Dynamic Self-Assembly of Rings of Charged Metallic Spheres

Bartosz A. Grzybowski,* Jason A. Wiles, and George M. Whitesides*

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138

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This Letter describes dynamic self-assembly in a system of stainless steel spheres (~1 mm in diameter) rolling on a flat dielectric surface under the influence of an external magnetic field that rotates parallel to the plane of the surface. As the spheres move, they charge triboelectrically. Self-assembly is mediated by two types of electrostatic interactions among these charges: (i) attraction between negatively charged regions of the surface and positively charged spheres and (ii) repulsion between the like-charged spheres. The spheres organize into highly ordered rings as a result of these electrostatic interactions.

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Dynamic self-assembly (DySA)—that is, self-assembly that requires continuing dissipation of energy [1,2]—occurs on length scales from molecular to global, and underlies processes ranging from the transfer of genetic information [3] to the creation of ordered vortex flows in oceans [4]. Although dynamic self-assembling systems are ubiquitous, few are understood in quantitative detail [5–8], and little is known about the general principles that govern them. We have previously suggested that competition between attractive and repulsive forces (at least one of which depends on the flux of energy through the system) provides one basis for DySA [9,10]. Here, we describe a dynamic system in which spontaneous development of order is mediated by competing electrostatic interactions and by feedback. The components of this system move in an environment that they themselves have modified, and the system evolves in response to its own history. Although the symmetries of the final, ordered structures are always the same (e.g., concentric rings), their internal characteristics (e.g., occupancies of the rings) vary between experiments: this system is complex [11,12] in the sense that the knowledge of the dynamics of its *isolated* components is insufficient to determine their *collective* behaviors.

Superparamagnetic spheres ($n = 25$–1000) made of type 316 stainless steel [Small Parts (http://www.smallparts.com), Catalog No. B-BNMX-1M, 1 mm in diameter, sphericity $= 0.0025$ mm; $\rho = 7.972$ g/cm^3] were placed in a polystyrene (PS) Petri dish (VWR, Catalog No. 25384-056) [Fig. 1(a)]. A permanent bar magnet of dimensions 5.6 cm $\times$ 4 cm $\times$ 1 cm and magnetization $M \sim 1000$ G along its longest dimension was placed at a distance $h = 1$ cm below the bottom of the dish, and rotated with angular velocity ω between 300 and 1100 rpm (revolutions per minute). Under the influence of the time-dependent magnetic field generated by the rotating magnet, the spheres rolled in circular paths on the dielectric surface (see Ref. [13] for more information). As they did so, remarkably, they organized themselves into concentric rings (Fig. 2). The origin of this organization was triboelectric charge separation [14–16] between the moving spheres and the substrate. This charging gave rise to two electrostatic interactions: (i) an attraction between negatively charged regions of the surface and positively charged spheres and (ii) a repulsion between the positively charged spheres. Because the amount of charge accumulated on the spheres increased with time, the magnitudes of both of these interactions also increased with time. The time-dependent interplay between these interactions led to the formation of ordered structures.

Figure 2 illustrates the time evolution of an ensemble of 500 spheres. In the absence of the rotating magnetic field, the spheres formed stationary, orderless clusters above the poles of the magnet [Fig. 2(a)]. When the magnet rotated, these clusters moved in the counterclockwise direction of rotation of the magnet. The clusters elongated along the direction of motion and their thickness in the perpendicular direction decreased [Fig. 2(b)]. Approximately ~10 s after setting the system in motion, the forward and the trailing ends of the clusters met and formed a thick ring (a swarm) with little local order [Fig. 2(c)]. As the spheres continued to accumulate more charge, separate orbits developed within the swarm. At first, these orbits were ill-defined and spheres exchanged between them [Fig. 2(d)]. After roughly 1 min, the rings became distinct, and exchange stopped. Within each ring, at this stage, the spheres were still not distributed uniformly; it took another 2–5 min before the separations between spheres within a ring equalized [Fig. 2(e)]. The assembly remained stable for another several minutes, until one (or several) sphere(s) adhered to the surface, stopped, and blocked the motion of the remaining spheres on the same ring so that they collapsed into an arc structure [Fig. 2(f)]. The ordered dynamic structure during the later stages of the experiment ($t \gtrsim 2$ min) could also be frozen without disrupting the ordering of the spheres by slowly decreasing ω (and, consequently, the precession rate Ω of the spheres around the dish) until a static structure ($\Omega = 0$ rpm) was obtained.

