

Phase separation of 2D meso-scale Coulombic crystals from meso-scale polarizable “solvent”†‡

George K. Kaufman, Samuel W. Thomas III, Meital Rechtes, Bryan F. Shaw, Ji Feng and George M. Whitesides*

Received 5th August 2008, Accepted 25th September 2008

First published as an Advance Article on the web 16th October 2008

DOI: 10.1039/b813590h

This paper describes the phase separation of millimetre-scale spheres based on electrostatic charge. Initially, polymeric (Teflon, T; Nylon-6,6, N) and metallic (gold-coated Nylon-6,6, Au^N) spheres are uniformly mixed in a two-dimensional (2D) monolayer on a gold-coated plate. Oscillating the plate vertically caused the spheres to charge by contact electrification (tribocharging). Positively charged N and negatively charged T spheres attracted each other more strongly than they attracted the capacitively charged, Au^N spheres. The T and N spheres formed 2D Coulombic crystals, and these crystals separated from the Au^N spheres. The extent and rate of separation increased with increasing amplitude of agitation during tribocharging, and with decreasing density of spheres on the surface. At high surface density, the T and N spheres did not separate from the Au^N spheres. This system models the 2D nucleation of an ionic crystal from a polarizable liquid.

This communication describes the separation of a mixture of ~3 mm spheres (Nylon-6,6, N; Teflon, T; and gold-coated Nylon, Au^N)—on agitation in two-dimensions—into an ionic crystalline, two-dimensional (2D) phase having the composition T[−]N⁺, and a disordered phase comprising Au^N spheres.¹ Teflon and Nylon spheres, when agitated together, charged oppositely by contact electrification.^{2,3} These polymeric spheres aggregated and separated from the gold-coated spheres, which were, on average, electrically neutral (Fig. 1). The objectives of this research were: (i) to test our prediction that mixtures of oppositely charged objects would crystallize and separate from non-charged objects when agitated, and (ii) to explore the effects of experimental parameters (*e.g.*, amplitude and frequency of agitation, and density of spheres) on the separation.

Contact electrification is the process by which electrostatic charge transfers between objects when their surfaces contact and separate.^{2,3} When charged, one object has a positive charge and the other a negative charge. From our work with ionic electrets—materials that have a covalently bound ion and a mobile counterion—we have shown that the transfer of ions can lead to contact electrification.^{3,4} We have demonstrated that contact electrification can direct the self-assembly of micron-sized ionic electrets into ordered three-

dimensional microstructures,⁴ and millimetre-sized spheres into ordered 2D rings and lattices.^{5,6}

This work, which describes the separation of ordered 2D Coulombic crystals of charged, millimetre-sized T and N spheres from less-charged Au^N spheres, is important for at least three reasons: (i) the system of charged and uncharged spheres provides a simple, physical model for nucleation of crystals, and thus for phase separation by formation of a crystalline, ionic phase—the pattern of T and N spheres we observe upon self-assembly resembles the (100) plane of a face-centered cubic lattice; (ii) as with a previous system involving electrets,⁵ it demonstrates our ability to predict complex behaviors in multi-component systems based on an understanding of electrostatics; and (iii) the electrostatic separation of mesoscopic particles, charged by contact electrification, from a heterogeneous mixture is important in a number of technologies:⁷ examples include the purification of coal^{8,9} and the sorting of mixtures of plastics for recycling.¹⁰ Other methods for the separation of mesoscopic particles are based on separation by size,¹¹ magnetic forces,¹² and thermal adhesion.¹³

