TRIBOELECTRIFICATION OF GRANULAR MATERIALS

by

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*We also certify that written approval has been obtained for any proprietary material contained therein.
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Triboelectrification of Granular Materials

Abstract

by

KEITH MITCHELL FORWARD

Triboelectric charging, also known as contact charging, is a process that occurs when two initially neutral surfaces are in contact, transfer charge, and upon separation, remain electrically charged. This charging occurs in a wide range of contexts, including industrial applications such as fluidized beds, pharmaceuticals, dust explosions and pneumatic conveying, and natural phenomena such as sand storms, dust devils, lightning and volcanic plumes. The mechanism of triboelectrification of granular materials is poorly understood, especially in single component systems.

Triboelectric charging of chemically uniform, insulating granular materials with a broad size distribution is generally known to exhibit bipolar charge segregation, characterized by smaller negatively-charged particle and larger positively-charge particles. This study focuses on the development of experiments to validate previously accepted theory and experimental observations of bipolar charging in these systems. Samples of soda lime glass beads with bimodal size distributions are initially charged in a flow apparatus that induces only particle-particle interactions in a controlled environment. Particles are separated and characterized by their charge polarity and sized using optical methods. Charging behavior is found to be intimately coupled to the relative
size and mass concentration of the particle size distribution with smaller particles tending to charge negatively and larger particles charging positively. Several single component systems are examined where this phenomenon occurs including polyethylene resin particle, glass beads, and Mars simulant (JSC-1 Mars simulant). These results are explained by a population balance model, in which the charge segregation occurs from an asymmetrical transfer of a negative species (i.e. electrons or hydroxide ions) between small and large particles.
1.1 What is Triboelectrification?

Triboelectric charging, also known as triboelectrification, is a process that occurs when two initially neutral surfaces are in contact, transfer charge, and remain charged after separation. Typically, when the surfaces contact, there is lateral motion (or rubbing). When there is no lateral motion, this is known as contact electrification. The polarity of the surface charge is a result of different material properties (e.g. electronic properties, hydrophility, surface roughness, surface stress/strain, impurities and other properties) and has been described empirically by the triboelectric series which is not fully understood.

Ancient Greeks coined the term *tribo*, which means “rub,” and *electricity*, which originates from the Greek word for “amber” to explain the charging produced after rubbing amber with fur. In this case, the fur charges positively and the amber charges negatively. In a similar sense, triboelectric charging occurs when rubbing a balloon against your head or arm with the balloon charging negatively and the hair from your head or arm charging positively. The resulting charge on the balloon can be on the order of 10s of kilovolts resulting in a discharge or spark if the balloon is placed near a grounded surface. While triboelectric charging is a commonly observed phenomena, it is unclear why such large quantity of charge transfer occur between the surfaces.

Shaw first developed the triboelectric series in 1917 to explain charge transfer between materials\(^1\). He rubbed various materials together and used an electroscope to measure the charge on their surfaces. He showed that some materials are more likely to charge negatively than positively, and vice visa (Figure 1.1). Based on these results, Shaw suggested that for a given pair, the material that charged negatively would be the one more likely to acquire electrons, and the material that charged positively would be
**Dr. P. E. Shaw.**

Table showing the Tribo-electric Normal Series, Column 2, with Variations for Matt, Abnormal, Pressed and Flexed States in Columns 3, 4, 5, 6, and 7 respectively. The more important materials are in capitals. Metals are in italics.

**GROUP A.**

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<tr>
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<tr>
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<td>31</td>
<td>Gutta Percha</td>
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<td>Pt, Mg, Au</td>
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<td>Izediarubber</td>
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Figure 1.1 Tribo-electric series produced by Shaw in 1917.
the one more likely to give up electrons. Over the past century, this model based on electron transfer between materials has been heavily debated against alternative mechanisms involving other charged species. Nonetheless, the fundamental work done by Shaw has been instrumental to our current understanding of contact charging$^1$.

Triboelectrification is often associated with electrostatic charging; however, electrostatics refers to the interaction between two stationary electric charges and is independent of the mechanism of how the charge is deposited. It is possible to charge a surface without contacting it with another surface (i.e. not triboelectrification). For example, to produce a charged conductive surface, the material is biased or floated with a separate voltage source. A charge can also be deposited on an insulator surface in contact with a plasma (i.e. gas discharge) which contains electrons and ions. While these charged surfaces are examples of electrostatic charging, they are not classified as cases of triboelectric charging. Triboelectric charging is restricted to charging due solely to contact between surfaces (or close proximity to allow for electron or ion tunneling between surfaces).

1.2 Impact and Consequences

As triboelectrification occurs in a wide range of consequences, understanding the mechanism would be extremely beneficial to a broad range of applications. In particular, triboelectric charging often involves granular material systems. This is due to the large surface-to-volume ratio associated with granular materials as compared to bulk materials which results in a larger contact area and, therefore, enhances charge transfer. The large
charge to mass ratio can then cause problems in several different fields. Some examples are presented in more detail in the following discussion.

1.2.1 Pharmaceutical industry

The pharmaceutical industry is one example of an area impacted by the triboelectrification of particles. Many pharmaceuticals are produced in granular form in a flow process involving a series of pipes and hoppers. During transport of the material, the particles collide with each other and other surfaces, causing triboelectric charging. The charged particles tend to aggregate because of charging, resulting in non-uniformities and quality control issues for the final pharmaceutical product. When the material sticks together, it is difficult to control the manufacturing of accurate amounts of the desired drug. In fact, eighteen percent of Federal Drug Association (FDA) recalls are due to potency/content uniformity.

In addition to pharmaceutical production, a similar problem exists in Dry Power Inhalers (or PDIs). PDIs contain a mixture of small drug particles (<5 microns) that are supposed to adhere and large additive particles (63 to 90 microns) to deliver a controlled dose of drug. However, the small particulates can become highly charged due to contact with the device and other particles in the PDI. As a result, the small particle aggregates adhere to the device and cause problems for drug delivery, drug disposal, and dosage.
1.2.2 Polyethylene natural gas pipeline

Another example of triboelectric charging is in natural gas piping which is typically made of high density polyethylene. Polyethylene pipe is lighter, cheaper and easier to work with than its older counterpart, copper. However, one of the problems with polyethylene is its ability to triboelectrically charge.

Dust particles or other small contaminants often found in the pipeline can cause extremely large amounts of charge to build up because of contact charging between one another or with the pipe wall. These impurities enter when the gas is being extracted, either during maintenance or from other sources. As the gas flows though the pipeline, the particles travel along the polyethylene pipe and triboelectrically charge the inside of the pipe. The charge also builds up on the outside of the pipe, which is equal and opposite to the one on the inside of the pipe. The accumulation of charge can reach up to 60 kilovolts or greater! This charge build-up can result in physical damage to the polyethylene pipe if the electrical fields generated are large enough to cause dielectric breakdown. This generates extreme amount of heats (on the order of 2500°C) and leads to melting and pinhole formation in the polyethylene pipe. Natural gas can then leak from the pinholes, and over a period of time as the gauge pressure in the pipe decreases, result in increased costs from lost product and maintenance.

In addition to maintenance, there are significant safety issues with the charging of the natural gas piping. Since the pipe is buried and the charge is not isolated from ground, when a worker touches the charged surface, the electrons can now flow through the worker to ground. Even worse, an explosion may occur if the pipe is leaking and a spark forms. In addition to natural gas, a similar charge build up has been observed in liquid
fuel, such as petroleum, toluene and iso-octane. Understanding the mechanism of triboelectric charging in polyethylene natural pipes would be extremely beneficial for the natural gas field.

1.2.3 Polyethylene resin production

The triboelectric charging of polyethylene powders has been found to occur during their synthesis in large polymer reactors. These reactors are normally large vessels (~120 feet and 16 inches in diameter) with gas reactants and small catalyst particles (~10 microns) flowing inside. As the gas reacts on the catalyst particles, polyethylene particles nucleate and grow. The polyethylene particles typically stay in the reactor for 4 to 6 hours and usually range from 20 microns (fine) to 2 millimeters (coarse) in diameter. Due to the nature of these particles, collisions occur between them and the reactor wall, resulting in triboelectric charging. As the particles acquire charge, they aggregate and adhere to the reactor wall. The reactor is operating close to the melting point of polyethylene (~176°C), the coating of particles on the wall can disturb the flow dynamics in the reactor. In addition, the resin melts to the reactor wall and continues to polymerize. If the charge buildup is not treated, stagnant zones develop in the reactor and lead to poor heat removal from the reactor. Ultimately, a coating of polymer is deposited on the reactor wall, known in the industry as sheeting, and the reactor must be shut down to remove the polymer sheets. The downtime is dependent on the size of the reactor and the type of polymer; typically, the time is between 18 to 30 months of continuous operations, with a downtime of 3 to 8 weeks. Understanding the triboelectric charging in fluidized reactors could eventually lead to decreased downtime or eliminating the sheeting behavior all together,
and have a profound effect on the thousands of polymerization reactors in operation worldwide.

1.2.4 Dust explosions

Dust explosions have also been linked to triboelectrification. When grains or other flammable materials flow into silos, they collide with each other and accumulate charge. In particular, when fine particles contact each other and the silos’ wall, they become charged, often in the form of a cloud. The charge can build-up to the point of breakdown which produces heat and ignites the flammable material\textsuperscript{12,13}. Since the particles are floating in air, there is an abundance of oxygen, allowing rapid combustion. Coal and metal powders are also capable of producing dust explosions\textsuperscript{14}. Dust explosions are unpredictable and often cause large amounts of damage. The triboelectrification of combustible powders is a safety concern.

1.2.5 Dust devils and sand storms

Triboelectrification is also commonly observed in natural contexts. Field studies have shown that dust particles in dust devils\textsuperscript{15} and sand storms\textsuperscript{16,17} charge significantly (Figure 1.2). When the wind blows, sand particles are picked up from the ground and the force of the wind causes particles to collide and drive charge transfer\textsuperscript{18,19}. This phenomenon is not just limited to Earth; it has been considered when planning starcraft missions to Mars where sand storms are more common than on Earth\textsuperscript{20}. The large potential created by Martian sand storms could disable electronics and charged dust may adhere to solar cells and prevent solar power production\textsuperscript{21}. 
1.2.6 Volcanic plumes and lightning

Lightning and volcanic lightning are the result of triboelectrification of ice particles and volcanic ash, respectively, producing large enough potentials to cause atmospheric breakdown. In large clouds, heat gradients generated from condensing water out of air and the decrease in pressure at higher altitudes drive the convective flow of dust and ice particles. A similar mechanism occurs in volcanic plumes, were ash is propelled into the sky. The eruption causes ash particles to collide and exchange charge. The charged ash particles are capable of producing atmosphere breakdown (Figure 1.3).
A recent article suggests that the origin of life may have been a result of volcanic lightning\textsuperscript{26}. To simulate the conditions in Earth at this time, a spark was generated in a glass vessel containing a mixture of various gases (CO\textsubscript{2}, NH\textsubscript{3}, and others gases). The spark was found to breakdown the gas into different ions that reacted with each other to form several different amino acids. Overall, the experiment hints that volcanic lightning may have produced amino acids and led to life. The amino acids could accumulate in local tidal areas, and from exposure to carbonyl sulfide (often found in volcanic environments), create peptides which are the basic constituents of proteins and RNA\textsuperscript{26}.

Figure 1.3 Volcanic lightning from Sakurajima on May 18\textsuperscript{th}, 1991\textsuperscript{27}.
1.2.7 Xerography

While triboelectrification often plagues many fields in an undesirable manner, xerography processes benefit from this phenomenon. The toner in Xerox machines is made from a clear thermoplastic with colorant and charge control agents. The charge control agent determines the polarity and amount of charging when mixed with the carrier beads\(^{28}\). The toner usually ranges from 5 to 10 microns in diameter. Carrier beads usually triboelectrically charge the toner particles, and this mixture is known as a developer. To copy an image on a sheet of the paper, a charged is deposited on the paper using a corona discharge in the pattern of the image. The triboelectrically-charged toner electrostatically adheres to the image charge on the paper. The sheet of paper is then heated and thermoplastic melts to the paper surface, producing the desired copy\(^{29}\).

1.3 Summary

These are just a few examples of the role of triboelectrification in charging granular systems. The aim of the project is to gain further insight on the mechanism behind triboelectrification, particularly in granular insulator systems.

1.4 References


13 B. Maurer, “Discharge due to electrostatic charging of particles in large storage silos” Ger. Chem. Eng. 4, 189 (1979)


22 NASA, “Phantoms from the sand: Tracking dust devils across Earth and Mars” web date 10/07/05 www.nasa.gov/vision/universe/solarsystem/2005_dust_devil.html


27 Sakurajima Volcananological Observatory (5/18/1991)


II. BACKGROUND

Triboelectrification, also known as contact charging, describes the process of two surfaces coming in contact (or close proximity) with each other and transferring charge. As discussed in chapter I, triboelectric charging occurs in a wide range of situations and applications. Triboelectric charging is often split into two categories: conductor contact electrification and insulator contact electrification. Conductor contact electrification involves electron transfer between surfaces and its mechanism is universally accepted. In contrast, the mechanism for insulator contact electrification has not yet been developed; for example, it is unclear whether electron and/or ion transfer occur during contact. In this chapter, the accepted mechanisms for conductor contact electrification and current models for insulator contact electrification are presented. Also, the proposed mechanisms for single component triboelectrification are explained.