After the structure had formed, we visualized the distribution of electrostatic charges on the surface by

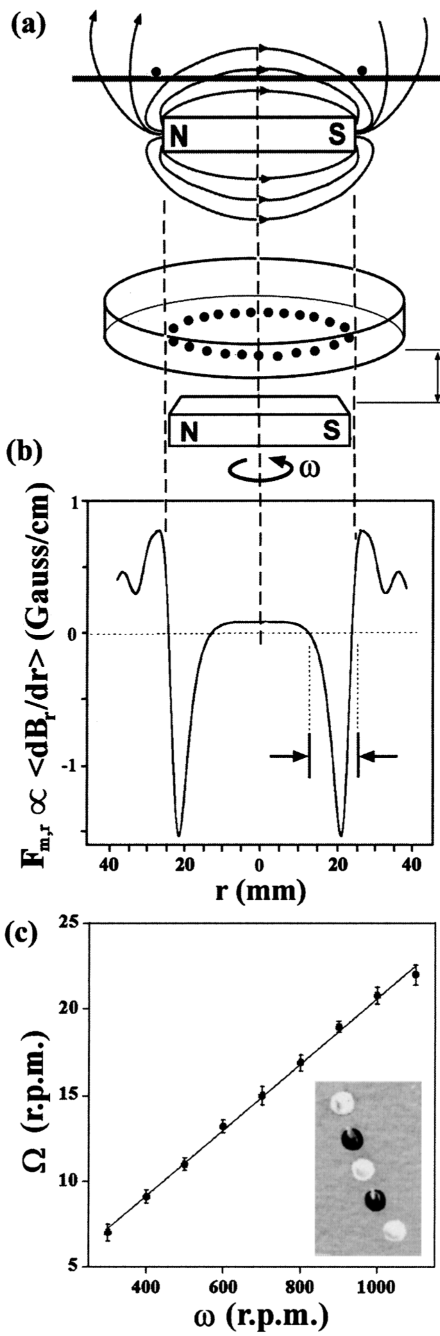

FIG. 1. (a) Stainless steel spheres roll on a dish made of PS under the influence of the magnetic field produced by a rotating permanent bar magnet, and so separate charge triboelectrically. The forces acting on an isolated sphere are shown in the inset. The curves in (b) give the time average (over one revolution of the magnet) of the radial derivative of the magnetic induction $\partial B_r/\partial r$ as a function of r, evaluated at $h = 10$ mm. This average is proportional to the radially directed magnetic force $F_m(r)$ acting on the metallic spheres in the plane of the PS support. (c) The spheres roll on the surface under the influence of the azimuthal component of the rotating magnetic field, and travel one rotation per one revolution of the magnet. The inset has five snapshots showing a rolling motion of a 1 mm sphere that was painted half black and half white.

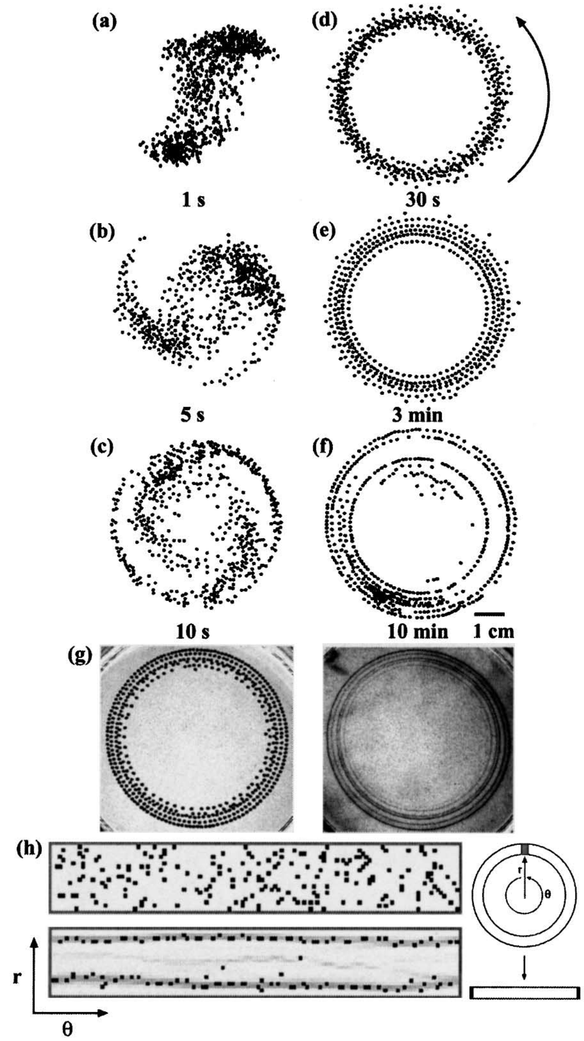

FIG. 2. (a)–(f) Evolution of dynamic ring structures formed by 500 stainless steel spheres rolling over a flat surface of PS at $\Omega = 20$ rpm ($\omega = 900$ rpm). (g) The picture on the left shows a stable, rotating ring structure formed by 500 spheres. In the picture on the right, the spheres were removed, and the surface was dusted with graphite powder. (h) Computer simulation of the evolution of 200 randomly distributed spheres (upper picture) into two rings (lower picture). The charges on the spheres and surface are indicated by shading: uncharged spheres, black; highly charged spheres, dark gray; uncharged surface, white, highly charged surface, light gray.