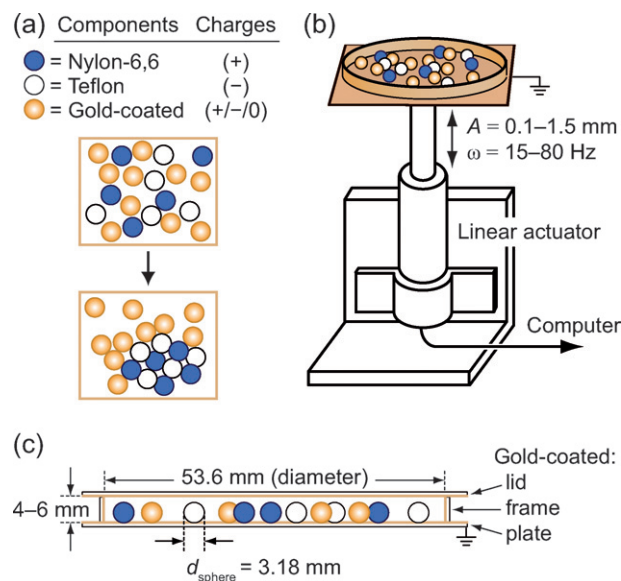


Fig. 1 Experimental design. (a) Separation in a two-phase system: strongly interacting, positively charged Nylon-6,6 (N) spheres and negatively charged Teflon (T) spheres form an ordered ionic cluster and exclude the less-charged, gold-coated spheres (Au^N) from that cluster. (b) N, T, and Au^N spheres on a grounded, gold-coated plate (within a circular frame). A computer controlled the amplitude (*A*) and linear frequency (ω) of a magnetic linear actuator that was connected to the base of the plate. A glove bag (not shown)—which contained dry air—surrounded the spheres, plate, and actuator. (c) We placed a gold-coated aluminium lid on the frame, which was 4–6 mm tall.

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge MA, 02138, USA. E-mail: gwhitesides@gmwhgroup.harvard.edu; Fax: +1 (617) 495-9857; Tel: +1 (617) 495-9430

† This paper is part of a *Soft Matter* theme issue on Self-Assembly. Guest editor: Bartosz Grzybowski.

‡ Electronic supplementary information (ESI) available: Experimental procedures; derivation of eqn (1), the limits of separation (Φ), and the scaled separation (Φ^*); Fig. S1–S6, and Tables S1–S3. See DOI: 10.1039/b813590h

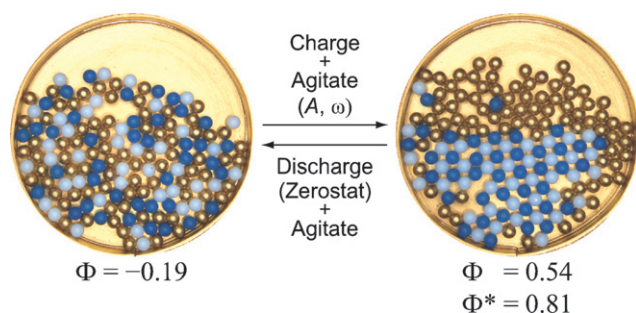


Fig. 2 Photographs of T (white), N (blue), and Au^N (gold) spheres in a gold-coated, circular dish. As the agitated spheres charged, the T and N formed a 2D Coulombic crystal and expelled Au^N from that crystal (left → right). When we neutralized the electrostatic charge on the spheres while the dish was oscillating, the spheres re-mixed (right → left).

The triboelectric series guided our selection of materials.¹⁴ We used spheres made of Teflon (T), Nylon-6,6 (N), and gold-coated Nylon (Au^N). When T, N, and Au^N come into contact on a conductive (gold) surface, T charges negatively, N charges positively, and Au^N charges capacitively either positively or negatively, depending on its immediate electrostatic surroundings.

At the beginning of an experiment, we placed T and N spheres between pairs of Au^N spheres on a grounded, horizontal, gold-coated plate, surrounded by a frame (Fig. 2, left), and we neutralized the electrostatic charge on the surfaces of the spheres and the plate. To charge the T, N, and Au^N spheres by contact electrification, we secured a lid on the plate, and agitated it vertically for selected values of time (*t*), amplitude (*A*), and linear frequency (*ω*) (Fig. 1b). During agitation, collisions between the spheres also drove them to move horizontally across the surface of the plate, within the circular boundary that the frame defined. The horizontal (2D) motion of the spheres depended on the density (*ρ*, proportional to the number of spheres per mm²) of the spheres on the plate: when the spheres were densely packed, their lateral motion was sharply hindered. The lid prevented the spheres from forming 3D aggregates, and from being expelled from the plate when agitation was vigorous (Fig. 1c). With the spheres constrained to remain in 2D, there was a controlled, constant fraction of the surface covered by spheres (*ρ* = constant).

