

Phase separation of two-dimensional Coulombic crystals of mesoscale dipolar particles from mesoscale polarizable “solvent”

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This letter describes the formation of two-dimensional (2D) crystals of dipolar particles (TN) made of electrostatically charged, joined, millimeter-scale Teflon (T) and nylon-6,6 (N) spheres, and the separation of these crystals, as a distinct phase, from a mixture of TN and similar, capacitively charged particles that were coated with gold (Au_2). The extent of separation increased with increasing amplitude of agitation, and with decreasing density of particles. Above a threshold in the amplitude of agitation, the crystals broke apart and the particles remixed. This system is a 2D model of the nucleation of crystals of polar molecules in a polarizable liquid. © 2009 American Institute of Physics. [DOI: 10.1063/1.3052616]

This letter describes the assembly of charged, dipolar particles (TN), each comprising two ~ 3 mm, electrostatically charged polymeric spheres—one Teflon (T) sphere and one nylon-6,6 (N) sphere—into two-dimensional (2D) Coulombic crystals that separate from particles of the same shape, size, and weight that were coated with gold (Au_2 , Fig. 1). On agitation, the polymeric spheres of TN particles charged by contact electrification,¹ while the Au_2 particles charged capacitively. The TN and Au_2 particles were both, on average, approximately electrically neutral.

We have demonstrated previously that charged millimeter-sized spheres can assemble into ordered 2D lattices.² We have also described the formation of 2D Coulombic crystals of T and N spheres, and the separation of these crystals from gold-coated spheres;³ the present work extends this study of charged spheres to dipoles. The formation of a Coulombic crystal, and the separation of this crystal from the disordered gold-coated particles, is a simple, physical model for the nucleation of a molecular crystal in a polarizable solvent.

Three features are central to the design of the present system:

- (i) When T, N, and gold (Au) are combined and charged by contact electrification, T develops a negative charge and N develops a positive charge; Au remains, on average, approximately neutral.⁴ Charged T and N spheres interact more strongly with each other than they do with Au.³
- (ii) We determined previously³ that Au spheres charged capacitively; their charge was $\sim 20\%$ that of the T and N spheres around them. In the present system, we attached one T sphere to each N sphere permanently to form TN particles. Each TN particle was approximately electrostatically neutral (Fig. S3), but had a significant electrostatic dipole (Figs. S4 and S5).⁶ We speculated that the net neutral TN particles would induce less charge on Au spheres than nonconnected,

charged T and N spheres did. These less-charged Au spheres should interact more weakly with (and separate with less agitation from) the TN electrostatic dipoles than with individual T and N monopoles.

- (iii) We wished the only difference between the TN and gold-coated particles to be their charge, to minimize contributions to phase separation from shape, mass, or other features that can also lead to separation of particles.⁵ We therefore attached gold-coated T spheres (Au^T) to gold-coated N spheres (Au^N) to form Au_2 (Au^TAu^N) particles (the gold coating was ~ 165 nm thick, and did not influence either the diameter or mass significantly; see Table S1).

We agitated mixtures of TN and Au_2 particles vertically on a

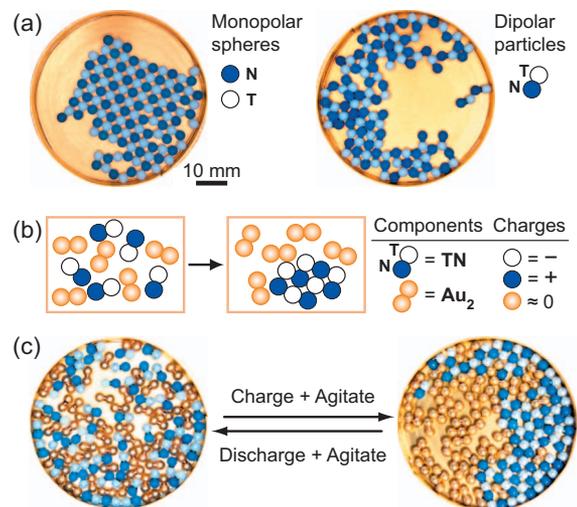


FIG. 1. (Color) Crystallization of TN (a), and separation of TN from Au_2 (b and c). (a) T and N monopolar spheres (left) crystallize. TN particles (right) form polycrystalline aggregates without Au_2 ; the crystals have edge defects near the circular frame. (b) The TN particles have dipoles formed by a negatively charged sphere (T, white) and a positively charged sphere (N, blue). These particles interact more strongly with each other than they do with the less-charged particles of Au_2 (gold), and form a crystal that excludes Au_2 . (c) Photographs of TN and Au_2 particles on the plate within a circular frame.