2.1 Conductor Contact Electrification

The mechanism of electrification of conductors is well understood. The low resistivity (high conductivity) of electrons in conductors allows electrons to flow freely through the materials. Charged conductors do not typically retain charge because the excess charge usually flows to ground. However, conductors will remain charged after contact charging if the conductors are isolated from ground\(^1\).

2.1.1 Theory behind conductor electrification

The theory behind conductor contact electrification is based on the premise that electron transfer occurs such that thermodynamic equilibrium is reached. The transfer of
electrons is driven by the difference in chemical potentials for the electrons between the two materials. The contact potential difference, \( V_c \), is defined as the difference in the surface potential of the conductors\(^2\).

\[
V_c = (\phi_B - \phi_A)/e  
\]  
Equation 2.1

The workfunction, \( \phi \), is the amount of energy an electron loses going from the lowest energy vacant orbital state to a position an infinite distance away from the metal surface. The workfunction of a conductor is dependent on energy levels at the top of the valence band (Figure 2.1).

Electrons can tunnel between conductor surfaces to maintain a potential difference equal to the contact potential difference and establish thermodynamic equilibrium. Work has been done by Harper to explore the process of tunneling\(^3\)

\[
Q = C_o V_c  
\]  
Equation 2.2

where \( C_o \) is a capacitance of the system that is dependent on the shape of the contacting bodies. At distances larger than 1 nm, tunneling of electrons becomes negligible. Experimental work has been done to show that conductor-conductor charging is proportional to the contact potential of the conductors\(^4,5\).
2.2 Contact Electrification Between Insulators

Contact electrification between insulators has been frequently observed in both nature and industry. At first glance, it is non-intuitive that insulators would charge at all since the conductive and valance bands are separated by a large energy and electrons cannot flow as in the case of conductors or semiconductors. According to band theory electrons do not exist in the forbidden zone between the valance and conductive band (known as the band gap). Even if electrons were somehow able to travel from the valance to conductive band to transfer charge, it would be expected that the triboelectric series would correlate with the band gap of the material, which it does not (Figure 2.2). Why insulator charging occurs is not necessarily clear, but it does occur in the various systems as explained in the introductory chapter.
Figure 2.2 Insulator contact electrification. Electrons in the valance band of insulator A cannot flow to the valance band of insulator B because there are no unoccupied states available. The electrons do not have enough energy to flow to the conductive band of insulator B.

A typical range for charge density on an insulator is $10^{-5}$ to $10^{-3}$ C/m$^2$ which corresponds to approximately one elementary charge for every $10^4$ surface atoms. Thus, contact electrification affects only a small fractional area of the material surface. However, this charge density is easily capable of breaking down air at atmospheric conditions which requires electric fields of 30 kV/cm or greater$^1$. In addition, these fields are capable of bulk or surface breakdown in thin films of insulators in transistors and other electronic devices.

Although triboelectrification in insulator systems is widely accepted, the mechanism behind charging has been highly debated over the past century. Harper was the first to propose a mechanism for insulator contact electrification in the 1960s that charge transfer occurs through three pathways: electron transfer, ion transfer, and material transfer$^2$. He suggested that ion transfer contributed to contact charging for
insulators. More recently, Lowell has argued that contact electrification results from electron transfer between materials\(^1\). As a result of these conflicting theories, significant research efforts have been devoted to proving which transfer species is actually involved in moving charges between surfaces in contact (or close proximity) with each other. While it is still unclear if a single transfer species causes charge buildup on insulating surfaces brought into contact, there are convincing arguments for both mechanisms (ion and electron transfer).

### 2.2.1 Ion transfer mechanism

The current and most accepted mechanism for ion transfer has been proposed and validated by McCarty and Whitesides\(^6\), based on Diaz\(^7,8,9,10\) and his own work\(^11,12,13,14\). Diaz performed contact electrification studies with polymers that were functionalized with covalently bonded molecules that contained immobile ions and mobile counterions. Examples of these are shown in the figure 2.3 below.
Figure 2.3 Polymer and glass beads contain mobile ions on the surface. Materials containing mobile cations charge negatively and materials containing anion charge positively. The mobile ions are removed from the surface.

Figure 2.4 shows an illustrated example for the case of cations that are covalently bonded to the polymer and anions that are mobile and able to transfer to the adjacent surfaces. After contact electrification, the functionalized material acquires the same charge as the polarity of the covalently bonded ion. As the concentration of the covalently bonded ion increases, the magnitude of the surface charge on the triboelectrically charged material increases. These results suggest that the charging of insulator pairs consisting of ionic doped polymers is due to the loss of the mobile counterions of the surface. Similarly, Whiteside has extended these experiments to a
wide range of covalently bonded ion and mobile counterions. In these studies, the functionalized polymer and glass beads were triboelectrically charged with a grounded aluminum surface. While the lack of the mobile counterions explained the sign of the triboelectrically charged surface, it is unclear what *drives* the motion of the mobile counterions to the opposing surface.

![Figure 2.4 Ion transfer mechanism. Mobile anions are able to transfer to between surfaces due to Van der Waals and Coulombic forces.](image)

To explain their experimental observations, McCarty and Whitesides proposed a mechanism (adapted from Harper) that the potential energy of a mobile ion between two surfaces at different electrical potentials is given by the sum of three forces: two short-range interactions (one for each surface, with potential-energy curves shaped like a Lennard-Jones potential or Morse potential) and a long-range Coulombic interaction. When the two surfaces are in Van der Waals contact, the mobile ion experiences a single potential well between the two surfaces. As the surfaces move apart, the potential-energy surface evolves into an asymmetric double-well potential. Thus, one well is associated with each surface and, as the surfaces move apart, a fraction of the mobile ions will be trapped in the adjacent surface, resulting in charge transfer between the two surfaces (Figure 2.5).
Based on this model, a simple calculation can be done to predict the number of mobile ions actually transferred to the unfunctionalized adjacent surface. At equilibrium, the ratio between numbers of transferred mobile ions per unit area is given by a Boltzmann distribution

\[
\frac{n}{N-n} = \exp\left(\frac{n d e^2}{\varepsilon_o k T}\right)
\]

Equation 2.3

where is \( n \) is the number of transferred mobile ions per unit area, \( N \) is the total number of ionic functional groups per unit area, \( d \) is the distance between surfaces, \( e \) is the elementary charge, \( \varepsilon_o \) is the permittivity, \( k \) is the Boltzmann constant and \( T \) is temperature. Two force fields drive equilibration between the mobile ion distribution on the surfaces: (1) electrostatic forces, which tend to keep the mobile ion close to its counter-ion (which is immobile) and (2) entropy, which tends to equalize the number of mobile ions on the two surfaces. McCarty and Whitesides\(^6\) suggested that approximately 3% of mobile ions would transfer from the functionalized surface to the unfunctionalized surface at equilibrium. From this transferred ion density, the charge density was approximated to be 1 elementary charge for every 300 atoms (3000 ca per square micron), which is almost two orders of magnitude greater than the typically observed laboratory experiments (both by Whitesides and Harper). This shows that it is theoretically possible to produce a large charge density; however, the dielectric breakdown of the surrounding medium ultimately limits the final stable charge density on
2.2.1.1 Role of water

Almost all surfaces are covered in a thin film of water when exposed to atmospheric moisture. Even fluorocarbons, which are extremely hydrophobic, adsorb some water. Teflon has been shown to sequester around two monolayers of water in air with 80% RH (relatively humidity)\textsuperscript{15} The adsorption of water does affect (in most cases, increases) the surface conductivity and likely affects contact electrification. Additionally, the monolayers of water can act as a bridge between the surfaces to increase the effective area of contact.

2.2.1.2 Role of water for triboelectrification of materials with mobile ions

In studies done by Diaz and co-workers with polymers containing mobile ions, it was observed that almost no contact charging occurred at 0% RH, and maximum charging was observed at 30% RH and began to decrease at 40% RH. Based on these results, it is suggested that water is required for contact charging to produce good contact
between surfaces. Also, at high humidity, the increase in monolayers of water produces increased surface conductivity and allows the charge to dissipate along the surface, possibly discharging to ground\textsuperscript{16}.

Water allows for mobile ions to diffuse to the adjacent surface. If the water thickness is less than 1-2 nm, the water bridge is thinner than the typical Debye length of most aqueous solutions. This means that the aqueous ions have access to both surfaces and are not spatially dependent. The entropic tendencies of mobile ions are on the same order as the electrostatic force to the non-mobile counterion, thus the mobile ions will distribute throughout the thin film of water\textsuperscript{6}. When the surfaces are separated, a proportion of the mobile ions are trapped on the unfunctionalized surface, producing two charged surfaces.

\textbf{2.2.1.3 Role of water for triboelectrification of nonionic materials}

For the case of materials that do not contain mobile ions, a key question is what are the nature and source of ions that are allowed to be transferred between surfaces? Recently, several reports have concluded that, generally, anions (in particular hydroxide) tend to accumulate at the interface between water and organic polymers\textsuperscript{17,18,19,20,21,22,23}. This generation of anions on the interface appears to be independent of hydrophilicity of the organic polymer. In the case of hydroxide, ions accumulate at the interface, leaving hydronium ions solvated. For contact charging of two different polymers, the thin film of water acts as a bridge between surfaces. The hydroxide ions redistribute and stabilize on the polymer with the greatest affinity for hydroxide ions once in contact. Finally, the surfaces are separated and the polymer with more hydroxide ions will acquire a negative
charge. This may explain the triboelectrification of non-ionic materials (Figure 2.6). In addition, surface contaminants will also contribute other ions and may change the triboelectrification behavior. Whiteside and colleagues\textsuperscript{24} have also performed experiments on polystyrene in varying pH environments and showed that charging increases in basic environments as compared to acidic environments. These results support the idea of ionic transfer since hydroxide ions are more likely to adsorb on polymers in a basic environment than in an acidic one. The hydroxide-adsorption model has been used to explain the contact charging in non-mobile ion containing materials. However, McCarty and Whiteside\textsuperscript{6} acknowledged that further research is required to determine why hydroxide segregates to the interfaces and explain how other factors such as temperature and surface roughness affect the dispersal of the ions in monolayers of water\textsuperscript{6}.
2.2.2 Electron transfer mechanism

Lowell and coworkers have argued that electron transfer is the most likely mechanism for insulator electrification based on an analogy between chemical potentials of insulators and workfunctions of conductors\(^1\). As described earlier, the mechanism for conductor contact charging is based on electron flow from one surface to the other due to the difference in workfunctions. Similarly, in insulators, electrons flow between surfaces to reach thermodynamic equilibrium.

Figure 2.6 Hydroxide adsorption model\(^6\).
Lowell performed a series of experiments to examine the surface contact charging between conductor and insulator surfaces. Based on his observations, he determined that electron transfer occurs in insulators similarly to conductor contact electrification\textsuperscript{25,26,27}. However, it remains unclear how electron transfer would occur in insulators (dielectric materials) since there are no free electrons. The band gap that separates the conductive and valences bands in dielectric materials is large; thus, electrons are unable to flow in the conductive band to allow for electron transfer. In insulators, electrons are spatially independent from each other. While this theory is appropriate for “perfect” insulators, as we will explain, real insulators are not necessarily crystalline and defect free.

It has been shown that trapped electrons can exist in defect states in the band gap of insulators. In the case of polymers, the entanglement of the carbon chains produces trapped electron states, along with surface defects and chemical defects\textsuperscript{28,29,30,31}. In other crystalline materials, defects in the crystal structure and impurities will create trapped electron systems. Thermoluminescences has been used to determine the density of trapped electrons in polymers\textsuperscript{32,33}. These experiments have been performed on materials with electrons in high energy states that can exist for periods of years to centuries\textsuperscript{34}. In addition to trapped electrons, vacant energy states can also exist in the band gap as a result of defect states in the material. Trapped electrons and vacant energy states are spatially independent from each other, making it impossible for electrons to move to lower states which explains why the electric conductivity remains poor in insulators\textsuperscript{35,36}.

In the theory proposed by Lowell, two surfaces are brought in contact with one another such that trapped electrons on one surface can transfer to a lower vacant energy state on the adjacent surface. Once the surfaces are separated from each other, the
electrons have transferred from one surface to another producing an imbalance of charge on the two surfaces (Figure 2.7)\textsuperscript{24-26,34,35}.

Other research groups have independently shown that insulators contacted with different conductors exchange charge proportionally to their respective workfunctions\textsuperscript{2,37,38}. These experiments have been performed in a vacuum to avoid surface contaminants and water. The effective workfunction of various insulators was then determined by interpolating to the zero charge value. The idea behind these experiments is that electrons flow from the conductor surface to vacant low energy states in the insulator to establish thermodynamic equilibrium between the surfaces. An implicit assumption is that that the effective workfunction in insulators is a surface property when considering triboelectrification\textsuperscript{39}. In this regard, it has been shown that lapped (or roughed-up) surfaces tend to charge greater than the same material after annealing\textsuperscript{40}. A
similar behavior has been observed with high stress/strain materials where the increase of stress/strain has been found to increase the density of trapped electron states in the materials, resulting in a high effective workfunction, and, thus, increasing charge transfer. The theory of charging behavior originating from defects in the forbidden gap of insulators has been termed ‘surface state theory.’