Such agitation led to efficient charging of all spheres, formation of a 2D Coulombic crystal of T and N spheres, and separation of that crystal from Au^N spheres. Wiles *et al.* demonstrated that the initial rate of charging of stainless steel spheres, rolling on a polystyrene surface, increased with higher values of relative humidity (RH).¹⁵ Because the extent of separation of the T and N spheres from the Au^N spheres did not depend on humidity in the range of RH = 8–30% at room temperature, we performed all our experiments at RH = 8%.

After agitation, we removed the lid from the plate and measured the positions of the spheres. Each experiment resulted in a particular configuration of the T, N, and Au^N spheres on the plate. In order to compare numerically each configuration of spheres, we quantified the extent of separation or mixing (*Φ*) of T, N, and Au^N spheres according to eqn (1), which we adapted from Stambaugh *et al.*¹² In eqn (1), $\langle n_{\text{Au-Au}} \rangle$ is the average number of Au^N spheres that neighbor each Au^N sphere (Au–Au neighbors), $\langle n_{\text{P-P}} \rangle$ is the average number of polymeric (P = T or N) spheres that neighbor each polymeric sphere (P–P neighbors), and *n*_{tot} is the total—constant—number of neighbors that we counted for each sphere. To avoid any dependence of *Φ* on the density of spheres on the plate, we defined the “neighbors” of

a sphere to be the six spheres closest to that sphere, regardless of their actual distance from that sphere (Fig. S2†).¹⁶ That is, we arbitrarily set *n*_{tot} = 6 for our calculations (*n*_{tot} was the *same* for each sphere, and equal to the maximum number of spheres that can physically touch each sphere in a close-packed configuration). Other values of *n*_{tot} changed the values of *Φ* quantitatively, but the qualitative trends in *Φ* remained unchanged.

$$\Phi = \frac{\langle n_{\text{Au-Au}} \rangle}{n_{\text{tot}}} + \frac{\langle n_{\text{P-P}} \rangle}{n_{\text{tot}}} - 1 \quad (1)$$

Eqn (1) describes how many neighboring spheres were, on average, of the same phase (“like” neighbors). This equation has the limiting behaviors that *Φ* = 0 for a random mixture of spheres, or for an infinite dilution of one phase (either Au^N or T and N) in the other, and that *Φ* = 1 for completely separated phases.¹⁷ For the configurations of spheres in which we intentionally placed T and N spheres between pairs of Au^N spheres, as in Fig. 2 (left), *Φ* < 0 (about −0.20).

Since the frame confined the spheres to move within a fixed area on the plate, the spheres never completely separated, and *Φ* < 1. We therefore defined a different upper limit for the separation of the spheres ($\Phi_{\text{max}}^{\text{C-S}}$), in which the T and N spheres occupied the center, and the Au^N spheres occupied the surround of a center-surround configuration.¹⁸ The value of $\Phi_{\text{max}}^{\text{C-S}}$ increases with increasing density of spheres (Fig. S3†). To compare quantitatively the separation for different densities of spheres, we divided the value of *Φ* by $\Phi_{\text{max}}^{\text{C-S}}$ to obtain *Φ** for each experimentally observed configuration of spheres. The value of *Φ** depended on (at least) five variables: charge, *t*, *A*, *ω*, and *ρ*.

To verify that the separation of the T and N spheres from the Au^N spheres required electrostatic interactions among the spheres, we separated a mixture of 45 T, 45 N, and 90 Au^N spheres by agitating them at *A* = 0.6 mm and *ω* = 60 Hz for 15 min (Fig. 2). We then neutralized the charge on the spheres and continued to agitate them for 10 s. After 10–15 cycles of neutralization and agitation, the spheres re-mixed to a state similar to that of Fig. 2, left. Continued agitation without neutralization caused the spheres to re-separate to a state similar to that of Fig. 2, right. We therefore conclude that separation of the T and N spheres from Au^N spheres required that the T and N spheres be charged, and that the electrostatic (and hard-sphere) interactions guided the assembly of the spheres.

