Effect of particle size distribution on the polarity of triboelectric charging in granular insulator systems

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Abstract

Triboelectric charging occurs in granular insulating systems even when all particles are composed of identical material. A simple model is used here to address triboelectric charging in such systems. The basis of the model is the existence of electrons trapped in high-energy states, which can be released during collisions with another particle and transferred to the other particle. This model shows that triboelectric charging in insulator systems composed of particles of identical material can be attributed to a distribution of particle sizes, such that smaller particles tend to charge negatively and larger particles tend to charge positively. This polarity of charging has been observed in field studies of sand storms, dust devils and volcanic plumes, and most laboratory experiments on triboelectric charging in granular systems.

Keywords: Triboelectric; Insulators; Granular

1. Introduction

In many phenomena the agitation of systems of insulating granular particles causes the particles to develop electrostatic charges. This triboelectric charging occurs in natural events such as sand storms [1], dust devils [2,3], and volcanic plumes [4], in industrial processes such as fluidized beds [5] and pneumatic conveying [6], and in pharmaceutical dispersal devices such as dry powder inhalers [7]. A number of studies suggest that in these systems the smaller particles charge negatively while the larger particles charge positively. The present paper proposes a simple mechanism for this polarity of charging based on particle size.

Field studies of natural phenomena imply that small particles charge negatively and large particles charge positively. Dust devils [8–12] and sand storms [10] are found to generate dipolar electrical fields perpendicular to the ground, with the negative pole at higher altitudes. Since the particles at higher altitudes tend to be smaller due to gravity, the implication is that smaller particles charge negatively and larger particles charge positively. This polarity of triboelectric charging in these systems has been the basis of modeling studies of these phenomena [13–15]. In volcanic plumes the electric fields are more complicated due to the existence of gas and aerosol at high altitudes, but again positively charged larger particles at the lowest altitudes and negatively charged smaller particles at higher altitudes contribute to the electric field [16].

Recent laboratory experiments have measured the charges on particles in granular systems as a function of particle size. These studies, carried out on polymer materials with industrial relevance, also show that smaller particles charge negatively and larger particles charge positively [17–21], although charging with the opposite polarity has been reported in one case [18].

Despite the significance of triboelectric charging in granular systems, the reason why charging occurs when all particles are composed of the same material, and why smaller particles tend to charge negatively, is not clear. In metallic systems, which are better understood than insulator systems, charge transfer between two surfaces is proportional to the difference in workfunction of the...
surfaces and the capacitance of the system [22,23]. Thus particles of identical metal will not charge each other when they collide, because the workfunctions of the particles are the same.

Several hypotheses have been suggested to explain the particle-size-dependent charging in granular insulator systems of a single material. A particle-size dependence of the workfunction has been suggested [20,24], but based on the finite-size correction to the workfunction of a metallic sphere [25], the changes in the workfunction with particle size are less than $0.01\%$ for particles larger than $1\,\mu$m. The particle size also alters the capacitance of a particle pair, but again the magnitude of this effect with regard to triboelectric charging is very small [14]. Other proposed explanations include a composition variation with particle size [14], particle-size-dependent adsorption of workfunction-altering contaminants [20], and a particle-size-dependent particle roughness or shape that affects the inter-particle contact [20]; however, these mechanisms would be highly system dependent and would not lead to the apparently general behavior observed in a wide range of systems.

2. Theory

We propose here a simple theory to explain the tendency of smaller particles to charge negatively, based on the explanation of triboelectric charging for same-material systems suggested by Lowell and Truskott [26]. The physical basis of the theory is that electron states in insulators are spatially localized, so that electrons can be trapped in high-energy states even if vacant lower energy states exist elsewhere in the material, as shown schematically in Fig. 1. The presence of trapped high energy electrons in insulators is demonstrated by studies that show that ultra-violet irradiation generates phosphorescence that lasts for days following the cessation of irradiation [27]; i.e., ultra-violet irradiation excites electrons to high-energy trap states, and phosphorescence corresponds to the slow release of the trapped high energy electrons to lower-energy states. Furthermore, thermoluminescence experiments, in which trapped high energy electrons are detected by luminescence when heating the material releases the electrons, show that electrons can be trapped in high-energy states for periods of years [28] to centuries [29].

