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ELECTROSTATIC INSTABILITIES, CHARGING AND AGGLOMERATION IN FLOWING GRANULAR MATERIALS

by

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Abstract of the Dissertation

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The unpredictable behavior of granular materials is one of the largest stumbling blocks on the way to satisfactory design and control of many manufacturing processes. There are many factors which contribute to the complex behavior of granular materials, however, the effect of electrostatic forces is both one of the least studied aspects of granular materials as well as one of the most important. Electrostatics can cause agglomeration of otherwise free flowing powders, the adhesion of grains to equipment surfaces, and particles of differing composition or size to segregate. In addition, electrostatic discharges can ignite dangerous dust explosions. With a better understanding of the effects of electrostatics, as well as the processes at work during the charging of particulate flows, some of these issues can begin to be addressed. To these ends, we examine the charge and agglomeration of grains and investigate how flows of particles charge, and in turn, how they are affected by those charges.

In this work, we show that the behavior of flows of uncharged grains through chutes can be approximated by simple models, but when charging takes place the behaviors change dramatically, replacing fluid-like flow instabilities with significant agglomeration, making the flow much more difficult to model. To understand and predict these transitions from relatively simple flow to a more complex/agglomerated state requires that the distribution of charge amongst the particles, as well as the effect of large electric fields, produced by either charged surfaces or particles, be investigated.

It was found that highly nonuniform distributions of charge could be generated by flowing particles. This distribution can result in significantly different forces acting on charged and uncharged grains and suggests that many of the problems commonly encountered during powder handling may be due to a small fraction of the particles.

Lastly, significant agglomeration was observed when particles were subjected to nonuniform electric fields. Nonuniform electric fields, which are produced as particles charge, cause polarization of the particles and attraction between grains. The resulting forces acting on the particles (referred to as dielectrophoretic forces) were large enough to produce both large agglomerates of powder, as well as adhesion to equipment surfaces. These forces may also be utilized to control particle behavior as this adhesion depends on the presence of an easily controlled external electric field.

Preface

In the pharmaceutical industry, as well as in other industries, there is a need not only for better control and predictive capabilities when it comes to powder handling but also new methods for controlling powders on a large scale. By investigating electrostatics it may be possible to move toward both of those goals. In the pharmaceutical industry the unpredictable nature of electrostatic interactions can lead to segregation and agglomeration and can cause expensive batch failures. At the same time, other industries have learned to use electrostatics to obtain consistent results from what would otherwise be very complicated operations. For example, electrostatics is used to separate particles by composition or size in both the recycling and mining industries, and electrostatics is also used to apply uniform coats of paint to surfaces. These applications show that if the full potential of electrostatic forces could be utilized in all industries there is the potential to solve many of the current problems with variability of products due to not only electrostatic effects but also segregation, poor mixing, and flow instabilities.

We began this research by focusing on the instabilities generated in an inclined chute. However, as we examined the patterns produced by these instabilities we noticed new and complicated patterns, which occurred whenever we neglected to take steps to prevent electrostatic charging. These new patterns were quite different than the patterns produced by the flow of the grains alone and yet their presence suggested the relative strength that electrostatic forces can have on the motion of the particles. Studying these patterns lead us to attempt to answer several questions raised by the behavior of these particles. Questions such as how did the particles manage to form large agglomerates when their apparent charges were too low to create significant forces. It seems likely that either distributions of charge on the particles themselves or the electric field produced by the chute were to blame for the agglomeration of the particles.

To investigate the distribution of charge on particles a simple cylindrical tube was chosen as it allowed us to control the particle motions easily. We could then determine how distributions of charge are developed by a flowing particulate material. The forces created by an external electric field were also studied and it was found that nonuniform electric fields can induce large forces in even uncharged grains. These experiments have allowed us to examine the effects of electrostatics on flowing materials.

