Spontaneous Separation of Charged Grains

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(Received 4 April 2007; published 31 July 2007)

In 1867, Lord Kelvin described an experiment in which two streams of water droplets were connected so that each stream amplified the charge on the second stream [W. Thomson, Proc. R. Soc. London **16**, 67 (1867).]. We present here a complementary effect in flowing grains that spontaneously separates similar and well-mixed grains into two charged streams of demixed grains. This effect has important consequences for industrial and natural processes.

DOI: 10.1103/PhysRevLett.99.058001 PACS numbers: 45.70.Qj, 05.45.Df, 46.55.+d

Electrostatic charging of particles is widely applied industrially, for example, in conventional printing [1], electrocoating [2], and filtration [3], as well as in more modern applications such as crystal self-assembly [4]. Electrification of grains is equally important in nature, where it influences Aeolian sand transport [5] and geological sedimentation patterns [6,7]. Surprisingly, after centuries of study, some of the most elementary properties of contact and frictional electrification continue to defy satisfactory explanation. Two examples illustrate this point.

First, it has long been recognized that insulators, which lack free charge carriers, transfer charge readily, while conductors charge more weakly. This paradoxical effect is known to be distinct from the ability of conductors to carry charges to ground [8,9], and led to prolonged confusion beginning in the 18th century, when researchers distinguished ''electrics'' that charge (e.g., dry glass or silk [10]) from ''nonelectrics'' that do not (e.g., moist glass or iron [8]). Although we can adequately explain charge transfer in conductors and semiconductors [11], to this day we remain unable to explain, even qualitatively, how insulators recruit charges during contact or rubbing [12].

Second, the best models that do exist for contact electrification rely on differences between the two materials in contact—notably between work functions of the materials [9,13]. Yet in common atmospheric lightning, large charge separations result from interactions between chemically *identical* water molecules [14]; likewise desert sands acquire large charges with little to rub against beyond other sand [5]. Indeed, measurements have revealed that rubbing of carefully prepared identical polymers can tribocharge one another [15].

Apparently, our understanding of contact electrification remains inadequate to explain, in even the simplest and most commonplace of situations, how materials lacking free carriers charge strongly, or why apparently identical materials tribocharge. Our deficient understanding has particular repercussions in granular flow, where as we will show we cannot even correctly predict when grains may mix or separate due to charging effects. Granular experiments are especially suited to elucidating charge effects because the grains themselves can be used to visualize charge separation—indeed, xerography is founded on this observation.

Our experiment is conceptually similar to Lord Kelvin's 19th century arrangement. In Lord Kelvin's experiment, each of two streams of water droplets were charged by induction which, in turn, was established by the charge on the second stream [16]. A complementary, if simpler, granular experiment using only a single stream appears in Fig. 1(a), where we show a commercial vibratory feeder (Eriez Manufacturing, Erie, PA) that meters grains into a nearby charged acrylic cylinder of diameter 20 cm and height 44 cm. The grains consist of equal parts mechanically indistinguishable ''art sand'' of mean diameter 250 μm. Granular flow and mixing experiments using these grains have been reported frequently in the literature [17]. We compare sizes and shapes of the two colors of grains in Fig. 1(b): in the main plot we show two replicates of size measurements obtained by sieving, and in the insets, we include micrographs of sampled grains displaying similar shapes.

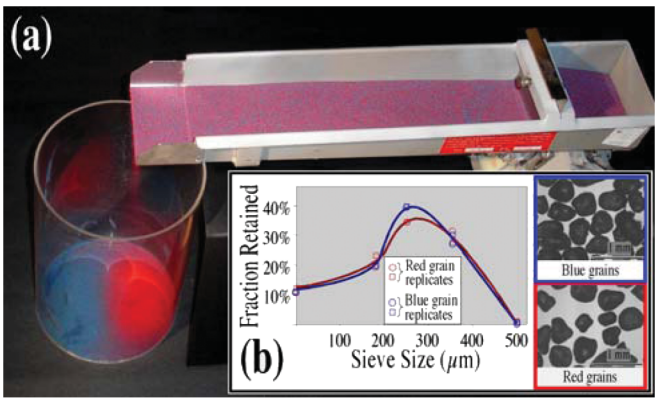

FIG. 1 (color). Demixing of mechanically similar grains. (a) Overview of experiment: grains are supplied by vibrating feeder (top) into charged acrylic collecting cylinder (left). (b) Size distributions of red and blue grains, obtained by passing grains through sequential sieves. Insets to right show micrographs of grains, illustrating similar shapes.