removing the spheres with a strong magnet, and dusting the surface with fine (1–2 μm) graphite powder. Because the electric field produced by surface charges induced electric dipoles in the graphite dust particles, they deposited preferentially onto the regions of the surface with highest charge density. These regions were rings that corresponded to the orbits of the spheres, and the amount of graphite in each ring correlated with the number of spheres that had occupied that orbit [Fig. 2(g)]. The rings of graphite did not form when the surface was discharged by an electrostatic gun prior to dusting.

The patterns in Fig. 2 reflected the interplay between magnetic and electrostatic interactions acting in the system. Using a standard current-sheet method (see Ref. [13]), we calculated the average magnetic field produced by the rotating magnet and derived from it the magnetic force $F_{m,r}$ that acted along the radial direction on all spheres on the PS surface. Because, as we verified experimentally, the positions of the spheres did not change substantially (~ 3 mm) during one revolution of the magnet, $F_{m,r}$ could be well approximated as centrosymmetric. The magnitude of this force was proportional to the time average—over one revolution of the magnet—of the gradient of the radial component of magnetic induction at the location (r, θ, z) of a sphere: $F_{m,r} \propto \langle \partial B_r(r, z)/\partial r \rangle$. Figure 1(b) shows the profile of $F_{m,r}$ in the plane of the PS surface: the spheres localize in the annular region around the radial location where $F_{m,r}$ reverses sign ($r \sim 15$–20 mm).

The induced magnetic moments of the spheres confined to this region interacted with the magnetic field produced by the rotating magnet. For every complete revolution of the magnet, each sphere performed one full rotation around the axis joining its center and the center of the magnet. Consequently, the rotating spheres rolled on the surface along circular paths and in the direction of rotation of the magnet. The precession rate Ω of the spheres around the axis of rotation of the magnet was proportional to ω, with the proportionality coefficient approximately equal to the ratio of sphere diameter and the diameter of the circle traced by the spheres [Fig. 1(c)].

As the metal spheres rolled across the PS surface, spheres and surface developed opposite charges. To investigate the kinetics of separation of charge, we performed a set of experiments in which we allowed different numbers of spheres to roll on a PS support for increasing intervals of time; we then measured the charges of these spheres by transferring them into a Faraday cup connected to an electrometer. We found that the charge developed on each sphere varied approximately exponentially with time, $q(t) = q_{\max}[1 - \exp(-kt)]$, where $q_{\max} \sim 0.5$ nC and $k \sim 0.045$ s^{-1}.

The emergence of well-defined orbits is the consequence of the circular motions of the spheres. After the first full revolution around the dish, the spheres revisit the parts of the PS support with which they had previously separated charge, and their orbits change in response to the distribution of surface charge they encounter. Because an exact analytical solution of the equations of motions for a system that is composed of so many interacting components and is so dependent on its own history is impossible, we analyzed the formation of the ring patterns numerically. In our simplified model (see Ref. [13]), the spheres moved over a surface represented as a union of rectangular cells [Fig. 2(h)]. Based on the experimentally observed exponential kinetics of charging of a single sphere rolling on the PS support, we assumed that the amount of charge transferred per unit time between a surface cell of charge q_S and a sphere of charge q_B depended exponentially on the difference of these charges, i.e., $\Delta q/\Delta t \propto \exp(q_S - q_B)$.

Initially, the spheres were randomly distributed over the surface (or parts of the surface); we calculated the forces that acted on them. These forces included (i) the Coulombic attraction between the spheres and the charged surface cells, (ii) pairwise Coulombic repulsions between the spheres, and (iii) constant azimuthal magnetic force (“motive force”) that acted on all spheres. New positions of the spheres were calculated from the net forces on each sphere. The charges on the spheres and on the surface cells below them were updated according to the first order kinetics (see above), and the simulation cycle was repeated.