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Chapter 1 Introduction

1.1 Motivation

Particle handling operations are ubiquitous within most manufacturing industries, and yet their unpredictable nature makes them difficult to adequately design, predict and control. With the current state of the art, industrial processes involving gas or liquid phases can, to a large extent, be accurately modeled and predicted, allowing for efficient and accurate design, operation and control of most fluid based operations [1]. However, processes that require the use of particulate materials make up the majority of industrial operations [2]. The behavior of particulate material is complex, and while often analogous to that of gases or liquids, has thus far defied attempts at accurate theoretical description [2]. The host of particle attributes which play a significant role in the macroscopic behavior of granular materials and the discrete nature of the particle interactions has stymied attempts to bridge the gap between the microscopic understanding of the individual particle interactions, such as friction, energy dissipation, deformation, fluid drag, liquid-bridging, as well as van der Waals and electrostatic forces, and the larger scale behavior of granular materials. The effects of each individual interaction on the bulk material must be understood to accurately predict material properties and flow under all conditions. While many particle interactions have received considerable attention, the effects of electrostatics have not been studied in great detail. This is in spite of the ability of electrostatic forces to alter, or cease the flow of grains [3], segregate mixtures of materials [4, 5, 6, 7], agglomerate otherwise free flowing materials [8, 9] and even cause extremely dangerous dust explosions [10].

The pharmaceutical industry, more than other industries, is especially vulnerable to particle handling problems, including those created by electrostatics. With the pharmaceutical industry's need to reliably mix small amounts of active drug particles with much larger quantities of excipient, any segregation or flow problems can result in unacceptable product concentrations [11]. At best these problems can cause costly batch failures and product delays. At worst, defective tablets that make it to market could deliver either an underdose of drug, so that patients do not receive the full medicinal effect of the drug, or an overdose, which can result in severe health issues. The ability of a material to flow readily is also essential in pharmaceutical processing. High speed tablet presses require powder to flow easily into the press dies, so that they can be compressed accurately. Flowability issues can lead to tablet non-uniformities, which may make their appearance, dissolution, or shelf life unacceptable [11].

While many mechanisms can lead to these powder handling problems, electrostatic forces can contribute significantly to both segregation and unpredictable flowability. At present there is no consensus on the best methods for preventing electrostatic charging. Several commonly used methods for controlling the charge picked up by grains, including: grounding equipment [12], the use of electrostatic eliminators [13, 14], and raising the relative humidity [15, 16], have had their effectiveness debated.

Some industries have developed methods to utilize electrostatics to control large quantities of particles simultaneously. Electrostatic separation is currently used to separate materials based on their conductivity or charge [17, 18], as well as to filter aerosol particles from gas streams [19]. The photocopying industry has been using electrostatics to place toner particles on paper controllably for over 60 years [20]. Electrostatics has also improved the efficiency and speed of applying paint and other coatings [21]. The ability of electrostatics to accurately control the motions of grains could be used to develop new technologies to improve many particle handling operations.

To truly tackle the particulate handling problems facing many industries, a fundamental understanding of particle mechanics must be developed. Currently, experimental investigations are slowly determining how electrostatic charges are produced and affect granular behavior. To achieve these goals many questions, such as "under what conditions do electrostatic forces dominate over other effects," and "how is charge distributed within a material," as well as, "how do external electric fields affect granular behavior," will need to be answered.

1.1.1 Granular materials

The dynamic behaviors of fluids are well characterized by the theory of Navier-Stokes. However, no theoretical framework has been capable of completely describing all granular material behaviors [2]. These materials have proven especially difficult to characterize largely due to their extremely broad range of behaviors, from those analogous to gases to those of solids, depending on density and the amount of energy applied to the system. Several of these "phases" can coexist in one system and regions of a granular flow can dynamically switch between them [22, 23]. Their behavior is further complicated by distributions of grain size and shape, the inelastic nature of granular collisions, and the lack of scale separation between grain and system dimensions [24, 25, 26].

The modern study of granular materials began with an attempt to understand geophysical features [27]. Many geophysical systems depend on the mechanics of granular materials, including many which impact human lives and property. For example, avalanches and lahars can quickly bury individuals or whole communities [28]. While volcanoes [29], sand dunes [30], and even lightning [31] all depend on granular materials and can be extremely important for both humanity and the environment. Research has since grown to include many other systems of both scientific and industrial interest, such as chute flows, fluidized beds, vibrated systems, as well as granular packing and pattern formation. Granular materials have also been recognized as one of the most import factors for planetary exploration, as most nearby planetary bodies, such as the Moon and Mars, are almost totally dry. Any attempts to utilize resources on these bodies will require processing granular materials in large quantities [32].