Lowell and Truskott suggest that contact between surfaces provides a way to release electrons trapped in high-energy states. This contact may bring an occupied high-energy state on one surface in close proximity to a vacant low-energy state on another surface, which allows the high energy trapped electron to be released from the high-energy state to the vacant low energy state on the other particle.

Experiments support the ideas underlying the Lowell and Truskott theory. In particular, polyethylene normally charges negatively in interactions with gold, but charges positively in interactions with gold after undergoing ultra-violet irradiation [30]. This behavior can be understood in that irradiation increases the number of electrons trapped in high-energy states in polyethylene, which are then transferred to the gold during contact. Also, annealing has been shown to decrease the extent of triboelectric charging [31], which can be understood in that heating enables the release of trapped high energy electrons (as in thermoluminescence [28,29]). The theory is also consistent with the result that humidity decreases electrostatic charging [32]. Humidity allows a conducting layer of water to form on the insulator surface, through which trapped high energy electrons can escape to lower-energy states on the same surface; the resulting decrease in the number of electrons trapped in high-energy states decreases the extent of triboelectric charging.

The charging behavior that follows from the theory is investigated in two ways:

1. The theory is implemented in an analytically tractable model for a binary mixture, which addresses the average charging behavior.
2. The theory is addressed in deterministic particle dynamics simulations. These simulations address the time dependence of the processes and distributions of charges on the particles, rather than just the average charge per particle.

The simulations are carried out for impenetrable spherical particles with radius $R_i$ (for particle $i$), which do not interact, except for the steric interaction associated with their impenetrable character. The simulations include 864 particles that are confined in a cubic box with impenetrable walls. All collisions, both particle–particle and particle–wall, are elastic. Standard techniques for hard-particle dynamics are used to find the particle trajectories [33], which the following steps: (i) the time interval until the first collision occurs is determined from the positions and velocities of the particles; (ii) all particles are moved at constant velocity for the time interval up to the collision; and (iii) upon collision, the velocities of the

![Fig. 1. Schematic representation of the process of electron transfer upon contact of two insulators. (a) Electrons on the surface of an insulator can be trapped in high-energy states. (b) These electrons can be released from the high-energy states when a collision brings a low-energy state on another particle in close proximity.](image)
colliding particles are changed in accordance with conservation of energy and momentum. These three steps are then repeated to obtain the particle trajectories over a period of time.

The particle dynamics simulations incorporate the triboelectric charging theory proposed here as follows. Each particle $i$ has $n_{\text{high}, i}$ trapped high energy electrons and $n_{\text{low}, i}$ low energy electrons. Initially $n_{\text{low}, i}$ is set equal to zero, and $n_{\text{high}, i}$ is set to a value proportional to the surface area of the particle, which corresponds to the case in which the surface charge density of trapped high energy electrons is equal for all particles. At each particle–particle collision, one trapped high energy electron is transferred from each particle to the low-energy state on the particle it collides with, provided that a trapped high energy particle is present in that particle. For example, if particles A and B collide where $n_{\text{high}, A} > 0$ and $n_{\text{high}, B} > 0$, then an electron is transferred from A to B and one from B to A, and there is no net transfer of electrons between particles. However, if A and B collide where $n_{\text{high}, A} > 0$ and $n_{\text{high}, B} = 0$, then an electron is transferred from A to B but not B to A, and there is a net transfer of an electron from particle A to particle B. Note that we have chosen the simplest possible protocol for transferring electrons during collisions, but we note that other protocols (e.g., a probability of electron transfer at each collision) would not alter the conclusions.

3. Results

3.1. Analytical application of theory to model of binary mixture

A binary mixture of small (S) and large (L) particles is considered. There are $N$ particles, and the number fractions of small and large particles are $x_S$ and $x_L$, respectively ($x_S + x_L = 1$). The radii of the particles are $R_S$ and $R_L$ ($R_L > R_S$).