2.2.2.1 Evidence of electron transfer

A recent article has found through experiments that electrons may be the charge transfer species involved in contact charging of Teflon-like materials (polytetrafluoroethylene)\(^43\). Liu and Bard attacked the problem from an electrochemical standpoint and performed several different experiments on the charged Teflon. In one experiment, Lucite (polymethylmethacrylate, known as acrylic) was used to charge the Teflon surface and resulted in the Teflon charging negatively (accumulating electrons) and the Lucite charging positively (giving up electrons).

A piece of charged Teflon was also immersed in an acidic solution and found to change the pH and evolve hydrogen gas. In the experiments, the pH of the solution (3 ml of 0.1 mM HCl) increased from 4 to 6.2 after the charged Teflon was immersed. Although this alone does not indicate electron transfer since it is possible for H\(^+\) or another anion to adsorb on the surface during charging and cause a pH change, additional measurements by mass spectrometry were used to confirm hydrogen production from the reduction reaction of H\(^+\) + 2e\(^-\) → H\(_2\). The appearance of D\(_2\) for charged Teflon and the absence of the same peak for uncharged Teflon is clear evidence of electron transfer reactions resulting from contact charging involving Teflon.
In addition to the reduction of H⁺, Liu and Bard investigated electrodeposition of copper. Charged Teflon was immersed in a solution of CuSO₄ to reduce Cu²⁺ and deposit Cu metal. The electrodeposition of Cu metal on charged Teflon implies electron transfer, since reduction of Cu²⁺ by hydroxide (according to Whitesides’ hydroxide adsorption model)⁶ would produce Cu(OH)₂, which would remain dissolved in solution.

The suggested model of electron transfer rather than ion transfer was further validated by experiments focused on the redox reaction of Fe(CN)₆³⁻. Cyclic voltammograms of solutions of Fe(CN)₆³⁻ before and after immersing charged Teflon showed a decrease in the plateau which correlates to a single electron reaction: 

\[
\text{Fe(CN)}_6^{3-} + e^- \rightarrow \text{Fe(CN)}_6^{4-}
\]

This apparent decrease in current is associated with an increase in the number of electrons in the initial solution.

2.3 Dielectric Breakdown

Dielectric breakdown of the surrounding gas limits the maximum stable surface charge that a dielectric material can acquire. When a charge is deposited on an insulator via triboelectric charging or corona discharge, an electric field is generated from the charge. When gaseous ions or electrons are accelerated towards (or away from) the surface due to the electric field, charged species in the gas phase (i.e. electrons or ions) will collide with neutral gas molecules. If the collisions have sufficient energy, ionization events will occur, leading to more charge species. Overall, this mechanism will result in a cascade event, known as gas breakdown, which ultimately allows current to flow to the dielectric surface and neutralize some or all of the surface charge⁴⁴. The threshold for dielectric breakdown in atmospheric air is 30 kVcm⁻¹ which correlates to a
uniform charge density of approximately $10^4 \text{ C/m}^2$ on a planar insulator. This limit explains why there is an upper bound for stable charge on insulator surfaces.

It should be mentioned that gas breakdown is dependent on pressure and gas species as well which is summarized by the Paschen curve\textsuperscript{45}.

2.4 Single Component Triboelectrification

Although the above mechanisms suggest an explanation for triboelectrification of different materials, they do not clearly show why charging occurs in single component granular material as discussed in the introductory chapter.

2.4.1 Evidence of size dependence bipolar charging

Triboelectrification in large silos is often a concern due to the possibility of dust explosions. Over a period of time, an electric field has been known to exist such that a negative pole is at the top and a positive pole at the bottom of the silo. It has been hypothesized that the fine particles charge negatively and the large particles charge positively\textsuperscript{46}. In addition to storage silos, particulate systems with a broad size distribution are also known to produce bipolar charging behavior.

Field studies on dust devils have shown that large dipolar electric fields exist and orient themselves such that the negative pole is at higher altitude and the positive pole is near the ground (Figure 2.8)\textsuperscript{47,48,49,50,51}. The widely accepted interpretation of this result is that the smaller particles charge negatively and larger particles charge positively, and that the wind blows the smaller particles higher. This size dependence of polarity has been the basis of a number of modeling studies of dust devils\textsuperscript{52,53,54}. A similar hypothesis of small
particles charging negatively and rising to higher attitudes has been proposed to explain the electric fields that develop in volcanic plumes that lead to volcanic lightning\textsuperscript{55}.

![Dust devil electric field](image)

**Figure 2.8 Dust devil electric field.** Electric dipole moment is generated by the segregation between small and large particles\textsuperscript{50}.

In addition, a number of laboratory experiments have surmised that small particles charge negatively and large particles charge positively when triboelectrically charged with each other\textsuperscript{45,56,57,58,59,60,61}. In these studies, a wide range of materials (polymeric, glass, alumina) appearing at different locations along the triboelectric series were examined. Although many laboratory-scale experiments have shown smaller particles charge negatively and larger particles charge positively, no systematic study has been performed to explain what factors contribute to charge segregation in single component granular systems.

### 2.4.2 Theories for charge segregation

Theories have been proposed to explain why small particles tend to charge negatively and large particle charge positively. It has been suggested that these tendencies are due to a difference in the effective workfunction of the different sized
particle. It has been well documented that size distribution plays a role in triboelectric charging of granular material\textsuperscript{45,55,56,57,58}.

Castle and Inculet have explained why bipolar charging segregation may occur in polydisperse granular materials\textsuperscript{56,62}.

1. Inherent differences in workfunction exist between small and large particles.
2. Microscopic surface differences (e.g., surface roughness, shape) change the extent and nature of contact.
3. Large surface increases the probability for submicron-size contaminants to absorb on the surface.
4. There is a difference in surface energies existing between small and large particles (i.e., curvature effect changes the surface energies of the material).

Mazumder has suggested that the increase in area of large particles increases the amount of surface contaminants and oxidation, which could produce a change in workfunction. The difference in the workfunction between small particles and large particles would then create the bipolar charging\textsuperscript{60}.

\textbf{2.4.3 Asymmetric contact}

Based on work done by Lowell and Truscott\textsuperscript{63,64}, a simple theory has been proposed to the explain charging of same-material systems. Electron states are spatially and energy independent from each other in an insulator. Electrons in high energies are unable to flow to lower energy states due to the low electric conductivity in insulator materials. This model assumes that there are a larger number of vacant low energy states than high energy trapped electrons in a single insulator.
Based on Lowell and Truscott’s model, high energy state electrons are able to transfer to low vacant energy states when in close proximity. In their study, asymmetric charging is compared to a sphere rolling or sliding along a plane surface of the same material. The sphere produced a net negative charge and the plane a net positive charge because the area of sphere that is in contact with the plane is smaller than the area of the plane in contact sphere. The finite number of high energy trapped electrons on the sphere are quickly transferred to lower vacant states on the plane as it slides along the surface. Similar, the high energy trapped electrons are continuously transferred to the sphere as it slides along the plane\textsuperscript{63,64}. This has been verified experimentally; the charge on the sphere increases linearly with the distance that the sphere travels up to a maximum charge governed by the dielectric breakdown of the surrounding gas.

Although asymmetric charging has been shown with spheres and planes, it has not been clearly shown in single component granular materials. It has long been hypothesized that small particles charge negatively and large particles charge positively in particle mixtures characterized by broad size distributions. This is suggestive of asymmetric contact charging that could lead to the bipolar charge distribution. Since the particle surface contains a finite number of electrons, the number of electrons will scale with the size of the particle (i.e. larger particles have more electrons to give up). Initially, the density of the high energy states are the same for all particles; as the particles collide with each other, electrons are transferred. Because the large particles have a larger number of electrons to transfer to lower vacant energy states, they are more likely to lose electrons and, thus, charge positively. Simulation studies have been done using Lowell and Truscott’s model\textsuperscript{64} of asymmetric contact showing this behavior; however, no
experimental study has been able to confirm that small particles charge negatively and large particles charge positively.

Lacks et al. proposed the idea of a surface state theory applying to granular materials, which explains the bipolar charging in powders and granular materials. The model assumes an equal density of high energy trapped electrons on both small and large particles. As collisions occur, high energy trapped electrons will transfer to the low energy vacant state on other particles. As the collisions continue, the small particles will lose their high energy electrons quickly due to the smaller amount present on the surface. Large particles tend to give up electrons to the small particles, leading to bipolar charging.\textsuperscript{65,66,67}

The currently proposed hydroxide-adsorption model (ion transfer) does not completely support the Lowell and Truscott\textsuperscript{64} mechanism of asymmetrical charging in a single component system. Because the mechanism that allows the hydroxide ions to accumulate at the interface water-surface is still unknown, there is no apparent driving force that would promote the hydroxide ions from one surface to the other in a single component system.

2.5 \textbf{Summary}

Although much work has been done on triboelectrification of materials, a mechanism has been accepted for conductor contact charging, but not in the case of \textit{insulator} contact charge. While theories for insulator contact charging have been proposed, a universally-accepted mechanism remains elusive. Recent work by Liu and Bard\textsuperscript{43} has proposed an electron transfer model, validated with experiments on charged
Teflon. In contrast, Whiteside and colleagues have used a series of ionic electrets that contain mobile ions to suggest that ion transfer is a possible explanation for contact charging.

2.6 Additional Thoughts

I would like to add some of my own thoughts on the matter of triboelectrification of insulators. Both proposed models have some flaws associated with them which include that they do not recognize the complete role of water involved in the mechanism. For the case of the hydroxide adsorption model, it is determined that water is required for charge transfer. However, many triboelectric charging experiments have been successfully performed in a high vacuum environment that is void of moisture. Also, there are several observations that would contradict the requirement for water; for example, polyethylene reactors and natural gas pipelines (as discussed in chapter 1) are void of moisture. Although I believe that water does influence charging behavior, it may not be necessary for charge transfer. Further experiments will be required to understand the chemical adsorption ion of hydroxide and other anions in the role of charging in a water-free environment.

For the case of the electron transfer mechanism, there is no mention of the role of water in the charging behavior. Adsorption water will increase the ionic surface conductivity, which allows for greater mobility for electrons to either flow to lower energy states or ground. In this sense, any continuous monolayer of water should produce
zero charge transfer because trapped electrons could reduce the various ions that are found in the monolayer of water. Many of the experiments that advocated for the electron transfer were performed in a high vacuum environment (Lowell\textsuperscript{1,25,26,35,36}, Truscott\textsuperscript{63}, Akande\textsuperscript{27}) where water is absent.

The importance of the hydrophilic material must be taken in account when studying the triboelectrification of insulator materials. The experiments performed by Liu and Bard\textsuperscript{43} were carried out in atmospheric conditions where moisture is present. However, their investigation of Teflon, an extremely hydrophobic material, is unlikely to be covered in a continuous monolayer of water. The bare surface of Teflon is likely to be exposed when charging with the Lucite surface (which is also hydrophobic). In this system, it is probable that water did not play a role in the charging behavior. Lui and Bard strictly reported on the reduction reaction evolving the charged Teflon. However, no experiments were done on the oxidation of Lucite that was depleted of electrons. It would be interesting if a similar series experiments were performed on polyester or polyurethane, which are hydrophilic and charge negatively in the triboelectric series. (Alternatively, instead of using Lucite, glass which is also hydrophilic, could be used.) It is difficult to avoid the role of water in contact charging because it is likely to affect the surface conductivity and surface chemistry.

A model must be developed that accounts for the excess and absence of water during contact charging. For the case of excess water, ion transfer is likely to occur due to the aqueous ions suggested by Whitesides\textsuperscript{6} and Diaz\textsuperscript{10}; vice versa, for an absence of water, electron transfer is likely to occur due to the trapped electrons based on the idea of Lowell\textsuperscript{1}. Based on these ideas, it may not be possible to develop a universal mechanism
for insulator triboelectrification because the material properties and environmental conditions govern whether electron or ion transfer dominates in insulator triboelectrification.

However, it has been observed that small particles tend to charge negatively and large particles tend to charge positively in single component granular systems. As explained in the previous sections, this has been surmised to be independent of material type. Also the two models suggest that a negative transfer is responsible for charge transfer. In the case of waterless (or hydrophobic) systems, such as in polyethylene production, electron transfer will cause charge segregation whereas, for water-containing (or hydrophilic) systems, such as in lightning or dust storms, ion transfer (hydroxide ions or other anions) will cause charge segregation. In these means, it is necessary to consider both electron and ion transfer as probable explanations for charge segregation in a single component system. In this dissertation, I establish the groundwork to gain a fundamental understanding of the charge segregation that occurs in single granular component systems.

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III. TRIBOELECTRIC CHARGING OF GRANULAR MIXURES


Triboelectric charging is widely observed in granular systems, but the physics underlying the phenomenon is not well understood. A critical challenge for experimental studies of triboelectric charging is to obtain reproducible data that can be linked to theoretical predictions. Towards this end, we develop and perform experiments on the triboelectric charging of granular mixtures with varying composition. A bench-top particle flow apparatus has been constructed which operates under low vacuum (70 Torr); performing experiments in a clean and controlled environment reduces the effects on charging caused by contaminants, humidity, etc. The apparatus is designed such that only particle-particle interactions occur (i.e. no particle-wall interactions). A non-contact method of measuring charge is employed to limit probe-particle charging (or discharging). Both time-dependent and steady-state behaviors are investigated. Various granular insulator materials are studied to investigate the effect of system composition on the triboelectric charging. In all cases, the binary mixtures produce much greater triboelectric charging than the single component systems. This work has previously been presented1.