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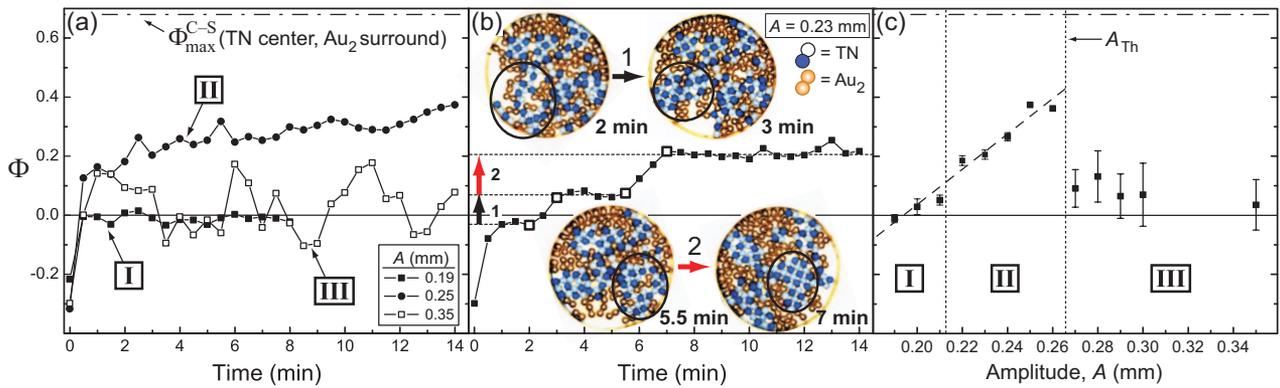


FIG. 2. (Color) Separation (Φ) of 50 TN from 50 Au_2 particles as a function of time (t) and amplitude (A). (a) Behavior of $\Phi(t)$ for agitation at $\omega=60$ Hz, $A=0.19$ mm (I), 0.25 mm (II), and 0.35 mm (III); see the text for a description of I–III. The solid line at $\Phi=0$ corresponds to that for a random mixture of particles, and the dashed-dotted line corresponds to $\Phi_{\text{max}}^{\text{C-S}}=0.68$ (Fig. S6) (Ref. 6). (b) For some amplitudes, $\Phi(t)$ increased in discrete steps (white squares) between plateaus. These steps coincided with the formation of clusters of TN and the expulsion of Au_2 from these clusters. In the photographs of the particles, we have drawn a ring around the cluster of TN formed during each step. (c) Separation as a function of A , at $\omega=60$ Hz for 14 min. The vertical dotted lines separate the amplitudes according to those that led to behaviors I–III. The lengths of the error bars represent the standard deviation about the mean value of Φ for $t>0.5$ min (I and III), or for the last plateau in $\Phi(t)$ (II). There are no error bars for $A=0.25$ or 0.26 mm because $\Phi(t)$ increased approximately continuously from the value at $t=0$ to the value indicated by the square ($t=14$ min). The dashed line represents a linear, least-squares fit of the data for $0.19 \text{ mm} \leq A \leq 0.26 \text{ mm}$.

grounded, horizontal, gold-coated plate, within a circular frame, at a selected amplitude ($A=0.1\text{--}1.5$ mm) and frequency ($\omega=15\text{--}80$ Hz) (Fig. S2).^{3,6} Collisions between particles induced horizontal motion, and resulted in the contact electrification of the particles. The electrostatic interactions among the particles guided their assembly into 2D configurations that varied in the extent of separation (Φ) or mixing of the TN and Au_2 particles.