The simulations suggested that ring patterns formed by a self-amplifying process. The parts of the surface that initially had more spheres rolling over them than others charged preferentially and acted as “funnels” that attracted more spheres moving in their vicinity. The more spheres entered the funnel regions, the more charged these regions became and, in turn, the more spheres were attracted towards them. This process reinforced the trajectories (orbits) passing through the funnel regions, and ultimately all spheres moved in several (2–5 in our simulations) well-defined rings. Once confined to a ring, the spheres minimized electrostatic repulsions by equalizing their separations.

Although the mechanism of ring formation was independent of the initial configuration of the spheres, the radii and the occupancies of the rings (and in some cases even the numbers of the rings) varied both in experiments and in simulations with the same numbers of spheres (see Ref. [13]). The localization of potential funnels on the surface, and ultimately also the radii of the resultant rings, depended on the number of spheres that rolled over them in the early stages of the evolution of the system.

Because the system was highly sensitive to initial conditions, we expected that additional small perturbations would have large effects on the final structures. We introduced these perturbations by modifying the PS surfaces, inscribing thin (~ 100 μm) lines or dots into the surface [Figs. 3(a)–3(e)]. Initially, when the spheres were weakly charged, they traveled unhindered over these incisions. As the charging progresses, the density of negative charges in the incisions became higher than on the flat portions of the surface [Fig. 3(f)], and Coulombic interactions at these incisions dominated the motions of the spheres. Grooves perpendicular to the direction of motion presented barriers capturing spheres, and those aligned along the direction of motion served as “rails” guiding the spheres. The complex patterns that emerged reflected the influence of these electrostatic barriers on the evolution of the ensemble.

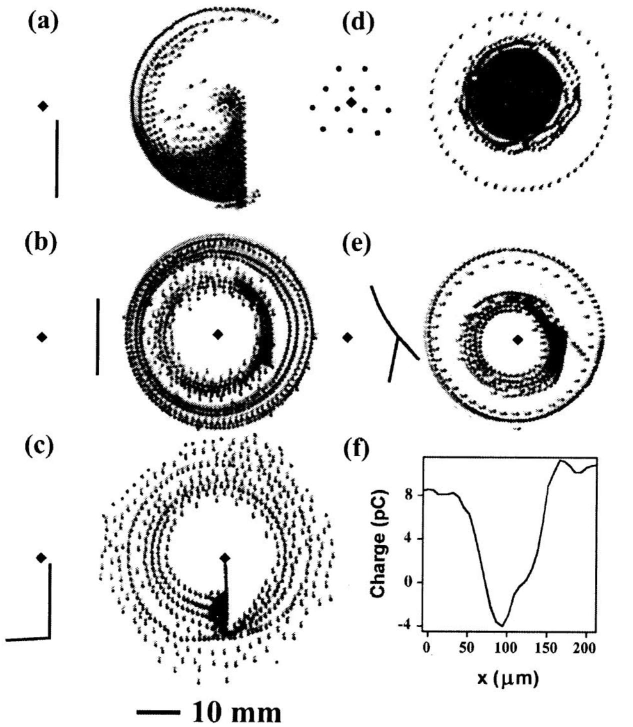

FIG. 3. Formation of noncentrosymmetric patterns of stainless steel spheres on PS surfaces that were modified by making ~100 μm incisions into them by using a scalpel. The pictures were taken ~3 min after setting the system in motion; the rotation rate ω of the magnet was 900 rpm. The scale and geometry of the incisions are illustrated schematically by lines adjacent to each image; the locations of the axis of rotation of the magnet are indicated by solid diamonds (◆). The graph in (f) is a Kelvin probe image of a surface charge across the width of an incision charged by rolling 100 spheres over it for 1 min.

This Letter described a *rationally* designed, dynamic self-organizing system, whose remarkable feature is the partial unpredictability of the ordered structures it forms; this unpredictability is the consequence of the strong dependence of the system on its own history. We believe this system is an interesting candidate with which to study the evolution and controllability of multibody ensembles. In particular, the dynamic circular aggregates could model formation of circular swarms by large numbers of self-propelled organisms [17,18]. We suggest that the principles that underlie self-organization in our system, that is, competition between attractive and repulsive interactions, and feedback, provide a general strategy with which to engineer nonequilibrium self-organization and evolution. Dynamic systems—analogous to the one we described—that evolve into structures of markedly different morphologies in response to small external perturbations are plausible precursors to *adaptive matter* [19,20]. This work can also have practical ramifications. We have recently verified that the degree of order which developed in the system correlates with the magnitude of the charge separation between the rolling spheres and the surface; this system is thus an analytical tool for studying and *quantifying* contact electrification.

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*To whom correspondence should be addressed.

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