As shown in Fig. 1(a), the initially well-mixed blend spontaneously separates into red and blue streams. The cylinder was lightly rubbed with low-powder nitrile gloves prior to performing the experiment. This reproducibly generates a positive charge on the acrylic that we have measured using a null voltmeter probe (Trek Inc., Model 344 with probe 6000B-7C, Medina, NY). The colored grains are also positively charged, and despite being mechanically similar, the blue grains charge more positively than the red grains (described next). We analyze the cause of demixing shortly; for now we emphasize that it is unexpected that the *more* positively charged, blue, grains separate *away* from the metal feeder and toward the positively charged cylinder.

Charge densities on the grains are measured using an electrometer (Keithley, Model 610CR, Cleveland, OH) connected to a Faraday cup that collects the output stream and sits on a digital scale. As shown in Fig. 3(b), when metered separately through the feeder, the blue grains acquire a charge density of 0.64 ± 0.01 s C/g, while the red grains charge to 0.11 ± 0.01 s C/g. Similarly, when metered through the feeder in a blended state, the blue half of the heap is measured using the voltmeter probe to be more positively charged than the red half. The demixing effect is robust provided the cylinder is positively charged: the experiment shown was performed in an environmental chamber with controlled temperature and humidity (70°F, 30% relative humidity), but has been reproduced in experiments performed under higher humidity, with the experiment enclosed in a grounded Faraday cage, and at different granular flow rates.

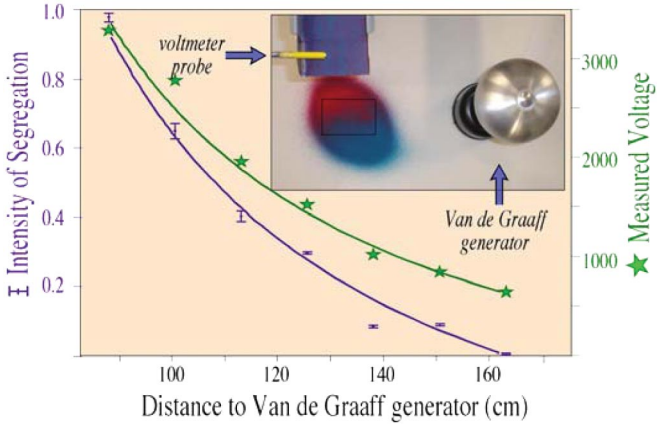

FIG. 2 (color). Correlation of charge separation of colored sand with externally applied voltage. Intensity of segregation I_S from processing of digital photos of sandpiles and measured voltage near feeder outlet vs distance from centerline of chute to nearest edge of a positive Van de Graaff generator. Error bars represent standard error over multiple trials. Inset: Geometry used; Van de Graaff generator is moved to right in orientation shown. The black box indicates the approximate location of rectangular array of 2×8 collecting vials used in the experiment of Fig. 3(a).

We confirm that the observed separation is associated with the proximity of the charged cylinder by replacing the cylinder with a positive Van de Graaff generator downstream of the flow as shown in Fig. 2 (inset). Provided there is a positive voltage source near the feeder outlet, we find a similar segregation profile. This is shown in Fig. 2, where we plot the intensity of segregation I_s of grains accumulated onto a flat surface beneath the feeder as a function of perpendicular distance to a +200 kV Van de Graaff generator (Hobbytron, Orem, UT). I_s is defined by [18]: $I_s = (\sigma^2 - \sigma_-{}^2)/(\sigma_+{}^2 - \sigma_-{}^2)$, where σ^2 is the variance of the hue measured from digital photographs, and $\sigma_-{}^2$, and $\sigma_+{}^2$ are its maximum and minimum, respectively. As shown in Fig. 2, I_s drops from almost perfectly segregated ($I_s = 1$) at a distance to the generator of about 90 cm to almost perfectly mixed ($I_s = 0$) at 160 cm. Also as shown in the figure, I_s is correlated with the voltage measured with the voltmeter probe mounted 5 cm above the chute as shown in the inset. When the voltage at the chute drops below about 500 V, demixing vanishes; similarly no demixing is seen if a negative Van de Graaff generator is used, or in experiments using the charged acrylic cylinder if the top of the cylinder is more than 20 cm away from the bottom of the chute. These experiments demonstrate that the segregation effect is associated with sufficient positive voltage near the feeder outlet.