To compare the configurations of particles numerically, we calculated Φ according to Eq. (1).^{3,6,7} In this equation, $\langle n_{\text{Au-Au}} \rangle$ is the average number of Au spheres that neighbor a Au sphere (Au–Au neighbors), $\langle n_{P-P} \rangle$ is the average number of polymeric ($P=\text{T}$ or N) spheres that neighbor a P sphere (P – P neighbors), and n_{tot} is the total number of neighbors around a sphere.⁸ As before,³ we presumed that Φ should have its maximal value ($\Phi_{\text{max}}^{\text{C-S}}$) when the TN particles occupied the center and the Au_2 particles occupied the surround of a center-surround configuration.⁶

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

Equation (1) describes how many neighbors there were, on average, among spheres of the same phase (“like” neighbors), and has the limiting behavior that $\Phi=0$ for a random mixture of particles, or for an infinite dilution of one phase in the other, and that $\Phi=1$ for completely (infinitely) separated phases.⁶

Separation of TN from Au_2 required that the TN particles be electrostatically charged. As we agitated the particles, the TN charged and formed a cluster (or clusters), and expelled Au_2 from that cluster [Fig. 1(c) left \rightarrow right]. The particles remixed [Fig. 1(c) right \rightarrow left] when we neutralized the charge on the particles while the plate was oscillating.

We measured the charges on the particles [after agitation at $\omega=60$ Hz, and $A=0.26$ mm for 3 min (Refs. 3 and 9)] to determine the magnitude of charge that was responsible for the separation of TN from Au_2 (Fig. S3).⁶ Consistent with our design, the *average* charge on agitated TN particles was indistinguishable from that of neutralized TN particles. As

previously observed for mixtures of Au, T, and N spheres,³ the charge on Au_2 (q_{Au_2}) reflected nearby charges: the distribution of q_{Au_2} depended on whether or not TN remained on the plate when q_{Au_2} was measured. If the TN remained on the plate during measurement of q_{Au_2} , then the distributions of charge on Au_2 and TN were similar [Fig. S3(a)].⁶ If the TN had already been removed from the plate, the charge on Au_2 was indistinguishable from that of neutralized Au_2 [Fig. S3(b)].⁶

After agitation, the magnitudes of the charges on T and N of TN were approximately half that of separate (nonglued) T and N spheres (Table S2).^{3,6} The maximal charge *per sphere* (i.e., the charge density) on Au_2 , in the presence of TN, was approximately one-third that on Au spheres in the presence of T and N spheres.^{3,6} These fractions of charge were consistent with our experimental design, and with the fact that not all of the surface area of each glued sphere was exposed for contact electrification [Fig. S1(b)].⁶

In addition to charge, the magnitude of separation (Φ) of TN from Au_2 particles depended on (at least) six variables (Table S3). We address these variables in the paragraphs that follow.

The separation of TN from Au_2 progressed with one of three different types of behavior [I–III, Fig. 2(a)] that depended on amplitude (A). (i) At low A , Φ was constant (I); (ii) at intermediate A , TN clustered, and $\Phi(t)$ increased (II); (iii) at high A , Φ fluctuated extensively about a constant mean value near that of a random mixture (III). For $A=0.22\text{--}0.24$ mm [Fig. 2(b)], Φ increased in a series of discrete steps. These steps coincided with the formation of clusters of TN and the expulsion of Au_2 from these clusters.

The rate of crystallization of TN particles, and separation of these crystals from Au_2 particles, increased with A , up to a threshold of agitation ($A_{\text{th}} \approx 0.26$ mm at $\omega=60$ Hz). Below A_{th} , the maximal value of Φ (by $t=14$ min) increased linearly with A [Fig. 2(c)]; above A_{th} , the crystals continuously broke apart and the particles remixed. Stambaugh *et al.* observed a similar linear increase in the maximal separation of a mixture of magnetic particles.⁷ They predicted—although