We hypothesized that charged T and N spheres attracted each other electrostatically more than they attracted Au^N spheres; that is, the charge on the Au^N spheres was less than that on the T or N spheres. To verify this hypothesis, we measured the electrostatic charge on the spheres and compared the electrostatic potential energy between pairs of spheres of different materials. We agitated a mixture of 100 Au^N, 50 T and 50 N for 3 min at *A* = 0.26 mm and *ω* = 60 Hz, and measured the charge on each sphere (Fig. S4†). At this combination of *A* and *ω*, 10–30 s was long enough for the average charge per sphere to reach a constant, maximal value, reported in Table S1†; these charges and the configuration of spheres remained constant for at least 68 h after agitation had ceased (Fig. S5†).

In the absence of charged T and N, the Au^N spheres were electrically neutral (Fig. 3a). In the presence of charged T and N, however, the Au^N spheres charged capacitively, and the sign and magnitude of their charge depended on their immediate electrostatic environment: the charges on T and N induced charges of opposite polarity on the Au^N spheres (Fig. 3b–c). In the presence of both T and N, the charges

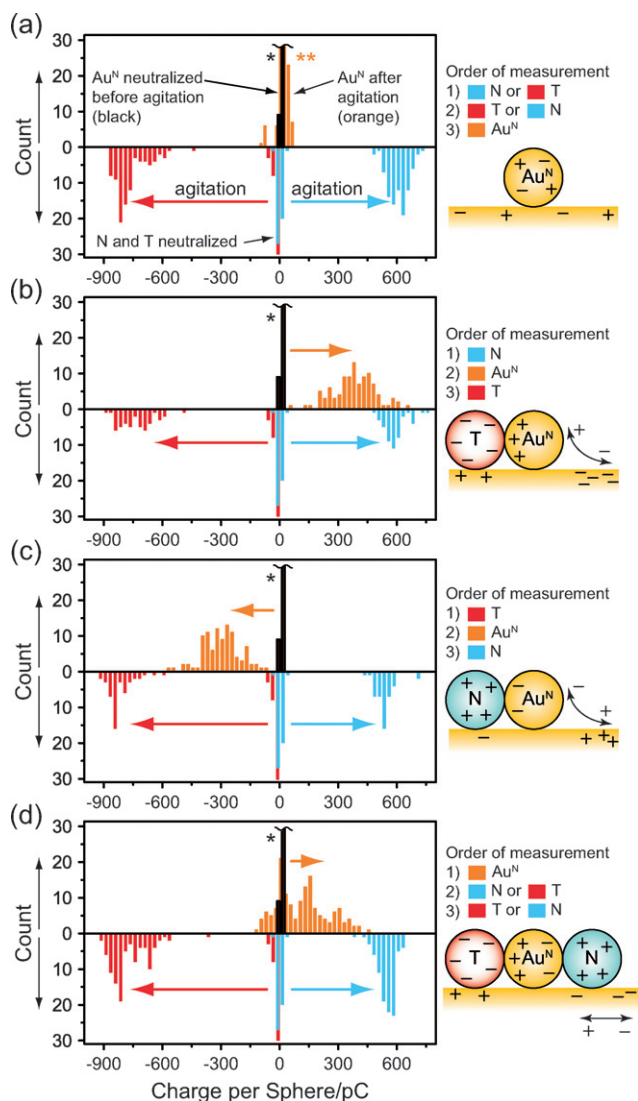


Fig. 3 A histogram of the charge (pC) on 100 Au^N, 50 N, and 50 T spheres after agitation for 3 min at $A = 0.26$ mm and $\omega = 60$ Hz (bins = 25 pC). The histogram points up for Au^N spheres, and down for T and N spheres. The charge on all spheres was approximately zero when neutralized with a Zerostat gun. After agitation, we measured the charge on all spheres of one type (e.g., T, red bars), then all spheres of a second type (e.g., N, blue bars), and then all spheres of the third type (e.g., Au^N, gold bars). The order of measurement is listed on each histogram, and the values of charge correspond to those reported in Table S1†. * Count of neutralized Au^N at 0 pC = 68. ** Count of agitated Au^N at 0 pC = 49.

on the T (-785 ± 26 pC) and N (590 ± 17 pC) spheres (averaged over the six experiments shown in Fig. 3) were ~ 5 – 7 times that on the Au^N spheres (120 ± 130 pC; Fig. 3d).¹⁹ To a first approximation²⁰ (treating the charges on a pair of spheres as point charges, q_1 and q_2 , located at the centers of the two spheres), their electrostatic potential energy (PE) is proportional to the product of their charges, $q_1 q_2$. We can therefore estimate, for example, that the energy of the interaction between T and N was ~ 5 times that between T and Au^N.