3.1 Introduction

The triboelectric charging of granular systems is poorly understood even though it has important consequences, as pointed out recently in both industrial2 and natural contexts3. Triboelectric charging, also known as contact charging, is a process that
occurs when two initially neutral surfaces come into contact, transfer charge, and remain charged with the opposite polarity when they are separated. The polarity is determined by the material properties (in a way that is not understood), as described empirically by the triboelectric series; the charging process is currently so poorly understood that it is not even clear whether it is the transfer of electrons or ions that causes the charging.

A wide range of consequences of triboelectric charging of granular materials arise in both industry and nature. In industry, intentional triboelectric charging forms the basis of many processes in the imaging industry, but unintentional triboelectric charging can cause problems in other processes. In fluidized bed reactors and pneumatic transport systems, triboelectric charging disrupts the desired flow patterns and can lead to problems such as the formation of polymer sheets in polymerization reactors and non-uniform dosages in pharmaceutical products. For pharmaceuticals used in powder form (e.g., with dry powder inhalers), triboelectric charging during dispersal can alter the drug delivery. In nature, lightning is caused by the charging of dust and ice particles, which produce large potentials leading to electrical breakdown. Similarly, volcanic lightning occurs when the ash particles in volcanic plumes triboelectrically charge, producing large electric fields sufficient for gas breakdown. The triboelectric charging of sand or dirt in dust devils generates bi-polar electric fields with potentials of several thousand kilovolts, which have the potential of damaging electronic equipment.

The present study addresses the triboelectric charging of granular mixtures arising specifically from particle-particle interactions, and relates the composition of the mixture to the magnitude of charging. In general, particles can charge from interactions with either the container wall (or its associated components) or with other particles; the
relative importance of these two contributions depends on the situation. In sand storms and dust devils, the particles seldom pick up charge from different materials at boundaries. In fluidized beds and pneumatic transport through pipes, the relative importance of these two factors will likely depend on the surface-to-volume ratio of the container as well as the properties of the materials involved; for example, in large silos or reactors, only a small proportion of the material is in contact with the walls.

While previous studies have elucidated the factors affecting electrostatic charging in single-component granular systems \(^\text{13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32}\), to the best of our knowledge, the composition dependence of triboelectric charging of granular mixtures arising only from particle-particle interactions has not been examined. The composition dependence of charging in granular mixtures has also been examined, in regard to electrostatic separations and pharmaceutical systems, but the charging behavior was unclear due to interaction of the particles with both other particles and the container walls\(^\text{33,34,35,36}\). Other studies examined the charging of particles in contact with larger beads of a different composition, in analogy with the toner charging process\(^\text{37,38,39,40}\). We are aware of one work that aimed to restrict charging to interactions only between particles (in single component systems), by lining the walls of the container with sheets of the same material being studied \(^\text{41}\); however, while ostensibly the same material, the sheets and particles may have somewhat different compositions (e.g., due to different processing methods).
3.2 Experimental Setup

We have developed a methodology to determine the triboelectric charging of granular mixtures as a result of particle-particle interactions. To do this, our apparatus creates particle flow in which the moving particles only come in contact with other particles, and we measure the electrostatic charging with a probe that does not contact the particles. Additionally, to eliminate particle charging from size variations, each particle sample is sieved to keep similar particle sizes for each material (note that previous work has shown that the particle size distribution can have significant effects on triboelectric charging\textsuperscript{15-19,31,38}). To improve the reproducibility, the experiments are carried in a controlled (low vacuum) environment.

3.2.1 Particle flow apparatus

As schematically shown in Fig. 3.1, a particle bed reactor was constructed from cast acrylic tubing and polyethylene. An acrylic tube 7” long with a 4” inner diameter was fixed inside a tube with a 4.5” inner diameter. A high density polyethylene rod was then machined to fix snugly into the bottom of the two-piece acrylic reactor. To evenly distribute the gas flow to the bed, the polyethylene was machined with a conical cavity. A channel was machined from the bottom of the cone to the side of the polyethylene plug to connect the gas flow. A distribution plate was machined from $\frac{1}{4}$” thick cast acrylic and sealed with an o-ring between the polyethylene plug and the acrylic. A single-hole distribution plate with a diameter of 120 $\mu$m was employed to ensure controlled flow of particles as compared to a more conventional multi-hole configuration: the single-hole configuration generates “fountain-like” flow in which the stream of particles does not
come into contact with the walls of the reactor. With this type of flow, the particles in contact with the distribution plate and the side walls are stagnant since only particles above the hole of the distribution plate are involved in the flow. As a result, only particle-particle contact is caused by the flow (see Fig. 3.1b). Furthermore, the particle flow is aligned with the electrostatic probe to measure particle charge directly.

Figure 3.1 Experiential apparatus (left) Schematic of the particle flow apparatus. (right) Image of the fountain-like flow that arises from a single-hole distribution plate.

An electrostatic probe, made from a 1/8” diameter stainless steel rod shielded with quartz glass, was used to measure particle charging. The probe was connected to a Keithley 6517A electrometer, which measures the current drawn from the bed at intervals of approximately 60 ms. The currents measured by the probe are induced by the charged particles that move in the vicinity of the probe. To minimize particle-probe interaction, the bottom of the probe was positioned approximately 10 cm above the settled bed.
The particle flow apparatus was placed in a cylindrical vacuum chamber (Laco Technology, Inc.), and enclosed by a Faraday cage to prevent interference from external electric fields. The vacuum chamber ensures a clean environment and minimizes the effects of impurities and humidity that can influence the charging behavior. An Edwards E2M1.5 vacuum pump was used to maintain a reduced pressure environment of 70 Torr. Two pressure transducers were used to measure the pressures in the vacuum chamber and of the inlet gas flow, respectively; the difference in pressure was used to determine the pressure drop across the fluidized bed. The chamber pressure and inlet gas flow rate were regulated by mass flow controllers.

3.2.2 Granular mixtures

The triboelectric charging of binary mixtures composed of three different granular materials is investigated. Soda lime glass, aluminum oxide and polymethyl-methacrylate (acrylic glass) are used for this study. Granular materials with similar sizes are used in order to have similar fluidization characteristics and prevent particle size effects on charging behavior. Acrylic powder was obtained from Alfa Aesar with particle diameters of 70-85 µm. Soda lime glass (Dragonite®, Jayco Inc.) and aluminum oxide (Duralum®) powders were obtained in bulk samples with large size distributions; these materials were sieved to obtain particles with diameters of approximately 90-106 µm (170-140 mesh number). Scanning electron microscope (SEM) images shown in Fig. 3.2 confirm the size distribution and morphology of the particles. The compositions of the mixtures are given below in percents by volume.
3.2.3 Experimental Procedure

The height of the settled bed was maintained at 34 mm (330 mL) for each material. Before particles were placed in the bed, they were neutralized with an ion gun (Exair Inc.). The bed was then placed in the vacuum chamber and connected to the inlet gas flow of high purity nitrogen gas. The chamber was evacuated to 20 Torr and purged with nitrogen gas to remove water vapor and air. The electrometer current, chamber
pressure, and pressure drop were continuously measured over a period of 50 minutes. To perform experiments, the pressure was controlled at 70 Torr with flow rates in the range of 0.15 - .5 L/min. It should be noted that the flow rates required for fluidization under reduced pressure are much lower than those required at atmospheric pressure.

3.3 Results

An example of raw current data from an experiment is shown in Fig. 3.3. A positively charged particle moving towards the probe will induce a positive current that is measured by the electrometer. Each data point represents the total current induced from all charged particles moving near the probe. The fluctuations in the raw data occur because of changes in the number of particles near the probe, the magnitude and sign of the charge on each particle, and the direction each particle is moving with respect to the probe. If the particles do not touch the probe (and transfer their charge to the probe), the mean current will equal zero since the contribution from each particle as it approaches the probe will be cancelled by the contribution when it moves away from the probe. The magnitude of triboelectric charging observed in Fig. 3 can be quantified by the standard deviation of the current measurements.
To address the transient behavior of charging, we track the time dependence of the standard deviation of the current over a short duration. In Fig. 3.4, the results are shown for the standard deviation of the current calculated over 100 data points (total time=6 s). Results are shown for three different flow rates. For the lowest flow rate, no charging is measured (for reasons discussed below). However, at the higher flow rates, a time dependent response is clearly observed. Initially, the value of the standard deviation is low, which indicates little charge on the particles (note that the method of using 100 data points to determine a standard deviation prevents accurate results at very short times). As time increases, the value of the standard deviation increases, and it eventually reaches a steady state value (denoted $\sigma_{ss}$). The timescale for the charging to reach the steady-state value is $\sim$5-10 minutes, which is similar to the timescales found for the triboelectric charging of fluidized beds$^{29,30}$. 

Figure 3.3 An example of the raw current data measured by the electrometer as a function of time. The time axis extends over 1 minute (1000 data points).
Figure 3.4 Results for the standard deviation of the current obtained for 100 data points (6 s intervals). Results are for the 75%-25% aluminum oxide-acrylic mixture. The three curves, from bottom to top, represent results for pressure drops of 7.5 Torr, 9.2 Torr, and 10.1 Torr.

The dependences of $\sigma_{ss}$ on the imposed pressure drop are shown in Fig. 3.5. The value of $\sigma_{ss}$ is determined here as the standard deviation for the last 20,000 data points (i.e. when the charging in bed has reached equilibrium). For low flow rates (low pressure drop), the particles do not have sufficient velocity to be detected by the probe. However, at higher flow rates the value of $\sigma_{ss}$ increases essentially linearly with the pressure drop. The slope that describes this dependence, $d\sigma_{ss}/d\Delta P$, is used to characterize the charging behavior of a granular system. As shown in Fig. 3.5, the charging is much greater for the acrylic-aluminum oxide mixture than for the pure aluminum oxide system; this difference is quantified by the much larger value of $d\sigma_{ss}/d\Delta P$ for the acrylic-aluminum oxide mixture.
Figure 3.5 Steady state standard deviations of the current, $\sigma_{ss}$, as a function pressure drop, $\Delta P$. Diamonds are results for the 75%-25% aluminum oxide-acrylic mixture, and triangles are results for pure aluminum oxide. The results at higher pressure drops are fitted to a line, with slopes $d\sigma_{ss}/d\Delta P = 136.4 \pm 10.2$ pA/Torr for the mixture and $d\sigma_{ss}/d\Delta P = 1.9 \pm 0.2$ pA/Torr for the pure aluminum oxide.

The charging behaviors of the granular mixtures are assessed as a function of the composition of the mixtures. Figure 3.6 shows the results for $d\sigma_{ss}/d\Delta P$ as a function of composition for the three binary systems examined (acrylic-aluminum oxide, soda lime glass-acrylic, and aluminum oxide- soda lime glass). For all three systems, the mixtures charge much more than the pure components (i.e., have much larger values of $d\sigma_{ss}/d\Delta P$); in the case of the acrylic-aluminum oxide system, the charging of the mixture is more than 20 fold greater than the charging of the pure components. Also, the acrylic-aluminum oxide system charges significantly more than the other two systems.
Figure 3.6 Results for the change in the steady state standard deviation of the current with change in pressure drop ($d\sigma_{ss}/d\Delta P$), for the (a) acrylic-aluminum oxide system, (b) soda lime glass-acrylic system and (c) aluminum oxide- soda lime glass system.

The mean currents at steady state, $\mu_{ss}$, are also examined. As discussed above, the mean current will equal zero if the particles do not touch the probe. The observed mean
currents are on the order of ~0.1 pA, which is negligible compared to the instantaneous
currents that fluctuate on the order of 10-1000 pA. Figure 3.7 shows that the dependence
of the mean currents on the pressure drop for all mixtures are zero within experimental
error. Thus, it is concluded that the particles do not physically contact the probe and
transfer charge to a significant extent.
Figure 4.7 Results for the change in the steady state mean value of the current with change in pressure drop \( \left( \frac{\text{d}\mu_{ss}}{\text{d}P} \right) \), for the (a) acrylic-aluminum oxide system, (b) soda lime glass-acrylic system and (c) aluminum oxide- soda lime glass system.

3.4 Discussion

The experimental approach described allows the measurement of triboelectric charging of granular materials solely from particle-particle interactions by using a flow
apparatus that eliminates wall effects. The charging is measured with a contact-less
method to avoid particle charging (or discharging) through contact with the probe; the
charging is then studied as a function of time since charge is never removed from the bed.
The experiments are carried out in a low vacuum environment to minimize the effects of
humidity, dust and other contaminants.

The difference in the charging of single component systems as compared to
binary mixtures is clearly illustrated in Fig. 3.6: the binary mixtures charge much more
than the single component systems. This result is understandable theoretically since
charge transfer during contact between surfaces would be expected to be driven by
differences in the surface properties. For metals, the property that governs the charge
transfer is the work function (i.e., the energy needed to remove an electron from the metal
surface); electrons will be transferred from the metal with the lower work function to the
metal with the higher work function, and the driving force for this charge transfer will
increase with the relative difference in work function. For insulators, the situation is
more complicated and not well understood, and an empirical “triboelectric series”, which
orders materials by their propensity to gain positive charge triboelectrically, is used to
determine the direction of charging.