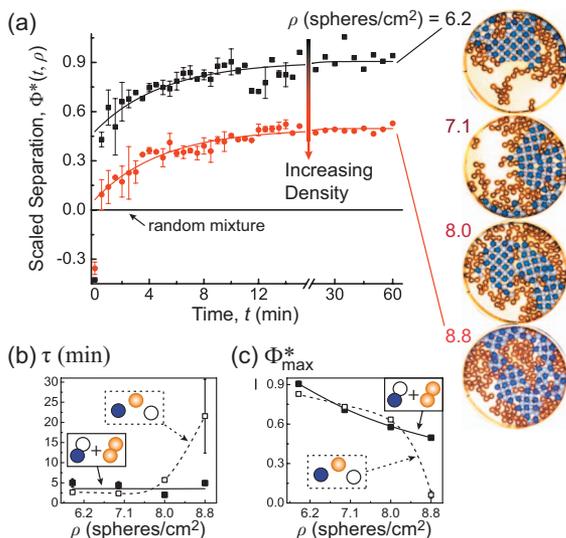


FIG. 3. (Color) (a) Scaled separation (Φ^*) as a function of density (ρ) and time (t) for mixtures of 50% TN and 50% Au₂, agitated at $\omega=60$ Hz, $A=0.25$ mm. For clarity, we show Φ^* for only two of the four values of ρ (Fig. S6) (Ref. 6). On the right are photographs of the particles at $t=14$ min. We fit the data for each density to Eq. (2) to obtain values of (b) τ and (c) Φ^*_{\max} . In (b) and (c), the filled squares represent values for TN and Au₂ particles, the open squares represent values for separate (nonglued) T, N, and Au^N spheres,³ and the lines are guides for the eye.

they never observed—that such a threshold should occur when the energy from agitation of the plate exceeds the energy of interaction between the particles. Calculation of these energies is beyond the scope of this letter; however, we believe that we have observed this predicted threshold.

We speculated that Φ did not reach Φ^*_{\max} for any amount of agitation because the particles lacked the ability to move efficiently past one another, and that they might separate more at a lower density (ρ , Table S3).^{3,10} When normalized for differences in density (Fig. S6),^{6,11} the separation ($\Phi^* = \Phi/\Phi^*_{\max}$) of four 1:1 mixtures of TN and Au₂ approached its upper limit (1.0) as ρ decreased [Fig. 3(a)].¹² We fit the data in Fig. 3(a) to Eq. (2) to obtain values of the time constant for separation (τ) and the maximal value of separation (Φ^*_{\max}); in this equation, t_0 was the time at which $\Phi^*=0$.³ After an initial increase in Φ^* that was inversely proportional to ρ , separation increased at a similar rate for all densities [$\tau \sim \text{constant}$, Fig. 3(b)], and reached a maximal value that decreased as ρ increased [Fig. 3(c)]. Unlike T, N, and Au spheres, which did not separate at high density ($\rho = 8.8$ spheres/cm²),³ Fig. 3 shows that TN and Au₂ do separate at this high density. We presume that the TN particles separated from Au₂ at $\rho=8.8$ spheres/cm² because their spheres were less charged than separate (nonglued) T and N spheres (Table S2).

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

We have demonstrated that dipolar particles (TN), on agitation, form 2D Coulombic crystals, and that these crystals separate from polarizable “solvent” particles (Au₂) of the same size, shape, and weight. These dipolar particles behaved similarly to charged, monopolar spheres³ (separation increased with the amplitude of agitation and decreased with the density of particles), except that we observed a threshold

of agitation, above which the crystals broke apart and the dipolar particles remixed with the polarizable solvent. Although the dipolar particles cannot model molecules accurately (the particles lack internal degrees of freedom, directionally specific hydrogen bonds, etc.), it will be instructive to compare the nucleation of crystals of dipolar particles among polarizable particles to that of polar molecules in a polarizable solvent (e.g., in the recrystallization of 9-fluorenone from hexane).¹³ Such studies will be useful for understanding molecular recognition and solvation—phenomena that depend greatly on electrostatic interactions, and that are central to topics as diverse as crystal engineering¹⁴ and rational ligand design for proteins.¹⁵

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⁶See EPAPS Document No. E-APPLAB-93-045851 for experimental details, measurement of charges, calculation of density (ρ), calculation and limiting behavior of separation (Φ) and scaled separation (Φ^*), and separation as a function of the number fraction of TN (χ_{TN}) and the angle of agitation with respect to gravity (α). For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.

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⁸To avoid any dependence of Φ on the density of spheres on the plate, we defined the “neighbors” of sphere n as the six spheres closest to sphere n , regardless of their actual distance from sphere n . For all the calculations in this paper, we set $n_{\text{tot}}=6$ (i.e., we considered only the six nearest neighbors of each sphere). Other values of n_{tot} did not yield qualitatively different results from those reported here.

⁹Previous work showed that at this frequency and amplitude, 30 s was long enough for the charge on each sphere to become constant.

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¹¹We calculated Φ^*_{\max} for each density (Fig. S6),⁶ and divided the values of Φ by Φ^*_{\max} to obtain Φ^* ; this normalization allowed us to compare directly the values of Φ for different densities of particles.

¹²We agitated the particles at the combination of A (0.25 mm) and ω (60 Hz) for which $\Phi(t)$ increased monotonically and most rapidly at $\rho = 8.8$ spheres/cm² (Fig. 2).

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