Colloids stick to fractal rules

John Rarity

A two-dimensional projection of a tree's root system looks remarkably like an overhead view of a river delta. Both are random fractals and the similarities arise from similar large-scale rules of growth which seem not to be influenced by their detailed constituents. The attraction of fractal theories of nature is that the application of such large-scale geometrical rules can lead to simple universal properties in many complex, random-growth processes. One such process that has been popular with the colloid scientist since the days of the Faraday gold sol is the phenomenon of colloidal aggregation. In their letter elsewhere in this issue (Nature 339, 360–362; 1989), M.Y. Lin et al. present electron micrographs of aggregates of colloidal gold, polystyrene and silica: the obvious similarities between these provide compelling visual evidence for universalities in their reactions.

Colloids, being suspensions of small particles in a fluid, are thermodynamically unstable to aggregation and survive only because of strong repulsive forces between the particles. Aggregation is thus inevitable when repulsive barriers are reduced, by various means specific to the constituents of the colloid. Two rate-limiting processes control the growth of random aggregates from the suspension. The first is the time taken for clusters to diffuse into contact with each other to allow sticking to occur; the second is the probability of sticking on contact.

The large-scale rule which leads to fractal properties of the aggregates is simply the geometrical limitation on close diffusive approach of two irregularly shaped objects. If particles stick on first contact and the bonds are stiff, one expects quite tenuous structures to evolve. If there is a low sticking probability per contact, the aggregates will have time to explore the contact surface and can interpenetrate somewhat before sticking, leading to less tenuous structures. The fractal nature of the resulting structure arises because each successful collision leads to a drop in the mean density of the aggregate and, on average, we can relate the mass contained in the aggregate to a measure of its radius \( R \) by a power law \( M \propto R^d \), where \( d \) is the fractal dimension, which can range from 3 for space filling objects (or aggregates whose density does not drop with mass) to 1 in the case of extremely tenuous reaction-limited aggregation (RLCA). Lin et al. measure the fractal dimension of large aggregates in suspension using static (elastic) light scattering. The inverse of the scattering vector \( q \), the difference between the input and scattered wavevectors, defines a length scale (for coherent scattering) and the light scattered from an aggregate depends on the amount of mass typically found within a box of these dimensions. As a result the scattered intensity \( I(q) \) falls with increasing scattering angle following the power law form \( I(q) \propto q^{-2} \). All three aggregated systems show fractal dimensions \( d \approx 2.1 \) for RLCA and \( d \approx 1.85 \) for DLCA as suggested by the micrographs.

There is also good reason to believe that the kinetics of the aggregation reaction is also universal. The present workers follow the kinetics using dynamic light-scattering measurements to estimate a mean aggregate radius \( R \) and show data which illustrate that \( R \propto t^\phi \) (implying linear growth of aggregate mean mass) for DCLA and exponential growth, \( R \propto e^\omega t \), for RLCA with all three systems studied. These data support the predictions of recent theory and simulations based on the simple rules of diffusion time and sticking probability governing the kinetics. Is that it? Is the aggregation reaction now well understood? The neatly wrapped results presented here contrast sharply with those of new work by J.P. Wilcoxon et al. (Phys. Rev. A 39, 2675–2688; 1989), who have been studying the aggregation of colloidal gold. Their article also reprints several earlier results from Lin et al. which at times disagree with those of the present work. Two main points of disagreement with the postulated universal kinetics are reported. First, Wilcoxon et al. point out that the strong optical resonance in aggregated gold at 680 nm can lead to measured fractal dimensions being wavelength dependent and report measurements of fractal dimensions ranging from 1.6 to 2 apparently uncorrelated with the aggregation kinetics. Second, they report a power-law growth of aggregate radius in DCLA with \( R \propto t^\phi \), when from the above we expect an exponent of...
1/d = 0.55. Both these results do not necessarily contradict the results of Lin et al. but do illustrate the difficulty of unambiguously interpreting light-scattering data.

Lin et al. made all their new measurements at a wavelength of 488 nm, well away from the optical resonance and thus should lead to a reasonable estimate of fractal dimension. In earlier work, lower values of the DCLA fractal dimension were reported which may be attributable to neglect of optical resonance and multiple scattering effects. Dynamic light-scattering data can be ambiguous because aggregating systems contain broad size distributions of randomly shaped aggregates. For these systems the technique measures an apparent radius dependent on scattering vector, because rotational motion of larger aggregates distorts the result. Lin et al. use a scaling approach based on multi-angle dynamic light scattering to estimate a true radius whereas Wilcoxon et al. use a simpler low-angle approach which may lead to distortion (in fact their data agree with uncorrected data from Lin’s group).

The paper by Wilcoxon et al. does, however, highlight the earlier inconsistencies of Lin et al., a typical problem of rushing into print in a rapidly moving field. Although Lin’s group may need a little chiding for having in the past published interpretations and results that had flaws, the present work conveys me of universality in colloid aggregation. But there are exceptions to every rule.