The magnitude of charging for the three mixtures studied was found to be in the
order (from most charging to least charging): (1) acrylic-aluminum oxide, (2) soda lime
glass-acrylic, (3) aluminum oxide-soda lime glass. It is understandable that the
aluminum oxide-soda lime glass system would charge the least, because these materials
are both oxides and thus would likely have somewhat similar surface properties.
Regarding the charging of the two oxides with acrylic, the triboelectric series usually
places silica glass further from acrylic than aluminum (we assume that studies on aluminum surfaces really address oxidized surfaces); thus the triboelectric series would suggest the soda lime glass-acrylic mixture would charge more than the acrylic-aluminum oxide mixture, in contrast to what we observe. Various factors can lead to this difference. For example, the position of a material in a triboelectric series is not invariant, but can depend on the surface texture, the details of the contact, the presence of contaminants, and temperature (which may affect the presence of contaminants)\textsuperscript{42}. Also, quantitative comparisons different systems are complicated by differences in fluidization. Since the density, shape and size distribution of the particles are different for each material, the fluidization behavior is somewhat different in all cases. For example, aluminum oxide is the densest of the materials and the most irregularly shaped, and higher flow rates were required to fluidize this material (see Fig. 3.5). Thus, there is some inherent error in comparing the values of $d\sigma_{ss}/d\Delta P$ for different systems because of differences in the nature of fluidization.

\textbf{3.5 Conclusion}

We present the first experiments that address the composition dependence of the triboelectric charging of granular mixtures arising only from the interparticle interactions. The results show that the amount of charging in the binary mixtures is much greater than in single component systems, which is in agreement with theoretical ideas regarding triboelectric charging.
3.6 Reference


2 L.B. Schien, “Recent Progress and Continuing Puzzles in Electrostatics” Science 316, 1572 (2007)


3.7 Appendix

3.7.1 LabView
**DAQ Assistant2**

DAQ Assistant
Creates, edits, and runs tasks using NI-DAQmx. Refer to the DAQ Quick Start Guide for information on devices supported by NI-DAQmx.

When you place this Express VI on the block diagram, the DAQ Assistant launches to create a new task. After you create a task, you can double-click the DAQ Assistant Express VI in order to edit that task. For continuous measurement or generation, place a loop around the DAQ Assistant Express VI.

For continuous single-point input or output, the DAQ Assistant Express VI might not provide satisfactory performance. Refer to examples\DAQmx\Analog In\Measure Voltage.lib\Cont Acq&Graph Voltage-Single Point Optimization.vi for techniques to create higher-performance, single-point I/O applications.

**Convert from Dynamic Data**

Convert from Dynamic Data
Converts the dynamic data type to numeric, Boolean, waveform, and array data types for use with other VIs and functions.

**DAQ Assistant2**

DAQ Assistant
Creates, edits, and runs tasks using NI-DAQmx. Refer to the DAQ Quick Start Guide for information on devices supported by NI-DAQmx.

When you place this Express VI on the block diagram, the DAQ Assistant launches to create a new task. After you create a task, you can double-click the DAQ Assistant Express VI in order to edit that task. For continuous measurement or generation, place a loop around the DAQ Assistant Express VI.

For continuous single-point input or output, the DAQ Assistant Express VI might not provide satisfactory performance. Refer to examples\DAQmx\Analog In\Measure Voltage.lib\Cont Acq&Graph Voltage-Single Point Optimization.vi for techniques to create higher-performance, single-point I/O applications.

**Convert from Dynamic Data2**

Convert from Dynamic Data
Converts the dynamic data type to numeric, Boolean, waveform, and array data types for use with other VIs and functions.

**DAQ Assistant3**

DAQ Assistant
Creates, edits, and runs tasks using NI-DAQmx. Refer to the DAQ Quick Start Guide for information on devices supported by NI-DAQmx.

When you place this Express VI on the block diagram, the DAQ Assistant launches to create a new task. After you create a task, you can double-click the DAQ Assistant Express VI in order to edit that task. For continuous measurement or generation, place a loop around the DAQ Assistant Express VI.

For continuous single-point input or output, the DAQ Assistant Express VI might not provide satisfactory performance. Refer to examples\DAQmx\Analog In\Measure Voltage.lib\Cont Acq&Graph Voltage-Single Point Optimization.vi for techniques to create higher-performance, single-point I/O applications.
This VI is used to control the Measure Layer (Trigger) settings and then read back the specified number of readings.

The function of the instrument will not be changed. To take measurements for a new function, you must first configure the instrument with that function’s VI.

The element of the array that stores readings is always 1 number less than the reading number. For example, the array starts at the number 0, while the readings start at 1.
IV. ELECTROSTATIC SEPARATION


Electrostatic separation has long been used to separate charged particulate materials. The mining industry has used electrostatic separation to separate metallic and non-metallic materials. The granular mixtures which were explained in the previous are now electrostatically separated. This work has previously been presented\(^1\).

4.1 Electrostatic Separation by Particle Polarity

After the particle flow is stopped, particles are collected by their polarity by applying an electric field above the bed. A 3” diameter copper disk was machined and attached to the probe tip. The bottom of the copper disk is covered with a 200 \(\mu\)m film of parafilm (Pechiney Plastic Packaging). A voltage (\(\pm 8\) kV) is imposed on the copper disk, and the copper disk is lowered to just above the bed (2-3 mm above the bed). The particles that are charged oppositely to charge on the disk are attracted to the disk, while similarly charged particles are repelled. Thus particles of a specified polarity are collected on the parafilm, which acts as a spacer between the charged disk and charged particles and prevents the particle charge from discharging; without the parafilm, charged particles could discharge upon in contact with the metallic surface and then fall back into the bed (and only a few particles will be collected). The disk is then removed from the bed and the particles are collected from the disk. In this methodology, particles are removed from the bed \textit{before} contacting any other surfaces (such contact could cause undesired charging of the particles). Both positive and negative biases are applied to the
copper disk in order to collect negatively charged or positively charged particles. The experimental setup is shown schematically in Figure 4.1.

![Figure 4.1 Schematic of charge separation apparatus.](image)

### 4.2 Results and Discussion

After the particle flow is stopped, particles of positive and negative charge are removed (separately) using the method described above. For experiments involving aluminum oxide, the shape of the particles is used to determine the identity of collected particles, since the aluminum oxide particles are non-spherical and the others are spherical (see Figure 4.2). Figure 4.2 shows optical images of the particles after electrostatic separation. For the aluminum oxide-acrylic mixture, all of the aluminum oxide particles (the non-spherical particles) charged negatively and virtually all of the acrylic particles charged positively (Figure 4.2c and 4.2d). The aluminum oxide-soda lime glass mixtures produced bipolar charging of both materials, but as seen in Figure
4.2a and 4.2b, the majority of the positively charged particles are aluminum oxide and the majority of the negatively charged particles are soda lime glass.

**Figure 4.2** Optical images of charge separated particles in experiments of granular mixtures (concentration 50-50 vol%).

In the case of the soda lime glass and acrylic mixtures, both types of particles are spherical, so that visual inspection cannot be used to distinguish particles of the two materials as done above. However, since the specific gravities of soda lime glass and acrylic are 2.5 g/cm³ and 1.18 g/cm³, respectively, the density difference can be used to separate collected particles. The collected particles are placed in a vial with saturated salt water (density of 1.4 g/cm³): the acrylic particles will float to the surface of the water, while the soda lime glass particles sink to the bottom of the vial. As shown in Figure 5.3, the negatively charged particles are soda lime glass and the positively charged particles are acrylic.
4.3 Density separation for particles collected from experiment on the soda lime glass-acrylic mixture (50-50 vol%). Collected particles with (left) negatively biased electrode (positively charged acrylic particles), and (right) positively biased electrode (negatively charged soda lime glass particles).

4.4 Conclusion

A methodology has been developed to investigate triboelectric charging of granular systems due solely to particle-particle interactions. The effects of particle-particle interactions are dominant for large systems where interactions with external surfaces are negligible, such as in large reactors, natural phenomenon, and other small area-to-volume ratio systems. We are currently using the techniques developed here to study the particle size dependence of the bipolar charging that occurs in single-component granular systems.
4.5 References


2 Jaygo Inc., personal communication.

3 Alfa Aesar, personal communication.
V. PARTICEL SIZE DEPENDENCE OF TRIBOELECTRICALLY CHARGED GRANULAR MATERIALS


Experiments are carried out to examine triboelectric charging in granular systems composed of particles that are chemically identical but differ in size. A methodology is developed so that only particle-particle interactions (but not particle-wall interactions) contribute to the charging. Since all particles are chemically identical, there is no apparent driving force for charge transfer, but charging occurs nonetheless, such that smaller particles tend to charge negatively while larger particles tend to charge positively. For bimodal systems, a model for the frequency of collisions of particles with different size predicts the concentrations for which the observed charge segregation is maximized. This is work has previously been presented¹.

5.1 Introduction

An interesting yet poorly understood phenomenon is the electrostatic charging of flowing granular systems with chemically identical particles. It is counter-intuitive that charging occurs at all, since charge transfer would seem to be driven by differences in chemical properties. Also, the charging appears to depend on the nature of the particle size distribution (as discussed below), which is surprising because the particles are macroscopic (10-1000 μm) and thus their sizes would seem to be irrelevant in regard to charge transfer. Nevertheless, this charging occurs in a wide range of contexts, including industrial applications such as fluidized beds² and pneumatic conveying³, and natural
phenomena such as sand storms\textsuperscript{4}, dust devils\textsuperscript{5,6} and volcanic plumes\textsuperscript{7}. One consequence of the charging is that it significantly alters the particle flows\textsuperscript{8,9,10}.

In granular systems with chemically identical particles, electrostatic charging occurs with some particles charging negatively and others charging positively. Previous work suggests that a particle size dependence exists for the resulting charge polarity. Field studies on dust devils show that large dipolar electric fields exist, and orient themselves such that the negative pole is at higher altitude and the positive pole is near the ground\textsuperscript{11,12,13,14,15}. To explain this result, it has been hypothesized that small particles charge negatively, and since they are lighter, are blown to higher altitudes\textsuperscript{9-16,17,18}. A similar hypothesis of small particles charging negatively and rising to higher altitudes has been proposed to explain the electric fields that develop in volcanic plumes\textsuperscript{19}. In addition, a number of laboratory experiments concluded that small particles charge negatively and large particles charge positively\textsuperscript{20,21,22,23,24}. However, these laboratory studies did not limit the cause of charging to only particle-particle interactions (i.e. the particles also interacted with container surfaces made of different materials), or investigate the effects of relative concentration of the various particle sizes.

In this Letter, we investigate the effect of the particle size distribution (PSD) on the electrostatic charging of granular systems with chemically identical particles. Our techniques address the charging due only to particle-particle interactions, so that these effects are decoupled from the effects arising from interactions with other material surfaces.
5.2 Experimental Procedure

We focus our investigation on three monodisperse samples of clear soda lime glass (Jaygo, Inc.) with mean particle diameters (standard deviations) of \( D = 78 \, \mu m \) (\( \sigma = 13 \, \mu m \)), \( D = 137 \, \mu m \) (\( \sigma = 22 \, \mu m \)) and \( D = 321 \, \mu m \) (\( \sigma = 22 \, \mu m \)). These monodisperse samples are obtained by sieving a polydisperse sample of soda lime glass, which ensures that all particles are chemically identical. Samples with a bimodal size distribution, hereafter referred to by the smaller particle diameter (\( D_S \)) and the larger particle diameter (\( D_L \)), are prepared by mixing two monodisperse samples at different mass fractions, \( w_L \) (\( w_L = m_L / (m_L + m_S) \)), where \( m_L \) and \( m_S \) are the masses of the monodisperse samples of large diameter and small diameter particles, respectively.

We have recently developed a methodology to study triboelectric charging resulting only from particle-particle interactions\(^{25,26}\). The granular material (approximately 350 mL) is placed on a distribution plate with a single hole at the center. Gas (dry nitrogen) flow through the hole fluidizes only a localized region of the bed (i.e., this granular material) near the bed center. This leads to fountain-like flow, as shown in Figure 7.1, in which the particles involved in the flow contact only other particles and no other surfaces (such as the container wall). This particle flow apparatus is operated in a controlled environment (70 Torr nitrogen atmosphere) to reduce contaminants and enhance reproducibility. The particle flow is operated for approximately 120 minutes (the charging appears to become time independent after about 10 minutes\(^{25}\)); all particles remain in the bed after the flow stops. After the particles are charged, the particle flow apparatus is removed from the vacuum chamber and a non-contact method is used to collect particles with specified charge polarity. A 2.5 cm diameter copper disk covered
with a 200 μm film of parafilm is suspended ~1 mm above the bed. The disk is held at a positive or negative voltage (10 kV) to extract negatively or positively charged particles, respectively, from the bed. The disk is smaller than the diameter of the flowing region of the bed (~8 cm), and is positioned above only this region, to ensure that only particles involved in the flow are collected. Particles are collected on the parafilm surface, which acts as a spacer so particles do not discharge through the copper disk and fall back to the bed; the particles thus remain attached to the disk as long as the voltage on the disk is maintained. The charging and collection process is performed three times for each trial, and a total of 0.5-1.2 g of particles (~5000-10000 particles) are collected with each polarity. After the particles are collected, digital pictures of the positive and negative particle samples are taken with an optical microscope, and the PSDs of each sample are determined (for > 1000 particles) by measuring the particle diameters in the images. In addition, the collected particles of each polarity are separated by size with a sieve and the mass of each size cut is obtained.

