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 (Au2). 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 (Au2). 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.

(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. Charged T and N spheres interact more strongly with each other than they do with Au.

(ii) We determined previously that Au spheres charged capacitively; their charge was ~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). 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. We therefore attached gold-coated T spheres (Au1T) to gold-coated N spheres (Au1N) to form Au2 (Au1T Au1N) 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 Au2 particles vertically on a circular frame.

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FIG. 1. (Color) Crystallization of TN (a), and separation of TN from Au2 (b and c). (a) T and N monopolar spheres (left) crystallize. TN particles (right) form polycrystalline aggregates without Au2; 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 Au1 (gold), and form a crystal that excludes Au2. (c) Photographs of TN and Au2 particles on the plate within a circular frame.

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grounded, horizontal, gold-coated plate, within a circular frame, at a selected amplitude ($A=0.1–1.5$ mm) and frequency ($\omega=15–80$ Hz) (Fig. S2).\textsuperscript{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 ($\Phi$) or mixing of the TN and Au$_2$ particles.

To compare the configurations of particles numerically, we calculated $\Phi$ according to Eq. (1).\textsuperscript{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), $\langle n_{pP} \rangle$ is the average number of polymeric (P=T or N) spheres that neighbor a P sphere (P–P neighbors), and $n_{\text{tot}}$ is the total number of neighbors around a sphere.\textsuperscript{8} As before,\textsuperscript{7} we presumed that $\Phi$ should have its maximal value ($\Phi_{\text{max}}^{C_S}$) when the TN particles occupied the center and the Au$_2$ particles occupied the surround of a center–surround configuration.\textsuperscript{5}

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\Phi = \frac{\langle n_{\text{Au-Au}} \rangle - 1}{n_{\text{tot}} - 1} + \frac{\langle n_{pP} \rangle - 1}{n_{\text{tot}} - 1} - 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.\textsuperscript{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→right]. The particles remixed [Fig. 1(c) right→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).\textsuperscript{5} 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,\textsuperscript{3} the charge on Au$_2$ ($q_{\text{Au}_2}$) reflected nearby charges: the distribution of $q_{\text{Au}_2}$ depended on whether or not TN remained on the plate when $q_{\text{Au}_2}$ was measured. If the TN remained on the plate during measurement of $q_{\text{Au}_2}$, then the distributions of charge on Au$_2$ and TN were similar [Fig. S3(a)].\textsuperscript{3} 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)].\textsuperscript{3}

After agitation, the magnitudes of the charges on T and N of TN were approximately half that of separate (nonglued) and N spheres (Table S2).\textsuperscript{3} 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.\textsuperscript{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)].\textsuperscript{3}

In addition to charge, the magnitude of separation ($\Phi$) 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 $A$, $\Phi$ was constant (I); (ii) at intermediate $A$, TN clustered, and $\Phi(t)$ increased (II); (iii) at high $A$, $\Phi$ fluctuated extensively about a constant mean value near that of a random mixture (III). For $A=0.22–0.24$ mm [Fig. 2(b)], $\Phi$ 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 ($A_{th} \approx 0.26$ mm at $\omega=60$ Hz). Below $A_{th}$, the maximal value of $\Phi$ (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.\textsuperscript{11} observed a similar linear increase in the maximal separation of a mixture of magnetic particles.\textsuperscript{1} They predicted—although
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 the \( \Phi \) did not reach \( \Phi_{\text{C-S}}^{*} \) 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 (\( \rho \), Table S3).\(^{3,10}\) When normalized for differences in density (Fig. S6), the separation \( \Phi^{*}_{\text{max}} = \Phi / \Phi_{\text{C-S}}^{*} \) of four 1:1 mixtures of TN and Au2 approached its upper limit (1.0) as \( \rho \) decreased [Fig. 3(a)].\(^{12}\) We fit the data in Fig. 3(a) to Eq. (2) to obtain values of \( \tau \) and \( \Phi_{\text{max}}^{*} \). 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 Au5 spheres,\(^{3} \) and the lines are guides for the eye.

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 spheres (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—phomena that depend greatly on electrostatic interactions, and that are central to topics as diverse as crystal engineering\(^{14} \) and rational ligand design for proteins.\(^{15} \)

![Fig. 3.](Image)

**Fig. 3.** (Color) (a) Scaled separation (\( \Phi^{*} \)) as a function of density (\( \rho \)) and time (\( \tau \)) for mixtures of 50% TN and 50% Au2, agitated at \( \omega = 60 \, \text{Hz} \), \( \Lambda = 0.25 \, \text{mm} \). For clarity, we show \( \Phi^{*} \) for only two of the four values of \( \rho \) (Fig. S6) (Ref. 6). On the right are photographs of the particles at \( t = 14 \, \text{min} \). We fit the data for each density to Eq. (2) to obtain values of \( \tau \) and \( \Phi_{\text{max}}^{*} \). (b) \( \tau = 14 \, \text{min} \) and \( \Phi_{\text{max}}^{*} \). We obtained the data for each density to Eq. (2) to obtain values of \( \tau \) and \( \Phi_{\text{max}}^{*} \). (c) \( \Phi_{\text{max}}^{*} \), as well as the support of EMBO and HFSP (M.R.), the American Cancer Society (S.W.T.), and the NIH (B.F.S.) for postdoctoral fellowships.


\(^{6}\) See EPAPS Document No. E-APPLAB-93-045851 for experimental details, measurement of charges, calculation of density (\( \rho \)), calculation and limiting behavior of separation (\( \Phi^{*} \)) and scaled separation (\( \Phi^{*}_{\text{C-S}} \)), and separation as a function of the number fraction of TN (\( \chi_{\text{TN}} \)) and the angle of agitation with respect to gravity (\( \alpha \)). For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.


\(^{8}\) To avoid any dependence of \( \Phi \) 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 \( n_{\text{max}} = 6 \) (i.e., we considered only the six nearest neighbors of each sphere). Other values of \( n_{\text{max}} \) did not yield qualitatively different results from those reported here.

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


\(^{11}\) We calculated \( \Phi_{\text{C-S}}^{*} \) for each density (Fig. S6), and divided the values of \( \Phi^{*} \) by \( \Phi_{\text{C-S}}^{*} \) to obtain \( \Phi^{*} \); this normalization allowed us to compare directly the values of \( \Phi^{*} \) for different densities of particles.

\(^{12}\) We agitated the particles at the combination of A (0.25 mm) and \( \omega = 60 \, \text{Hz} \) for which \( \Phi^{*} \) increased monotonically and most rapidly at \( \Lambda = 0.8 \, \text{cm}^{2} \) (Fig. 2).