We address the case in which all particles initially have identical surface density of trapped high energy electrons, $\rho_0$ electrons/unit surface area. Thus there are initially $N_{\text{S}}\pi R_S^2 \rho_0$ trapped high energy electrons on the small particles, and $N_{\text{L}}\pi R_L^2 \rho_0$ trapped high energy electrons on the large particles.

These trapped high energy electrons are released by collisions, and transferred to a low energy state in the colliding particle. Each particle collides with both large and small particles, and thus distributes its trapped high energy electrons to low energy states in both large and small particles. The fraction of the collisions undergone by a small particle that involve a large particle is represented by $f_{\text{S,L}}$, and the fraction of the collisions undergone by a large particle that involve a small particle is represented by $f_{\text{L,S}}$. The fraction $f_{\text{S,L}}$ is then obtained as

$$f_{\text{S,L}} = \frac{(R_S + R_L)^2 x_L}{(2R_S)^2 x_S + (R_S + R_L)^2 x_L}.$$  

In an analogous way, the fraction $f_{\text{L,S}}$ is obtained as

$$f_{\text{L,S}} = \frac{(R_S + R_L)^2 x_S}{(2R_L)^2 x_L + (R_S + R_L)^2 x_S}.$$  

These results for $f_{\text{S,L}}$ and $f_{\text{L,S}}$ are valid for all particle packing densities. The average charge on the small particles, $Q_S$, can then be evaluated using Eqs. (1) and (2), and is found to be

$$Q_S = -4\pi \rho_0 \left( \frac{R_S}{R_L} \right)^2 \left( \frac{x_S}{x_L} \right) \left( 1 + \frac{R_L}{R_S} \right)^2 \times \left\{ \left( \frac{R_L}{R_S} \right)^2 \left( \frac{R_L}{R_S} \right)^2 + 2 \left( \frac{R_L}{R_S} \right) - 3 \right\} \left\{ 4 + \left( \frac{R_L}{R_S} \right)^2 + 4 \left( \frac{R_L}{R_S} \right) + 1 \left( \frac{R_L}{R_S} \right)^2 \right\}.$$  

Note that the term inside the brackets is always positive since $R_L > R_S$ implies

$$\left( \frac{R_L}{R_S} \right)^2 + 2 \left( \frac{R_L}{R_S} \right) - 3 > 0$$

and

$$3 \left( \frac{R_L}{R_S} \right)^2 - 2 \left( \frac{R_L}{R_S} \right) - 1 > 0.$$
Thus, this analysis shows that $Q_S \leq 0$; the equality holds when all particles are the same size, and the small particles charge negatively when the particles are different sizes.

The tendency of smaller particles to charge negatively holds for all ranges of particle concentrations, even when there are many more small particles than large particles. This result is evident from Eq. (3).

The result derived here is valid for all particle packing densities, ranging from the low packing densities relevant to airborne particulate systems to the high packing densities relevant to pneumatic conveying and fluidized beds. This generality occurs because the collision fractions $f_{S,L}$ and $f_{L,S}$ derived here are valid for all packing densities.

We note that our analysis is not dependent on all trapped high energy electrons being transferred: the parameter $\rho_0$ could represent the density of trapped high energy electrons that are eventually transferred, rather than the total density of trapped high energy electrons.

3.2. Particle dynamics simulations

Particle dynamics simulations are carried out to probe the time dependence and distributions of particle charges. Simulations are also carried out to address continuous particle size distributions.

First, particle dynamics simulations are carried out for a bimodal particle distribution with $R_L/R_S = 5$, equal concentrations of large and small particles, and an occupied volume fraction of 0.23 (the occupied volume fraction is the volume occupied by the particles divided by the total volume). The simulations are run until 100,000 collisions occur, at which point all high energy electrons are transferred to low-energy states. As shown in Fig. 2a, the average charge on the small particles is negative, and the average charge on the large particles is positive. The magnitudes of these average charges, after all trapped high energy electrons have been depleted, are in quantitative agreement with the analytical results obtained above (Eq. (3)). Fig. 2b shows the distribution of charges on the small and large particles after all trapped high energy electrons have been depleted—note that some large particles even charge negatively.