![Schematic of the particle flow apparatus.](image1)

Figure 5.1 (left) Schematic of the particle flow apparatus. Note that due to the single hole distribution plate, the particle bed differentiates into a zone with flow and a stagnant zone, shown here with different colors. (right) Image of the fountain-like flow that arises from a single-hole distribution plate.
5.3 Results and Discussion

Figure 5.2 presents PSDs for the positive and negative particle samples obtained after charging mixtures with various mass fractions of $D_s = 78 \ \mu m$ and $D_L = 137 \ \mu m$ particles. For $w_L = 1$, it is seen that the large particles charge both negatively and positively. As $w_L$ decreases, charge segregation becomes apparent, and for $w_L = 0.77$, it is clear that the large particles tend to charge positively and the small particles tend to charge negatively. At $w_L = 0.5$, the results are similar to a monodisperse sample of small particles, where the small particles charge both negatively and positively.
Figure 5.2 Particle size distribution of negatively (—) and positively charged (—) particles, for $D_L/D_S = 1.9$ at various mass fractions ($w_L$) of large particles.
These results suggest that charge segregation depends on the relative proportion of the two particle sizes, which can be understood in terms of the probability for collisions between the two types of particles. In a time interval $\Delta t$, a particle with diameter $D_i$ moving at velocity $v$ “sweeps out” a volume $\frac{1}{4} \pi (D_i + D_j)^2 v \Delta t$ with respect to a possible collision with a particle with diameter $D_j$. The probability of a collision between particles of diameters $D_i$ and $D_j$, $p(D_i, D_j)$, is proportional to the product of this swept out volume and the number densities of particles, with a factor of $\frac{1}{2}$ in the case $i=j$ to eliminate double-counting of collisions. The number density of particles with diameter $D_i$ is given by $N x_i$, where $N$ is the total number density and $x_i$ is the number fraction of particles with diameter $D_i$. Therefore, $p(D_i, D_j) = \zeta_{ij} (N x_i)(N x_j) \frac{1}{4} \pi (D_i + D_j)^2 v \Delta t$ where $\zeta_{ij} = \frac{1}{2}$ for $i=j$ and $\zeta_{ij} = 1$ for $i \neq j$. The fraction of collisions occurring between a large particle and a small particle, $f_{L,S}$, is given as

$$f_{L,S} = p(D_L, D_S)[p(D_S, D_S) + p(D_L, D_L) + p(D_L, D_S)]$$

or

$$f_{L,S} = \frac{2 \left(1 + \frac{D_L}{D_S} \right)^2 x_S x_L}{x_S^2 + \left(\frac{D_L}{D_S} \right)^2 x_L^2 + 2 \left(1 + \frac{D_L}{D_S} \right)^2 x_S x_L}$$

Equation 5.1

The number fractions are calculated from the mass fractions based upon the assumption that the particles are perfect solid spheres,

$$x_L = \frac{w_L}{w_L + w_S \left(\frac{D_L}{D_S}\right)^3} \quad x_S = \frac{w_S \left(\frac{D_L}{D_S}\right)^3}{w_L + w_S \left(\frac{D_L}{D_S}\right)^3}$$

Equation 5.2

Figure 5.3a shows the collision frequencies as a function of $w_L$ for a sample with $D_S = 78 \mu m$ and $D_L = 137 \mu m$. Collisions between a small and a large particle will be most
prevalent at $w_L = 0.78$ (shown in Figure 5.3a), explaining why the most pronounced charge segregation in Figure 5.2 is observed for the experiments with $w_L = 0.77$. Figure 5.3b shows the values of $w_L$ that maximize $f_{L,S}$ as a function of $D_L/D_S$; the propensity for charge segregation is predicted to be the greatest at these concentrations.

![Figure 5.3 Collision fractions (see text for definitions) as a function of $w_L$, for $D_L/D_S=1.9$. (b) Mass fractions that maximize $f_{L,S}$, for a given $D_L/D_S$.](image)

Table 5.1 gives the results for all experiments carried out (the mass fractions examined should be considered in comparison to Figure 5.3b). The number fractions of large particles in the negatively charged sample, $x_{L}^-$, and in the positively charged sample,
$x_L^+$, are obtained by two independent methods. The count-based number fraction is obtained from the optical microscope pictures, and the mass-based number fraction is obtained from masses of the sieved samples; the two methods give consistent results. To quantify the extent of charge segregation, we define the charge segregation factor, $\xi$, as

$$\xi = \sqrt{\frac{x_L^+}{x_L^-} \frac{x_S^-}{x_S^+}}$$

(3)

The charge segregation factor represents the geometric mean of the deviations from overall neutrality for the small and large particles. In all experimental trials, large particles tend to charge positively and small particles tend to charge negatively, as indicated by values of $\xi > 1$. Note that for each bimodal system the most pronounced charge segregation occurs near the mass fractions predicted in Figure 5.3b.

<table>
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<tr>
<th>$D_L/D_S$</th>
<th>$w_L$</th>
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<th>$x_L^-$ by count</th>
<th>$x_L^+$ by mass</th>
<th>$x_L^+$ by count</th>
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<td>0.65</td>
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<td>0.78</td>
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<tr>
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<td>1.5 ± 0.4</td>
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</tbody>
</table>

Table 5.1 Results for the charge segregation in soda lime glass bimodal samples. The error estimate for the charge segregation factor is determined from the difference in results obtained using the mass-based and count-based number fractions.
Figure 5.4 compares the results for the three bimodal samples, each at the mass fraction that maximizes charge segregation (i.e., the value of \( w_L \) that maximizes \( f_{L,S} \), as shown in Figure 5.3b). As \( D_L/D_S \) increases, the charge segregation is enhanced, as evident in Figure 5.4 and Table 5.1 (\( \xi = 1.7, 3.8 \) and 4.3 for \( D_L/D_S = 1.8, 2.3 \) and 4.3, respectively). Figure 4 also shows that charge segregation depends on the relative size difference between particles, and not on the absolute particle sizes – e.g., the \( D = 137 \) μm sample tends to charge positively when mixed with the \( D = 78 \) μm sample, but tends to charge negatively when mixed with the \( D = 321 \) μm sample.
Figure 5.4 Particle size distribution of negatively (- - - - - - - - -) and positively charged (- - - - - - - -) particles as a function of $D_L/D_S$ at the mass fractions where charge segregation is most pronounced (see text). (a) $D_L/D_S = 1.9$, $w_L = 0.77$. (b) $D_L/D_S = 2.3$, $w_L = 0.85$. (c) $D_L/D_S = 4.3$, $w_L = 0.93$.

In addition to the soda lime glass samples, we studied the charging behavior of a polyethylene resin (Dow Chemical Company). Monodisperse samples of particles with $D = 605 \mu m$ ($\sigma = 99 \mu m$) and $D = 300 \mu m$ ($\sigma = 62 \mu m$) are obtained by sieving a polydisperse sample. Figure 5 shows results for the PSDs obtained for a mixture with $w_L$...
= 0.80. The results confirm that for polyethylene, as for soda lime glass, large particles tend to charge positively and small particles tend to charge negatively.

![Figure 5.5 Particle size distribution of negatively (---) and positively charged (- - -) polyethylene resin particles. The sample contained particles with D_L = 605 \(\mu\)m and D_S = 300 \(\mu\)m, at \(w_L = 0.8\).](image)

5.4 Conclusion

A key factor for the validity of our methodology is that identical particle size distributions are probed in the particle extraction process for the positive and negative particles. Since there is no sampling bias between the positive and negative samples, our conclusion in regard to the size dependence of the particle polarity is valid even if the particles sampled in the particle extraction process do not match the overall concentration of the bed. We note that the particle extraction process does not, in fact, sample the particles in the mixture uniformly – this is evident in the results in Table 5.1, which show that the \(w_L\)'s for the positive and negative samples are both smaller than the \(w_L\) for the overall mixture. This occurs because the particle extraction process preferentially
collects smaller particles as these particles are more easily pulled against gravity from the bed to the disk. While the fluidization process could cause non-ideal mixing of small and large particles (size segregation), our tests of the size distribution at the top of the bed after flow (obtained by scooping a layer) indicate that these effects are not significant. As stated above, since there is no sampling bias between the positive and negative samples, the conclusion that small particles tend to charge negatively and large particles tend to charge positively is unambiguous.

The driving force for particle-size-dependent charge segregation may result from the non-equilibrium dynamics of electrons\textsuperscript{27,28,29}. When the electrons cannot equilibrate between states on a particle surface (as is the case for insulators), and there is a distribution of rates of electron transfer between particles, collision-induced electron transfer generates a non-equilibrium electron accumulation on a particle-size-dependent subset of the system. The direction of net electron transfer depends on the initial electron distribution: electrons are systematically transferred from large particles to small particles when there is excess population in the higher energy states. Thus the non-equilibrium dynamics of electrons trapped in high energy states would give rise to smaller particles charging negatively, and larger particles charging positively, as observed in the present experiments.

5.5 References

\begin{enumerate}
\end{enumerate}


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5.6 Appendices

5.6.1 Procedure Notes

There are some tricks to producing reproducible results in this experiment. The parafilm is pulled over the copper disk and held in place with tape. This makes it easy to remove and replace the parafilm. When performing the electrostatic separation, the potential should be applied before the copper disk is lowered into the bed. The disk could be lowered over the center of the bed where fluidization had occurred and not near the acrylic side walls. The particles at the wall may have been charged undesirably by the wall and should not be collected. After collection, the copper disk is placed in a plastic Petri dish and the potential is removed. The particles are brushed off the parafilm and collected in the Petri dish. Then this process is repeated 3-5 times. The particles are then washed with the methanol to neutralize the charge. This makes handing the particles easier.

5.6.2 Null Experiment

A concern for this experiment is the packing effect which often effect broad size distribution. Smaller particles have been shown to migrate toward the both of the bed in large fluidized bed, this is unknown as the “brazil nut effect”. A null experiment was performed where the top proportion of the bed was scooped out after fluidization (without electrostatic separation). The sample was then sieved to determine the size distribution. The particle size distribution was the same as the overall prepared size
distribution. It appears that particle size segregation is not a factor from the top to the bottom of the bed.

5.6.3 Charge Decay

Another question which has been brought to our attention was stability of the charge on the particle surface. To address this, the particles were electrostatic removed from the bed but was not removed from the parafilm surface. The particles were then placed under an electrostatic voltmeter and surface voltage was recorded for several hours. The charge remained stable on the surface and decay slightly during a course of 14 hours. The charge is isolated from ground; therefore the charge remains stable since there is not flow of electrons or ions to discharge the surface. The slightly decay is probably do to atmospheric ions in the air which neutralize a proportion of charge over a long period of time.
VI. PARTICLE-SIZE DEPENDENT BIPOLAR CHARGING OF MARTIAN REGOLITH SIMULANT


6.1 Introduction

The regolith of Mars is believed to be electrostatically charged\textsuperscript{1,2,3,4}. While various processes (e.g. photoemission) could be responsible, triboelectric charging is believed to be the dominant process for charging of Martian dust\textsuperscript{5}. This charging can occur in the intense dust devils and dust storms that form on Mars, where dust devils reach over 6 km high\textsuperscript{6} and dust storms cover extensive portions of the planet for months\textsuperscript{7}. Furthermore, since the electrical breakdown of the Mars atmosphere is ~ 20kV/m (in comparison to ~ 3000 kV/m for Earth)\textsuperscript{8}, the charge buildup can lead to electrical discharges.

The electrostatic charge of the regolith has significant implications. In regard to robotic and human missions to Mars, charged dust can adhere to equipment and disrupt its operation (e.g., by covering solar panels) or cause permanent damage\textsuperscript{9}. In regard to atmospheric and geologic processes on Mars, the electrostatic charge of particles can lead to enhanced saltation\textsuperscript{4,10,11}, and the formation of geological features such as ‘razorbacks’ that have been observed\textsuperscript{12}. Electric discharges generated by the charged particles can activate chemical reactions and thus alter the composition of the Martian atmosphere, in particular, in regard to hydrogen peroxide\textsuperscript{13}.

The intense dust events on Mars are expected to generate large electric fields, as even the smaller terrestrial dust devils generate electric fields exceeding 100 kV/m\textsuperscript{14,15,16,17}. For electric fields to occur, there must be spatial segregation of positive
and negative charge. Based on the observed directions of these electric fields, it is generally surmised that the electric fields are caused by smaller particles charging negatively and larger particles charging positively, with gravity separating the particles by size\(^4,8,14,15,16,17,18,19,20,21\).

Previous studies have examined the electrostatic charging behavior of Martian regolith simulant in order to elucidate the mechanism of electrostatic charging. The effective workfunction of regolith simulant was determined in studies carried out by contacting the simulant with various other materials\(^22,23,24\). Experiments also examined the electrostatic discharges that develop from charging the simulant by stirring the particles with a rod\(^25,26\), and the electrostatic charging that develops during flow through a wind tunnel\(^27\). However, to the best of our knowledge, no previous work has directly demonstrated a particle size dependent charging of Martian regolith, arising from only particle-particle contact, even though this is the key factor that generates electric fields in dust events. In this letter, we carry out experiments to probe this effect in Mars regolith simulant.

