t)$ at low q is shown to be cooperative in nature. In previous publications [4, 5] we have shown other evidence that in RLCA the 2D colloidal system evolves in the direction of increasing intercluster disorder and inhomogeneity, including the distributions of intercluster separation and the cluster coordination number and various topological properties. This contrasts with DLCA, which leads to long-range order. While the analysis of intercluster organization becomes less straightforward when spanning clusters appear, the trends noted are consistent with progression towards a state exhibiting SOC. We have shown elsewhere that the distribution of cluster sizes in RLCA is a power law with a large size cut-off [10]. This again fits in with the hypothesis that RLCA is an example of SOC.

Further work is required to pursue the suggestion that RLCA leads to SOC. One focus of such work could be the temporal fluctuations expected for SOC. We know of no experiments or simulations adequate to address this point.

This work has been supported by the SERC. A helpful discussion with Dr P B Warren is gratefully acknowledged.

References

[1] Meakin P 1988 in *Phase Transitions and Critical Phenomena* vol 12, ed C Domb and J L Lebowitz (New York: Academic) p 335
[2] Carpineti M and Giglio M 1992 *Phys. Rev. Lett.* **68** 3327
[3] Robinson D J and Earnshaw J C 1993 *Phys. Rev. Lett.* **71** 715
[4] Earnshaw J C and Robinson D J 1994 *Phys. Rev. Lett.* **72** 3682
[5] Earnshaw J C and Robinson D J 1995 *Physica* A **214** 23
[6] Bak P, Tang C and Wiesenfield K 1987 *Phys. Rev. Lett.* **59** 381; 1988 *Phys. Rev.* A **38** 364
[7] Grinstein G, Lee D-H and Sachdev S 1990 *Phys. Rev. Lett.* **64** 1927
[8] Oddershedde L, Dimon P and Bohr J 1993 *Phys. Rev. Lett.* **71** 3107
[9] Bai Y, Lu C, Ke F and Xia M 1994 *Phys. Lett.* A **185** 196
[10] Robinson D J and Earnshaw J C 1992 *Phys. Rev.* A **46** 2045; **46** 2055; **46** 2065
[11] Hasmy A, Foret M, Pelous J and Jullien R 1994 *Phys. Rev.* B **50** 6006
[12] Hurd A J 1985 *J. Phys. A: Math. Gen.* **18** L1055
[13] Armstrong A J, Mockler A J and O'Sullivan W J 1986 *J. Phys. A: Math. Gen.* **19** L123
[14] See, e.g.,
Schaefer D W, Martin J E, Wiltzius P and Cannell D S 1984 *Phys. Rev. Lett.* **52** 2371
Dimon P, Sinha S K, Weitz D A, Safinya C R, Smith G S, Varady W A and Lindsay H M 1986 *Phys. Rev. Lett.* **57** 595
Lin M Y, Lindsay H M, Weitz D A, Ball R C, Klein R and Meakin P 1990 *Phys. Rev.* A **41** 2005