We hypothesized that separation of the crystal of T and N spheres from Au^N spheres should increase with time (t). We agitated T, N, and Au^N spheres for 30 s intervals at $A = 0.60$ mm and $\omega = 60$ Hz, and determined Φ^* at the end of each interval. Fig. 4 indicates that Φ^*

increased with time, although the rate of increase decreased with the density of spheres on the plate.

Efficient separation of materials requires that large numbers of particles can separate in a given amount of time. At increased densities, however, granular particles (*i.e.*, the spheres in the present system) experience jamming.²¹ Jamming is the process by which a system of particles becomes rigid, because the hard-sphere interactions between the particles prohibit the particles from moving past one another. We hypothesized that increasing the density of the particles would lead to an increase in jamming, and a decrease in the rate of separation of T and N from Au^N spheres. We defined the density (ρ) of the spheres to be the number of spheres (n_s) on the plate, within a given frame, divided by the number of hexagonally close-packed spheres that could fit on the plate within the same frame. For the circular frame we used ($d = 53.6$ mm), $\rho \approx n_s/260$.

To determine the maximal number of spheres we could separate on the plate, we prepared four mixtures of T, N, and Au^N spheres with different densities. As ρ increased, Φ^* increased more slowly and reached a lower maximal value (Φ_{\max}^*) than it did at the lowest density (Fig. 4). We fit the data in Fig. 4a to eqn (2) to obtain values of Φ_{\max}^* and τ (the time of agitation required to reach $0.63 \Phi_{\max}^*$; in this equation, t_0 was the time at which $\Phi = 0$).

$$\Phi^* = \Phi_{\max}^* [1 - e^{-(t-t_0)/\tau}] \quad (2)$$

Fig. 4 shows that when $\rho = 0.77$, the spheres were jammed— Φ^* did not change significantly—after they had charged fully ($t > 30$ s, see Fig. S5†). The small increase in Φ^* for $\rho = 0.77$ between 0 and 30 s, together with the lack of increase in Φ^* once the spheres had fully charged, indicates that the electrostatic interactions among the spheres—in addition to hard-sphere interactions—contributed to the jamming.

To determine if A affected the separation of T and N from Au^N, we agitated 40 T, 40 N, and 80 Au^N spheres at $\omega = 60$ Hz and a range of amplitudes. There was a slight increase in Φ^* with increasing A at low agitation (Fig. S6†); any trend was, however, noisy. Stambaugh *et al.* observed a similar increase in the separation of magnetic spheres with increasing agitation.¹²

We have shown that particles of the same composition (*e.g.*, Nylon-6,6) separate from one another based only on the properties of their surfaces: the presence or absence of a gold-coating, which comprises 1% of the total mass of the sphere. Separation required that the interaction (in the present case, electrostatic) between the Nylon-6,6 and Teflon be stronger than that between the gold-coated Nylon-6,6 and Teflon. Separation also required that the granular particles not be jammed, and therefore separation was more efficient at lower densities of spheres than at higher densities. Electrostatic separation of materials—for the recycling or purification of those materials—typically requires applied electric fields of ~ 4 – 15 kV cm⁻¹.^{9,10} Our method of separation requires no applied electric field, and may therefore be useful when such fields would be undesirable. As the size of the particles decreases, the electrostatic forces between them become increasingly greater than inertial forces; this technique is therefore not applicable to small particles (≤ 1 μ m), which adhere to surfaces non-specifically under similar conditions.⁴ Future work will include modeling systems that involve the interactions of charged species: these studies will include phenomena such as aggregation, solvation, and sedimentation of proteins.