6.2 Experimental Procedure

We have recently developed a methodology to investigate the triboelectric charging in granular materials \textit{due strictly to particle-particle interaction}\(^28,29,30\), i.e., the particles being examined have no contact with any surface besides that of other particles, until after they are separated by charge polarity and collected. In our experimental apparatus, a bed of particles (\(~350\) mL) sits on a distribution plate that has a single hole at its center (hole diameter 200 \(\mu\)m). The bed is sprayed with ionized air before each
experiment to neutralize any initial charge. A stream of gas (nitrogen) is then passed through the hole in the distribution plate, to fluidize the central region of the bed while the region near the container walls remains stagnant. This leads to a fountain-like flow, as shown in Figure 8.1a, in which the particles involved in the flow contact only other particles, and not any other surfaces such as the container wall. This particle flow apparatus is operated in a controlled low pressure (70 Torr) environment to reduce the effects of contaminants.

After the particle flow apparatus is run for a sufficient time to reach steady-state charge behavior (120 minutes), the gas flow is stopped and the bed is removed from the vacuum chamber. A non-contact method is then used to collect particles of a specific charge polarity. Particles are extracted from the bed using an electrically biased disk, 2.5 cm in diameter, suspended approximately 1mm above the center of the bed (i.e., the region of the bed that was flowing). The electrode is covered with parafilm that acts as a dielectric spacer to prevent the particles from losing their charge and falling back into the bed. A positive voltage (10 kV) is placed on the disk to extract negative particles from the bed, and a negative voltage (-10 kV) is placed on the disk to extract positive particles. Thus, the positively and negatively charged particles are extracted before touching any other surface (note that the particles touch the parafilm after they are extracted). This charging and collection process is repeated five times for a single experimental trial in order to collect a total of ~1.5 grams of particles for each polarity. After the particles are collected, they are rinsed with methanol to neutralize their charge. The size distributions of the positive and negative collections of particles are then determined with a Coulter LS 230 Particle Size Analyzer.
Figure 6.1 Left: Schematic of the particle flow apparatus that allows only particle-particle interactions. Right: Particle extraction set-up.

The experiments were carried out with JSC-1 Mars regolith simulant (Planet LCC), which is volcanic material collected from the southern flank of the Mauna Kea volcano in Hawaii. The simulant is mainly composed of SiO$_2$, AlO$_2$ and Fe$_2$O$_3$ (43.5 wt%, 23.3 wt% and 15.6 wt%, respectively) with grain size, density, porosity, reflectance spectrum, mineralogy, chemical composition, and magnetic properties similar to the regolith found on the Martian surface$^{26,31}$.

6.3 Results

We first present results of our control test where the particle extraction is performed before the fluid flow apparatus is operated. As shown in Figure 6.2a, very few particles are collected on the disk, because the particles are essentially uncharged at this point (the ionized air treatment neutralized the particle charges). In comparison, many
particles are collected on the disk when the procedure is carried out after the fluid flow apparatus is run, as shown in Figure 6.2b.

![Image of particle collection](image)

Figure 6.2 Particle collection with copper disk at -10 kV. Left: before particle flow. Right: after particle flow.

The particle size distributions for the samples of positive and negative particles are shown in Figure 6.3a. These results represent the average of three experimental trials, and the error bars represent the standard error of the results from the three trials. In Figure 6.3b, the particle size distribution for the original sample is compared with the total particle size distributions of the collected samples, obtained by averaging the size distributions of the positive and negative samples.
It is clear from Figure 6.3a that the measured size of negatively-charged particles tends to be smaller than the positively-charged particles. The mean diameter of the negatively- and positively-charged particles are estimated to be $296 \pm 21 \, \mu m$ and $400 \pm 31 \, \mu m$, respectively.

The comparison in Figure 6.3b shows that the particle size distribution of the collected samples does not exactly match that of the original sample. In particular, the collected samples are depleted of very large and very small particles. This result is
understandable, in that the very large particles are more difficult to extract due to gravity (their mass is larger), and the smaller particles are more difficult to extract due to their greater interparticle cohesive forces\textsuperscript{21}.

6.4 Discussion

It remains unclear why triboelectric charging would occur in a single component system such as the Mars dust. In particular, it is counter-intuitive that charging would occur at all, since charge transfer should be driven by differences in material properties (e.g., work function). However, the results found in this study suggest that particle size differences provide a driving force for charge transfer. This idea is also supported by previous reports of agitated samples of Mars regolith simulant producing more electrical discharges when there is a broad distribution size of the sample\textsuperscript{25}.

Our results also show that bipolar charging in the Mars regolith stimulant occurs such that smaller particles tend to charge negatively and larger particles tend to charge positively. We have recently demonstrated this result in both soda lime glass systems and polyethylene systems\textsuperscript{28}, and previous experiments by Castle, Inculet and co-workers have led to the same conclusion in various polymer systems\textsuperscript{32,33,34,35}. Furthermore, this size dependence of particle charges is consistent with the direction of electric fields observed in terrestrial dust devils\textsuperscript{14,15,16,17,18}. Thus, the phenomenon found for granular systems of a single material that the smaller particles tend to charge negatively and the larger particles tend to charge positively appears to be universal. However, the reason why charging would depend on the particle size is unclear because the particles are macroscopic (10-1000 μm) and thus their sizes would seem to be irrelevant in regard to
charge transfer (i.e., the chemical properties are not a function of physical size as may be
the case for nanoscale materials).

To explain the dependence of charging and polarity on particle size, we have
recently proposed a mechanism\textsuperscript{36,37,38}. The basic idea, which follows from Lowell and
Truscott\textsuperscript{39}, is that there are electrons trapped in high energy states in insulators, which can
relax during collisions to low energy states on the opposite particle at a rate proportional
to the surface density of these high energy electrons ($\rho^H$) on the donor particle. When
two particles collide, electrons can transfer in this way from either particle the other, but
there will be net electron transfer from the particle with higher $\rho^H$ to the particle with
lower $\rho^H$. Initially, $\rho^H$ is the same for all particles, and so the first collision between two
particles will not lead to net electron transfer. However, as shown in Figure 6.4, this first
collision generates a particle-size-dependent asymmetry, wherein the larger particle has a
higher value of $\rho^H$ than the smaller particle. Thus, subsequent collisions will lead to net
electron transfer from larger particles to smaller particles, thereby causing the larger
particles to charge positively and the smaller particles to charge negatively. Note that the
key to this mechanism is the non-equilibrium dynamics, in which the high energy
electrons can transfer to low energy states on another particle, but the low energy states
do not transfer (more generally, this effect occurs when there is a difference in rates of
transfer between the various states). This mechanism is addressed in more detail, and
more rigorously, in our previous papers\textsuperscript{36,37,38}. 
Figure 6.4 Schematic showing how non-equilibrium dynamics generate an asymmetry based on particle size, when two particles collide. The surface area of the large particle is exactly twice that of the small particle. Red dots represent electrons trapped in high energy states, and green dots represent electrons that are in low energy states. The surface density \( \rho_{\text{H}} \) is given as the number of electrons trapped in high energy states per surface area, for particle \( i \); initially, the two particles have the same value of \( \rho_{\text{H}} \).

(a) state of particles before collision; (b) state of particles at instant of collision; (c) during collision, the high energy electron on each particle near the point of collision relaxes to a low energy state on the other particle; (d) state of particles after collision. Note that the collision leads to an asymmetry in \( \rho_{\text{H}} \), even though there was no asymmetry prior to the collision and the electron transfer during the collision was symmetric.

8.5 Conclusion

We present the first results that show directly that flowing JSC-1 Mars regolith simulant undergoes triboelectric charging such that the smaller particles tend to charge negatively and larger particles tend to charge positively. This particle-size dependence of charge polarity underlies the charge separation that generates electric fields in Martian dust events.
6.6 References

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VII. INDUSTRIAL APPLICATIONS

In industry, polymer production and transportation are often plagued by triboelectric charging. Dow Chemical provided samples to differentiate the charging behavior of several polymeric materials. The technique we have developed has shown to be applicable for industrial testing. In this chapter, the charging behavior of single component systems; polyethylene and SARAN (polyvinylidene chloride) resin particles are presented.

7.1 Polyethylene resin analysis

As explained in the introduction chapter, the electrostatic charge build up in polyethylene reactors is a major consideration in polyethylene manufacturing. Using the technique we have developed, we are capable of determining the charging behavior of different polyethylene resins.

7.1.1 Particle Flow Apparatus

An apparatus has been designed for studying the triboelectric charging arising solely from particle-particle interactions. A vacuum chamber is used to reduce the effects of contaminants and humidity, and a single-hole distribution plate is used so that particles are mixed in a fountain-like flow. Only particle-particle interaction occurs in this flow, and there is no contact of the particles with the equipment surface or the probe surface.
7.1.2 Probe

The probe, which is modeled after a Langmuir probe, is a 1/8” diameter stainless steel rod shielded with quartz glass. The probe is positioned approximately 8 cm above the bed. At this height, the particles do not contact the probe to a significant extent. If particles did come into contact with the probe, charge transfer could occur between the probe and particles.

A Keithley 6517A electrometer is used to measure the current drawn from the probe. The electrometer measures the current approximately every 60 microseconds. The current is induced by the changes in the electric field generated by the moving charged particles. A positively charged particle will induce a positive current when moving towards the probe and it will induce a negative current as it moves away from the probe, thus the net current induced by a particle is zero. Note that the net current would not be zero if the particle came in contact with the probe, since some charge on the particle would discharge through the probe, and so the particle would not induce the same current as it traveled away from the probe (back toward the bed of particles).

Each data point represents the total current induced from all charged particles moving near the probe. The standard deviation of the current is determined over 20000 data points (~20 minutes), once the bed has reached steady state. As discussed previously in chapter 3, the magnitude of particle charging can be quantified by the standard deviation of the current measurements.
7.1.3 Particle Charging Methodology

In all experiments, the granular samples fill the bed to a height of 34 mm (330 mL). Before being placed in the bed, the particles are sprayed with ionized air from an ionizer gun (Exair Inc); the positive and negative ions produced by ionizer gun act to neutralize the particle surfaces. The particle bed is placed in the vacuum chamber, which is evacuated down to 20 torr and then purged with nitrogen. The particle flow is then generated by high purity nitrogen gas at various flow rates (.15-.5 L/min), at a chamber pressure of 70 torr. The current, chamber pressure, and pressure drop over the bed are measured for a period of 50 minutes.

Two polyethylene resin samples were obtained from Dow Chemical Company (PE1 and PE2). Each sample had a broad size distribution range from (70-2000 microns). The samples were sieved into control size distributions to examine the effect of size distribution on the polyethylene.

7.2.4 Polyethylene Resin

The PE1 resin was cut into 4 different monodisperse samples: 710-420 μm, 420-355 μm, 355-300 μm, and 300-210 μm. Each sample was run under the same parameters as in the mixture granular experiment:

Volume of granular material: 350 ml

Probe height above the bed surface: 10 cm

Chamber pressure: 70 Torr
The PE1 resin showed similar behavior to the granular mixtures where there was a linear relationship between pressure and standard deviation of current. In addition to each monodisperse sample, a broad size distribution sample was produced by mixing equal part of each monodisperse (210-710 μm).

Figure 7.1 PE1 resin (top) Steady state standard deviations of the current, $\sigma_{ss}$, as a function pressure drop, $\Delta P$ for different samples. (bottom) The slope of standard deviation and pressure drop which is relating to the charging behavior of each sample.
The results for the different monodisperse sample showed very similar charging behavior. The polydisperse sample charged on the same order of charging as the monodisperse samples. It appears for this sample that size distribution is not a factor in the triboelectric charging. In addition to the size effect, the charging behavior between PE1 and PE2 was examined.

![Figure 7.2 Comparison between PE1 and PE2 resin. PE2 (Blue diamond) and PE1 (red diamond).](image)

The PE2 resin charges \(\frac{d\sigma_{ss}}{d\Delta P} = 2.3 \text{ pA/Torr}\) more than the PE1 resin \(\frac{d\sigma_{ss}}{d\Delta P} = 1.2 \text{ pA/Torr}\). This behavior is similar to the charging characteristic which has been seen during operation in reactors\(^1\).

### 7.2 SARAN resin analysis

SARAN resin particles were also examined. It was suggested that SARAN resin particle charger greater than polyethylene resin. Static build during transportation of
SARAN resin has been observed to be a problem\(^2\). To better understand this behavior, we examined the charging behavior of several different SARAN resin particles and compared them to systems with known charging behaviors.

![Comparison of SARAN samples and other single component systems.](image)

The SARAN samples and both polyethylene samples had similar size distributions (300-355 μm)

The SARAN samples are labeled as S1-7 since the names are proprietary to Dow Chemical Company. Also, the differences between the SARAN samples were not disclosed to us. The method developed for measuring the charging behavior of single component system has been shown to be acceptable for various granular materials.
7.3 Reference

1 Personal communication with Tom Spriggs (Dow Chemical Company)

2 Personal communication with Karl Jacobson (Dow Chemical Company)
VIII. SURFACE TOPOGRAPHY OF SUB-MILLIMETER PARTICLES

[Published: K.M. Forward, A.L. Moster, D.K. Schwartz, D.J. Lacks “Contact angles of submillimeter particles: Connecting wettability to nanoscale surface topography,” Langmuir (2007) 24, 5255 (2007)]. This paper was a collaboration with Daniel Schwartz at University of Colorado at Boulder, who was responsible for the experimental setup. Amanda Moster contributed to developing the experimental procedure.