Colored sand is convenient because it provides easy visualization, but the demixing effect appears in colorless but practically important materials as well. As an example, in Fig. 3(a) we show that an initially well-mixed 50–50 blend of acetaminophen (APAP) and microcrystalline cellulose (MCC: a common pharmaceutical excipient) also segregate electrostatically in the same arrangement. In Fig. 3(a) we show that concentrations of APAP vary from 5 to 90% when sampled from locations shown in Fig. 2 (inset) and assayed using established spectroscopy methods [19]. Prior to testing, we mix the ingredients for 200

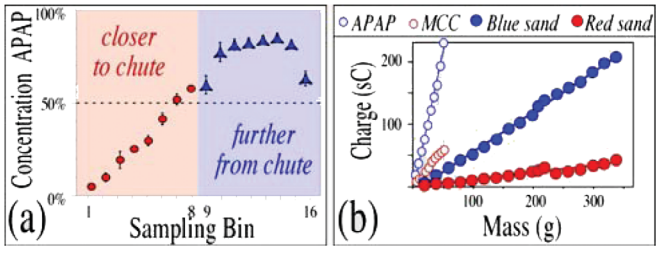

FIG. 3 (color). (a) Demixing in arrangement of Fig. 2 (inset) of initially mixed 50–50 blend of acetaminophen ("APAP": USP special grade, Mallinckrodt, Raleigh, NC) with a common pharmaceutical excipient ("MCC": PH-200, FMC BioPolymer, Philadelphia, PA). Powder is collected in sampling bins arrayed in ranks within the rectangle indicated in Fig. 2 (inset); bins in the further rank from the chute have consistently lower APAP concentration than bins in the closer rank. (b) Charge densities measured on grains collected in a Faraday cup at the feeder outlet.

revolutions in a tumbling blender, and in control experiments without the generator, we measure the concentration to be 51 ± 2% both before and after passage through the feeder. These two powders were as close as commercially available to the same size: the APAP and MCC are measured by sieving to be 310 ± 80 μm and 170 ± 130 μm in size, respectively. As with the colored sand, we have measured that both APAP and MCC are charged positively by the vibratory feeder, and that APAP is charged more strongly (6 s C/g) than is MCC (1.5 s C/g), as shown in Fig. 3(b).

We emphasize that the segregation effect that we report occurs only in grains larger than about 100 μm, and we speculate that below this size, cohesive (e.g., van der Waals) forces dominate, preventing electrostatic segregation. Also, we reiterate that segregation curiously appears when all charged materials are positive: this differs qualitatively from existing methods used to separate positively from negatively charged materials [20]. Finally, we note that the demixing that we report acts in the *opposite* direction from what one would predict using the most basic, Coulomb, law of electrostatics. That is, a positive voltage generator or charged cylinder placed nearby our grounded feeder chute should induce negative charges near the chute edge, producing an electric field directing positive test charges away from the positive source and *toward* the nearest edge of the grounded chute. Instead, the more positively charged grains paradoxically move *away* from the chute.

To identify the cause of the observed demixing, we note that grains segregate very near to the sharp outlet of the feeder [Fig. 4(a)]—where the electric field is concentrated—after which point they fall nearly passively, comparatively weakly influenced by applied fields. Thus the deposited heap segregates perpendicular to the centerline of the feeder, even when the voltage generator is placed at a right angle, as in Fig. 2 (inset), and similarly, in our experiments using the charged cylinder, we find that the segregation pattern of Fig. 1 does not change as the cylinder is displaced horizontally with respect to the stream of grains.

Therefore we concentrate on the flow of positively charged grains falling near a negatively charged edge. Scrutiny of the chute edge reveals that a "beard" of charged grains [Fig. 4(b)] adheres to the underside of the edge surface. This charged beard grows with time and applied field, but is typically 5–10 grains thick. We hypothesize that positively charged grains may adhere to the induced negative charges at the feeder edge, and that these grains may cause the paradoxical separation of subsequent falling grains.