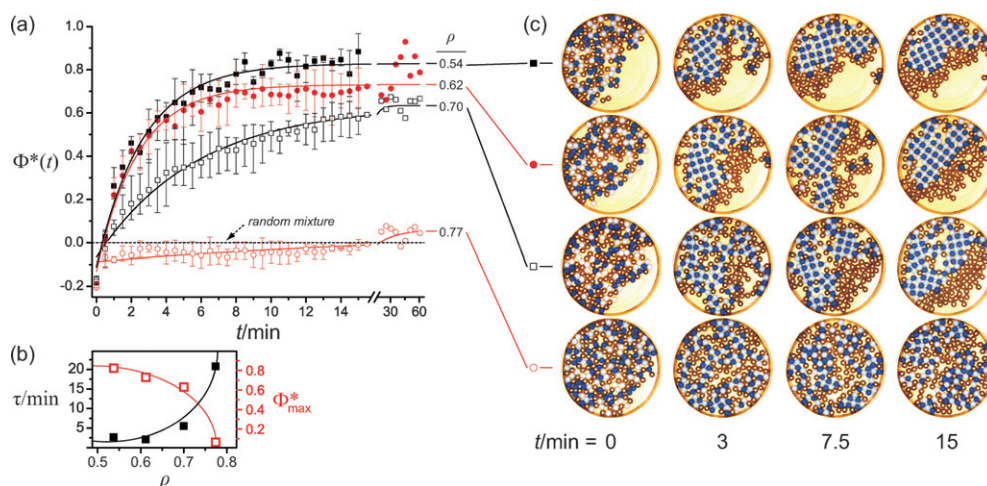


Fig. 4 (a) Separation of four densities (ρ) of the T, N, and Au^{N} spheres as a function of time, $\Phi^*(t) = \Phi(t)/\Phi^{\text{C-S}}_{\text{max}}$ (eqn (1); Fig. S3†). We agitated the spheres at $\omega = 60$ Hz, $A = 0.6$ mm. The reported values are the averages of $\Phi^*(t)$, and the lengths of the error bars represent the minimal and maximal values of $\Phi^*(t)$, for three trials at each density. The solid lines represent the least-squares fit of the data to eqn (2). The dotted line through $\Phi = 0$ indicates the value of Φ for a random mixture. (b) Values of $\tau_{1/2}$ and Φ^*_{max} [eqn (2)] as a function of ρ . The solid lines are guides for the eye. (c) Photographs of the spheres at $t = 0, 3, 7.5$ and 15 min for each density. All mixtures of spheres began with $\Phi < 0$ at $t = 0$ because we placed T and N spheres between pairs of Au^{N} spheres (Fig. 2, left).

Acknowledgements

This research was supported by the Department of Energy under award number DE-FG05-00ER45852. The National Science Foundation (CHE-0518055), DARPA/ARO (W911NF-04-1-0170), and the Xerox Corporation provided support for salaries. We thank Dick Co, Tom Hanisco, and David Wilmouth for assistance with the construction of the plates and frames used in this study, the NSF and MRSEC for a stipend through grant number DMR-0213805 (G.K.K.), as well as the support of the American Cancer Society (S.W.T.), EMBO and HFSP (M.R.), and the NIH (B.F.S.) for postdoctoral fellowships.

Notes and references

- 1 We used spheres that had a diameter $d \approx 3.18$ mm, because we could easily purchase, visualize, and manipulate them. The thin (~ 150 – 250 nm) gold-coating on a polymer sphere of this size does not add significantly to the mass of that sphere.
- 2 W. R. Harper, *Contact and Frictional Electrification*, Laplacian Press, Morgan Hill, CA, 1998; J. Lowell and A. C. Roseinnes, *Adv. Phys.*, 1980, **29**, 947–1023.
- 3 L. S. McCarty and G. M. Whitesides, *Angew. Chem., Int. Ed.*, 2008, **47**, 2188–2207.
- 4 L. S. McCarty, A. Winkleman and G. M. Whitesides, *J. Am. Chem. Soc.*, 2007, **129**, 4075–4088; L. S. McCarty, A. Winkleman and G. M. Whitesides, *Angew. Chem., Int. Ed.*, 2007, **46**, 206–209.
- 5 B. A. Grzybowski, J. A. Wiles and G. M. Whitesides, *Phys. Rev. Lett.*, 2003, **90**, 083903/1–083903/4.
- 6 B. A. Grzybowski, A. Winkleman, J. A. Wiles, Y. Brumer and G. M. Whitesides, *Nat. Mater.*, 2003, **2**, 241–245.
- 7 H. R. Manouchchri, K. H. Rao and K. S. E. Forssberg, *Miner. Metall. Process.*, 2000, **17**, 23–36.
- 8 R. K. Dwari and K. Hanumantha Rao, *Int. J. Miner. Process.*, 2006, **81**, 93–104; S. Trigwell, M. K. Mazumder and R. Pellissier, *J. Vac. Sci. Technol., A*, 2001, **19**, 1454–1459.
- 9 S. Trigwell, K. B. Tennal, M. K. Mazumder and D. A. Lindquist, *Part. Sci. Technol.*, 2003, **21**, 353–364.
- 10 V. Gente, F. La Marca, F. Lucci and P. Massacci, *Waste Manage. (Amsterdam, Neth.)*, 2003, **23**, 951–958; M. Lungu, *Miner. Eng.*, 2004, **17**, 69–75; C.-H. Park, H.-S. Jeon and J.-K. Park, *J. Hazard. Mater.*, 2007, **144**, 470–476; C.-H. Park, H.-S. Jeon, H.-S. Yu, O.-H. Han and J.-K. Park, *Environ. Sci. Technol.*, 2008, **42**, 249–255.