It is difficult to directly measure the triboelectric charging behavior of various insulator particles. The triboelectric charge has been show to be related to the wetting behavior of materials\(^1\). It is believed that wetting behavior is related to the Lewis acidity. The workfunction is related to the Lewis acidity because Lewis acidity is measurement of the propensity of accepting an electron. It is easier to determine the wetting behavior of particles than the triboelectric behavior. The idea of the wetting effects correlating to the static charging has been shown in experiments by Wiles et al\(^2\). He has shown that of contact angle and triboelectric charging of polystyrene prepared with different levels of oxidation. A large contact angle corresponds to an increase in triboelectric effects. Performing wetting experiment appears to be a suitable method for studying the triboelectric effects\(^3\). However, it is difficult to determine the contact angle of sub-millimeter resin particles. We have developed a methodology to measure the contact angle of sub-millimeter particles\(^4\).

8.1 Background

The wetting behaviors of particulate materials are influence by several factors such as surface topography and surface composition. The wettability of particulates is difficult to measure, due to the length scale of particulates (on the order of millimeters or
Thermodynamic equilibrium exists between the three phases: liquid (water droplet), solid (substrate or particle) and vapor (air). The chemical potential of the three phases are equal when in equilibrium. The Young Equation shows the equilibrium between the three phases.

\[
0 = \gamma_{SV} - \gamma_{SL} - \gamma \cos \theta
\]  
Equation 8.1

Where \(\gamma_{SV}\) is the interfacial potential of solid-vapor, \(\gamma_{SL}\) is the interfacial potential of solid-liquid, \(\gamma\) is the surface tension and \(\theta\) is the contact angle. The Young Equation can be rearranged and solved for the work of adhesion, \(W_{adh}\). The surface tension of water at 25 °C is 72 dynes/cm².

\[
\gamma + \gamma_{SV} - \gamma_{SL} = \gamma (1 + \cos \theta) = W_{adh}
\]  
Equation 8.2

The work of adhesion is the energy required to keep equilibrium between the three phases. The work of adhesion characterizes the wetting behavior of the surface.

Determining the contact angle of sub-millimeter particles has proven to be difficult. However, measuring the contact angle of a macroscopically-flat surface can be easily determined by sessile drop methods⁶. Several methods have been proposed for measuring the wettability of small particles. The Washburn method determines the wetting behavior of the particles by the uptake of the water in a packed particle bed. However, the analysis for determining the contact angles is based upon a pore model which requires addition arbitrary geometric parameter⁷. This method may have some inherent errors due the assumptions of the pore geometry. Tensiometry methods measure
the force of a particle as it moves through the vapor-liquid interface\textsuperscript{8,9}. However, the analysis for these types of measurements assumes spherical particles. These techniques may produce errors for non-spherical particles. In this study, we develop a methodology for measuring the contact angle of a sub-millimeter particle.

\textbf{8.2 Experimental Procedure}

The experimental setup is shown in figure 8.1. A drop of high purity (18 MΩ) water is placed between two microscope slides which were separated by a spacer. Small clamps are used to hold the slides and space together. The water was encased between the slides. In addition, the slides were placed on quarter-inch aluminum block above the microscope light to avoid heating the microscopes slides. The spacer was made of polyethylene with a thickness of 750 µm. Several types of microscope slides were investigated to produce the desired meniscus. Before each measurement, the slides were lightly clean with isopropanol (70%). Contact angles were measured for particles with diameters ranging from 200-600 µm. A particle is placed at the water-air interface. Particle position is adjusted to attain the equilibrium 3 phase boundary (water-air-particle) geometry. The equilibrium geometry is stable and the position of the particle does not change. Digital images are obtained of the water-air-particle interface. ImageJ image processing software was used to enhance and denote the edges of the particles. The software was used to obtain the size and contact angle. The contact angle measurement requires the user to draw the contact angle.
Figure 8.1 Experimental methodology for measuring contact angles. (a) View from the top, (b) view from the side, (c) view from the top, zoomed in, (d) view from the side, within the spacer. Yellow represents microscope slides, gray represents spacer, blue represents water drop, and black represents the polymer resin particle.

The precision on the contact angle measurement is dependent on the projection of the water-air interface when viewed from above. The wetting of the slides generates a meniscus which is produced from the hydrophilicity of microscope slides. An extremely hydrophilic or hydrophobic material creates a width meniscus. The material study was preformed to determine the appropriate slide material to produce a narrow water-air interface. The microscope slides were constructed from glycol-modified polyethylene terephthalate (PETG), acrylic, polycarbonate (PC) and polystyrene (PS). Figure 9.2 shows the effect of the hydrophobicity of the slide on the width of the water-air interface. The PC produces a narrower interface compared to traditional glass slides, thus allowing for clearer identification of the contact angle. The width of the water-air interface is given in table 8.1 of the various materials studied. The contact angle of polyethylene resin particles was determined by the method described above.
Table 8.1 Liquid-air interface thickness

<table>
<thead>
<tr>
<th>Slide Material</th>
<th>Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>173 ± 4</td>
</tr>
<tr>
<td>PETG</td>
<td>47 ± 3</td>
</tr>
<tr>
<td>Acrylic</td>
<td>67 ± 2</td>
</tr>
<tr>
<td>PC</td>
<td>29 ± 2</td>
</tr>
<tr>
<td>PS</td>
<td>38 ± 3</td>
</tr>
</tbody>
</table>

Figure 8.2 Pictures under microscope of resin at the water-air interface. (a) Low MW polyethylene particle with glass microscope slide; (b) Low MW particle with PC microscope slide; (c) Same as b, but with image enhancement; (d) High MW particle with glass microscope slide; (e) High MW particle with PC microscope slide; (f) Same as e, but with image enhancement.
The contact angles were also determined for the melt-polyethylene resins. The melt-polyethylene has the same composition as the resin particles, except the melt-polyethylene has a macroscopically flat surface. Standard goniometer techniques were used to measure the contact angles. High purity (18 MΩ) water was slowly applied and removed to the surface of the solid. The advancing and receding contact angle was measured.

Two types of the polyethylene were investigated, each demonstrating a different surface topography. Scanning electron microscopy (SEM) was performed to study the surface of the polyethylene particles and the surface of the melt-polyethylene resins. The surfaces of polyethylene are sputtered with 5 nm of Pd to produce a conductive surface for SEM. The SEM images show the contrast between the high molecular weight (MW) resin particle and the low molecular weight resin particle (figure 8.3). The high MW resin displays a higher surface roughness than the low MW resin.

8.3 Results

In this study, two types of polyethylene resins were studied with various surface topographies. The polyethylene resins differ in crystallinity and density. One polyethylene resin displays a high stress/rough surface (high MW resin particle) and the other polyethylene resin; a relaxed/annealed surface (low MW resin particle). However, the melt-polyethylene displays similar surface characteristics (figure 8.3). Table 8.2 shows the contact angle of the polyethylene resin particles and the associated contacting angle of the melt-polyethylene. Using Young’s equation, the work of adhesion is determined for each system.
<table>
<thead>
<tr>
<th></th>
<th>Low Molecular Weight Polyethylene</th>
<th>High Molecular Weight Polyethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin Particles</td>
<td>$104° \pm 4°$ (0.055 J/m$^2$)</td>
<td>$135° \pm 2°$ (0.021 J/m$^2$)</td>
</tr>
<tr>
<td>Melt (macroscopically flat)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Advancing</td>
<td>$100° \pm 1°$ (0.059 J/m$^2$)</td>
<td>$101° \pm 1°$ (0.058 J/m$^2$)</td>
</tr>
<tr>
<td>Receding</td>
<td>$78° \pm 2°$ (0.087 J/m$^2$)</td>
<td>$81° \pm 2°$ (0.083 J/m$^2$)</td>
</tr>
</tbody>
</table>

Table 8.2 Contact Angles (Work of Adhesion) of polyethylene
Fig. 8.3: Optical microscope images under microscope of resin at the water-air interface. (a) Low MW polyethylene particle with PC microscope slide; (b) High MW particle with PC microscope slide; (c) SEM image of low MW resin particle; (d) SEM image of high MW particle (e) SEM image of low MW polyethylene melt; (f) SEM image of high MW polyethylene melt.

8.4 Discussion

A successful methodology has been developed for determining the contact angle of sub-millimeter particles. Table 8.1 shows the importance of choosing the correct material which minimizing the meniscus thickness. Ideally, a material which does not have an affinity to water is preferred. In this case, polycarbonate produced the thinness
meniscus. This allowed for a clear view of the water interface of the particle. This effect is shown in figure 8.1, comparing the view of the interface for both polycarbonate and glass slides. The glass slide produces a wide meniscus due to the highly hydrophobic surface of the glass. Once the ideal slide material was determined, contact angles of individual particles were determined.

The low and high MW polyethylene resin particles display different wetting characteristics. However, the melt of each polyethylene shows similar wetting behavior. The contact angle of the melt polyethylene (macroscopically flat surface) was obtained. A goniometer was used to measure the advancing and receding angles. The advancing contact angles are 100° ± 1° for the low MW PE and 101° ± 1° for the high MW PE (the receding contact angles were 78° and 81°, respectively). Similar values have been gathered from literature reports for the contact angle of water on polyethylene surfaces of approximately 100° 10,11,12. Comparing the results for the resin particles and the melt polyethylene, it is clear that the resin particles are significantly more hydrophobic than the melt surfaces. From this, the wetting behavior for these resin particles is associated with the surface topographical and not the material properties of the polyethylene resin particle.

It is known that surface roughness increases the hydrophobicity of surfaces. This causes the apparent contact angle, \( \theta_{\text{app}} \), to exceed the intrinsic contact angle, \( \theta \), of a smooth surface. For complete wetting the Wenzel equation applies13,14.

\[
\cos \theta_{\text{app}} = r \cos \theta \\
\text{Equation 8.3}
\]
Where $r$ is a measure of the surface roughness ($r \geq 1$, $r = 1$ for a smooth surface).

Complete wetting is associated mainly with hydrophilic material since water is drawn into the surface feature due to capillary forces. In the case of incomplete wetting, the Cassie-Baxter equation applies\textsuperscript{15,16}.

$$\cos \theta_{\text{app}} = f \cos \theta - (1 - f)$$  \hspace{1cm} \text{Equation 8.4}

Where $f$ is the fraction of the surface wetted. For both cases, complete and incomplete wetting, the apparent contact angle exceeds the intrinsic contact angle for hydrophobic material ($\theta \geq 90^\circ$).

The increase of surface roughness has also been observed in nature to produce superhydrophobicity. The lotus leaf surface is covered with a nano-microstructure that gives the surface a rough structure. In addition to the nano-microstructure, the surface of the leaf is made of a waxy material which is hydrophobic. The combination of the waxy surface and the nano-microstructure creates a superhydrophobic surface. When water droplets form on the leaf, the droplets roll off and collect dust, small insects and other small particles. The superhydrophobic surface acts as a self clearing mechanism\textsuperscript{17}.

8.5 Conclusion

In conclusion, a useful method has been developed to measure contact angle of sub-millimeter sized particles. In addition, the wetting behavior of a high and low molecular weight polyethylene resins were investigated. The high molecular weight polyethylene resin surface contacts a nano-macrostructure. The surface roughness increases the hydrophobicity of the polyethylene. Similar wetting behavior is comparable to the lotus leaf, which is commonly known as the lotus effect.
8.6 References


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IX. CONCLUSION AND RECOMMENDATIONS

The knowledge presented in this dissertation has the potential to impact a wide range of industries. In addition, the techniques developed here allow for a better understanding of the fundamentals of triboelectrification. Single component granular materials are involved numerous applications. The particle flow apparatus is the first of its kind to strictly study particle-particle interaction without having the granular material contact any other systems. The fundamental study of bimodal particle distributions shows that relative, and not absolute, size difference determines the charge segregation in granular materials. By understanding the proposed mechanism for a single component system, it has been shown that it is possible to modify the composition of granular material to control the charge segregation.

In maintaining with the line of this work, I have several recommendations to continue to gather knowledge about the process of triboelectrification. The work done by Liu and Bard shows that electron transfer does occur in some insulator materials. Additional work is required to show which materials are dominated by electron transfer or ion transfer. I believe that this behavior is mainly dependent on the material type and the environment. The charge occurs in the environment where water is not present (i.e. Mars, polyethylene reactors systems, etc.), which would suggest that electron transfer is responsible. In the case of Liu and Bard, experiments were carried out on Teflon, which is very hydrophobic, and the water (ion transfer) was not an issue. A systematic approach similar to Liu and Bard's experimental procedure is required to examine which materials can show electron transfer in varying degrees of humidity. This study would give further
insight into the dominant transfer of electrons or hydroxide ions in the triboelectrification of insulator material.

In addition, to better understand charging in single component granular, more work is necessary to show how asymmetrical charge transfer occurs. I have developed an experiment, which uses two glass tubes. One tube rotates and the other tube is stationary against the rotating tube. The stationary tube represents a small particle, which is only in contact with the glass in a small, localized space, where the rotating tubes represent a large particle of which the whole circumference of the tube is in contact with. This setup is similar to the experiment performed by Lowell and Truscott, when they first examined single component charging. A wide range of experiments may be performed to understand asymmetrical charge transfer. One glass tube can be modified with various charge control agents (similar in to that in chapter 6), making it possible to examine ion transfer. Similarly, the tubes can be exposed to ultra-violet (UV) light to increase the density of trapped electrons. The stationary tube can be UV treated and contacted with a non-UV treated, rotating tube to obtain opposite charge segregation. These treatments can also be performed on the glass beads to produce different degrees of charge segregation. Experiments like these would gain important knowledge into triboelectric charging of single component granular systems.