The particle dynamics results provide a clear picture of the physical origin of the asymmetric charging. For short times in the simulation ($\leq 1500$ collisions), there is no charging of the particles (see Fig. 2a). This occurs because all particles initially have trapped high energy electrons, and so each collision involves a symmetric transfer of electrons between particles that does not lead to charging. However, after the trapped high energy electrons have been depleted on a particle, then a collision with a particle that still has trapped high energy electrons involves an asymmetric transfer of electrons, in which an electron is transferred from one particle to another, but not vice versa. Fig. 2c shows that the trapped high energy electrons become depleted in the smaller particles before becoming depleted in the larger particles. The fact that the smaller particles become depleted of trapped high energy electrons before the larger particles leads to the net transfer of electrons from the larger particles to the smaller particles.

Particle dynamics simulations were also carried out for a continuous polydisperse particle size distribution, at an occupied volume fraction of 0.05. The size distribution is shown in the inset of Fig. 3. The simulations were run until 100,000 collisions occurred, at which point all high energy...
electrons had been transferred to low-energy states. The results for the charges on each particle at the end of the simulation, as a function of the particle radius, are shown in Fig. 3. Consistent with the analysis above, on average the smaller particles charge negatively and the larger particles charge positively. Again, the dynamics simulations show that there is a distribution of charging.

4. Discussion

This negative charging of smaller particles agrees with field observations of natural systems [8–12,16], as well as most experimental studies of polymer powders [17–21]. However, two studies reported the opposite polarity of charging in granular systems: one experimental study of polymer powders found that the smaller particles charged negatively in one system but positively in another system [18], and a study of a fluidized bed of glass particles indirectly suggests that the smaller particles charge positively [34]. Additionally, we note that a related study showed that rubbing two differently sized sheets of the same polymer material caused the smaller sheet to charge negatively in three cases (in line with the present analysis), but positively in one case [31]. The positive charging of the smaller particles or sheets found in these few cases may be due to either experimental issues or theoretical issues associated with the present simplified analysis.

This analysis shows that a distribution of particle sizes is necessary for triboelectric charging to occur in granular systems, and that a system with a perfectly unimodal size distribution will not undergo triboelectric charging. This result concurs with recent experiments that show that the extent of triboelectric charging in dust and sand systems is significantly greater when the system has a broad particle size distribution [35,36].

The electrostatic charges that develop may alter the particle trajectories such that particles of the same charge will repel each other and tend to collide less. The consequences of this effect are easily addressed in the limit that the electrostatic charges dominate the particle trajectories. In this limit there are no collisions between particles of the same charge, and in terms of our analytic treatment of binary mixtures, \( f_{LS} = 1 \) and \( f_{SL} = 1 \). From Eq. (3), \( Q_s < 0 \) when \( f_{LS} = 1 \) and \( f_{SL} = 1 \). Thus, smaller particles charge negatively regardless of whether the particle trajectories are altered by the charging process.

We have intentionally kept our analysis as simple as possible, so as to focus on the behavior that arises from the most basic theoretical ideas. Of course, triboelectric charging is an extremely complex phenomenon, and many effects have been omitted from our analysis. For example, collisions may induce inter-particle transfers of electrons between states of the same energy, vacant low energy states may be limited and thereby affect the charge transfer, and processes may occur to replenish the concentration of trapped high energy electrons. Also, nonspherical particle shapes can affect the contact areas during the collisions, the charge distributions on a particle, and the efficiency of electron transfer during a collision. An inclusion of such effects would require a cumbersome many-parameter description. We believe that our analysis captures the fundamental physical process that causes smaller particles in granular insulating materials to charge negatively, and thus connects experimental observations from a variety of fields.

5. Conclusion

The present analysis describes a simple physical explanation for the tendency of smaller particles to charge negatively as granular insulating materials are agitated, as found in many field studies and laboratory experiments [8–12,16–21]. This explanation is based on the ideas that collisions allow electrons trapped in high-energy states on one particle to escape to low-energy states in another particle, and that the surface density of trapped electrons is initially the same on all particles. We have shown that these factors alone cause smaller particles to charge negatively (on average).

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References