We test this hypothesis by constructing a particle-dynamics simulation of positively charged grains flowing down an inclined and vibrated surface whose lower edge is negatively charged. Results of these simulations are shown in Fig. 4(c). Details of particle-dynamics methods appear

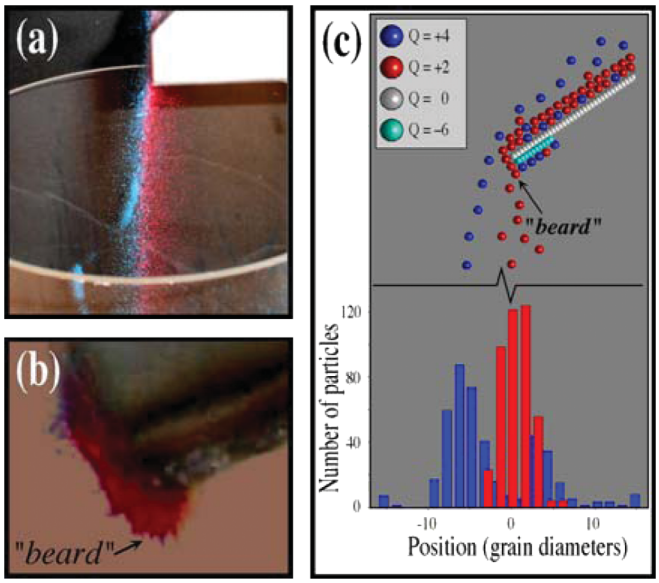

FIG. 4 (color). (a) Close-up of demixing in arrangement of Fig. 1 showing that blue and red charged grains separate at the outlet. (b) Detail of beard of adhered grains (experiment halted, and background digitally filtered to remove extraneous equipment). (c) 2D simulation of strongly (blue) and weakly (red) charged particles on an inclined and vibrated surface. Grains (cyan) fixed beneath the chute simulate induced negative charges. Simulation uses elastoplastic model of [21] integrated using Euler method for 2D particles with coefficient of restitution 0.16 and kinetic friction coefficient 0.2. Simulation shows state after 500 000 time steps. Computations use dimensionless units with grain diameter = 1, mass = 5, gravity = 0.01, and time step = 0.125. New positive grains are created every 500 time steps at randomized locations 25 ± 4 units upstream and above the chute. The histogram shows positions of all grains that have fallen 15 diameters below the chute, after which grains are removed from the simulation.

elsewhere [21]: in synopsis this model uses identically sized, elastoplastic grains with kinetic sliding friction, and permits grains to interact electrostatically as if their entire assigned charge were localized at the grains' centers. Grains are dropped a short distance onto the chute from an upstream location (not shown), and charges are assigned to new grains in equal numbers at random with magnitudes of either $Q = 2$ or $Q = 4$ computational units. The higher positive charges are shown as blue; the lower charges as red. Also shown in Fig. 4(c) are 10 fixed particles (cyan) placed beneath the chute to simulate induced charges; the charge on each of these particles is $Q = -6$ units. Particles making up the chute are moved up and down 1/10 particle diameter every other time step to simulate shaking the feeder. Other simulation values are included in the caption to Fig. 4.

As shown in Fig. 4(c), a beard forms spontaneously in the simulation as positively charged grains adhere to the negatively charged plate. After formation of the beard, the highly charged, blue, grains levitate above the charged bed

and cascade in a largely separate stream from the less charged, red, grains. Beneath the simulation snapshot of Fig. 4(c), we show the accumulated output of grains after 500 000 time steps. Without the beard (which can be eliminated in the simulations by reducing the negative charges on the chute), demixing vanishes. Evidently, the negative induced charges on the metal chute attract and retain positively charged grains, causing the edge of the feeder to become coated with a beard of positively charged material. This beard is the last thing that charged grains interact with before they enter free fall, and so the beard seems to cause the paradoxical repulsion of more highly charged grains, despite the naïve appearance that the mean applied field should attract them.

In conclusion, we have seen that charged grains, including both sand and pharmaceutical materials, segregate profoundly in very simple flow arrangements, to concentration extremes of 5% and 90%. This segregation occurs against the apparent electrostatic gradient, and direct simulations show that this effect is associated with the formation of a beard of opposite charges over the fixed charge region. It remains for future study to establish whether in other triboelectrification problems, local accumulations of charge may likewise cause a reversal of the field perceived by nearby free charges, leading to a consequent growth of charge separations.

This work was supported in part by the NSF ERC on Structured Organic Particulate Systems (C-SOPS), Grant No. EEC-0540855. We thank Pfizer, Inc. and Trek, Inc. for additional support, and David Maiullo and Maciej Noras for help and advice.

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