- 11 A. Kudrolli, *Rep. Prog. Phys.*, 2004, **67**, 209–247.
- 12 J. Stambaugh, Z. Smith, E. Ott and W. Losert, *Phys. Rev. E*, 2004, **70**, 031304/1–031304/6.
- 13 T. Saito and I. Satoh, *Polym. Eng. Sci.*, 2005, **45**, 1419–1425.
- 14 The triboelectric series is a list of materials ordered according to their tendency to develop a positive or negative charge when brought into contact with other materials on the list: A. F. Diaz and R. M. Felix-Navarro, *J. Electrostat.*, 2004, **62**, 277–290.
- 15 J. A. Wiles, M. Fialkowski, M. R. Radowski, G. M. Whitesides and B. A. Grzybowski, *J. Phys. Chem. B*, 2004, **108**, 20296–20302.
- 16 Stambaugh *et al.*¹² required that a “neighbor” of a sphere be approximately in physical contact with that sphere. This requirement worked for their system of magnetic spheres because all the spheres touched other spheres. This requirement is, however, problematic for our system because the Au^{N} spheres (which are, on average, uncharged) do not always contact other Au^{N} spheres because there is minimal driving force for these spheres to come into contact. The value of Φ calculated with Stambaugh’s definition of neighbors (all spheres less than a certain distance from the sphere) depends on the density of spheres in the plate (*i.e.*, the value depended on whether or not the spheres were close-packed).
- 17 For phases to be completely separated, the distance between any sphere of one phase (*e.g.*, Au^{N}) from any sphere of the other phase (*e.g.*, T or N) must be greater than the distance between each sphere of each phase and the six closest other spheres of that phase. We illustrate such complete separation in Fig. S2c†.
- 18 Nanoalloys of metals adopt a center-surround (core-shell) configuration when the cohesive energy of one metal (which occupies the core) is greater than that of the other (the shell). For a review on this topic see: R. Ferrando, J. Jellinek and R. L. Johnston, *Chem. Rev.*, 2008, **108**, 845–910.
- 19 The signs of these charges were consistent with the locations of Teflon, Nylon-6,6, and gold in the triboelectric series. The magnitudes of the charges on T and N were larger than what we measured previously for a similar system (B. A. Grzybowski, A. Winkleman, J. A. Wiles, Y. Brumer and G. M. Whitesides, *Nat. Mater.*, 2003, **2**, 241–245). In this study, we used tweezers made out of poly(butylene terephthalate) (PBTP)—as opposed to stainless steel, which we used previously, and which partially discharged the spheres (see Tables S2 and S3†).
- 20 Higher-order terms (induced dipoles, *etc.*) add about 10% to this energy.
- 21 H. A. Makse, J. Brujic and S. F. Edwards, *Los Alamos Natl. Lab., Prepr. Arch., Condens. Matter*, 2005, 1–53, arXiv:cond-mat/0503081; C. Song, P. Wang and H. A. Makse, *Nature*, 2008, **453**, 629–632.