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MATHEMATICS

Mock theta conjectures

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One of the most unusual people in the annals of mathematical research is Srinivasa Ramanujan, a self-taught Indian mathematician whose premature death left a rich legacy of unproved theorems. Ramanujan was preeminent in an un-fashional field — the manipulation of formulas. He tended to state his results without proofs — indeed on many occasions it is unclear whether he possessed proofs in the accepted sense — yet he had an uncanny knack of penetrating to the heart of the matter. Over the years, many of Ramanujan’s claims have been established in full rigour, although seldom easily. The most recent example, the ‘mock theta conjectures’, is especially striking, because the results are in question were stated in Ramanujan’s final correspondence with his collaborator Godfrey H. Hardy. The conjectures have recently been proved by Dean Hickerson (Invent. Math. 94, 639-660; 1988), following fundamental work of George Andrews and F.G. Garvan (Adv. Maths 73, 242–255; 1989).

The word ‘theta’ refers to a remarkable range of special functions, known as theta functions, investigated at great length by Carl Gustav Jacob Jacobi (1804–51). They arose during the nineteenth century and rapidly became a major research area. Attempts to calculate the length of a general arc of an ellipse using integral calculus led to simple-looking expressions which obstinately refuse to yield an explicit integral in terms of known functions such as polynomials or trigonometric functions.

The reason turns out to be that these integrals require a genuinely new breed of function, called ‘elliptic’ functions. In a sense, elliptic functions are generalizations of the trigonometric functions, because an ellipse is a generalized circle and arc-lengths of circles involve trigonometry. But they have a deeper mathematical property. Trigonometric functions are periodic, that is, they repeat their values if a constant, the period, is added to the independent variable. The period of the sine function, for example, is 2π, because sin(x+2π) = sin(x). Elliptic functions are doubly periodic: they have two independent periods, which in general are complex numbers, not real ones. This property singles them out and renders them worthy of serious study as pure mathematics, whereas their many applications to problems in number theory and dynamics make them useful enough to earn their keep in a competitive entrepreneurial environment. Although they have all but disappeared from the undergraduate mathematics course, they remain important at the frontiers of research.

Jacobi introduced four associated functions, the theta functions, which in the words of Morris Kline (Mathematical Thought from Ancient to Modern Times; Oxford University Press, 1972) are “the simplest elements out of which the elliptic functions can be constructed”. He also obtained expressions for them in the form of infinite series and infinite products and proved a number of remarkable identities.

Ramanujan’s last letter to Hardy (S. Ramanujan in Collected Papers, 354–355; Cambridge University Press, 1927) introduces ten new functions, occurring in two groups of five. They are defined by series which in some respects are similar to Jacobi’s, and Ramanujan asserted that they share many analogous properties, though, as usual, he gave no proofs. They are accordingly known as mock theta functions and said to be of the ‘fifth order’ to distinguish them from related functions found elsewhere in Ramanujan’s works.

But are they genuine mock theta functions, rather than ordinary Jacobi theta functions in some as yet unpenetrated disguise? Real fakes rather than fake fakes? It is a subtle question, but an important one. If Ramanujan’s mock thetas are really real thetas, they immediately lose any interest. Of course fancy combinations of genuine thetas behave like genuine thetas. As with certain art forgeries where the original artist has gone out of fashion but the forger has acquired notoriety, only a genuine fake is interesting. To put it another way: real thetas are interesting, and mock thetas share their remarkable properties, so provided that they are really new, mock thetas are also interesting.

And that is where the mock theta conjectures come in. Ramanujan recorded his results in a series of notebooks. One temporarily went missing, becoming the romantic ‘lost notebook’, but eventually turned up safe and sound. Following early work of G.N. Watson, George Andrews discovered a formula in the lost notebook which, if true, means that the mock thetas are genuine fakes. In his paper with Garvan cited above, he shows that this formula is equivalent to two slightly involved statements in number theory. These concern the partitions of a given integer — the ways of writing it as a sum of smaller integers. The original papers should be consulted for the details.

Hickerson has now proved these number-theoretic conjectures, so the mock thetas are genuine fakes and are therefore interesting new functions worthy of further study. The proof involves delicate manipulations of infinite series of a kind that would have delighted Ramanujan. The astonishing complexity of the proof underlines, yet again, the depth of Ramanujan’s genius. It is very hard to see how anyone could have been led to such results without getting bogged down in the fine detail. Hickerson has extended his methods (Invent. Math. 94, 661–677; 1988) to tackle the seventh order mock theta functions, also introduced by Ramanujan and equally enigmatic. They too prove to be genuinely mock.

Ramanujan was the formula man par excellence, operating in a period when formulas were out of fashion. Today’s renewed emphasis on combinatorics, inspired in part by the digital nature of computers, has provoked a renewed interest in formal manipulations. The half-forgotten ideas of Srinivasa Ramanujan are breathing new life into number theory and combinatorics.

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