1.1.2 Segregation

One of the many difficulties encountered when working with granular materials is segregation. Particles tend to spatially separate based on any one of a number of properties. Most theoretical segregation mechanisms are based primarily on particle size [33]. One of the most commonly observed segregation mechanisms occurs when a mixture of materials are vibrated. Counter-intuitively, large, heavy particles are often observed rising to the top of a vibrated container while smaller, lighter particles sink [34]. This is often referred to as the "Brazil nut effect." An example of this segregation mechanism can be seen in Figure 1.1(a). This behavior creates difficulties for any industry that requires the blending of particles with differing size distributions. Any vibration after the materials are blended can cause segregation, which produces concentration gradients in what would otherwise be a homogenous mixture.

Several segregation mechanisms have been investigated in vibrated systems. The segregation of particles by size has been attributed to both percolation [35], where small particles fall into spaces under large ones during vibration, eventually raising the larger particles to the surface, as well as convection [33], where, due to the drag of the container walls, both large and small particles rise near the center of the container but only the small particles can return to the bottom in the narrow descending regions along the walls. Interestingly, reverse buoyancy, in which large particles sink while small particles rise, has also been reported and is believed to be caused by differences in particle density [36].

Particle shape can also cause segregation. Shape affects a material's angle of repose and can cause segregation when powders are poured or tumbled in blenders [37], an example of which can be seen in Figure 1.1(b). Shape has also been shown to affect segregation in vibrated systems [38] and when particles are subjected to viscous drag [39]. Particle shape is especially difficult to model, as it requires much more computationally intense algorithms to calculate particle interactions [40].

Electrostatics can also cause particles to segregate, especially particles of different sizes or materials. As can be seen in Figure 1.1(c), red and blue art sand can be partially segregated by simply allowing them to charge as they pour down an inclined Teflon sheet. Electrostatic segregation can be so strong that it has been utilized in many industries to separate materials on a large scale [17, 18]. Electrostatic separators are widely used in recycling and mining industries. Segregation due to electrostatic effects is a common occurrence and has been documented in pipe flow [5, 6], vibrated chutes [41], mixers [7] and even the simple act of pouring charged grains from a container [4].

The conditions for dust explosions, which are often ignited by electrostatic discharges, are created by the segregation and lofting of fine particles [10]. Particle size, density and shape affect their ability to be fluidized. When in the presence of an interstitial fluid, smaller particles will tend to be carried by the fluid, thus separating small grains from larger ones. This mechanism is especially problematic in fluidized beds and while filling hoppers or blenders [24, 42]. For combustible materials, this lofting of fine particles can lead to dust explosions, commonly triggered by electrostatic discharges when a critical concentration of powder is mixed with air. Wheat flower, for example, contains more chemical energy per pound than TNT [43]. The discharge from

either charged particles or charged process equipment is often enough to ignite the cloud of particles, causing a dangerous explosion.

These dangers require that any facility working with fine powders must be carefully designed to prevent dust accumulation and electrostatic discharges. The design must also include methods to mitigate as much damage as possible if a dust explosion were to occur [44]. Materials must be constantly tested for their minimum exposable concentration as well as their minimum ignition energy, which is a measure of the amount of energy a spark must possess to trigger an explosion [10]. These design modifications are expensive and are subject to regulatory oversight. Understanding charging mechanisms could lead to better discharge prevention and explosion risk assessments.

1.1.3 Granular flow instabilities

Along with segregation, difficulties with flowing materials cause unpredictable behavior. Uniform particulate flows can become heterogonous spontaneously, leading to extreme variations in density, stress, and velocity. In polydisperse materials, unstable flow can cause or exacerbate segregation [45].

The clustering of grains due to inelastic collisions during flow is a well studied flow instability. As a material flows, grains collide and lose energy. Any high density region in the flow tends to have a higher frequency of collisions and therefore lose energy more quickly. Grains then collect in these regions, producing dense, slow moving regions of grains surrounded by low density regions [46, 47, 48].

Flows of material within commonly used particle handling devices, such as pipes, vertical channels, chutes, rotating cylinders, and Couette flows, have been observed to undergo several instabilities. Clustering has been examined in pipes and channels [46, 48] while vortices, as well as segregation, have been observed in Taylor-Couette geometries [49]. In chutes and inclined planes with roughened bottom surfaces, materials form long stripes as they flow (see Figure 1.2(a)) [50]. These patterns have been shown to be caused by longitudinal vortices within the flow created by density inversions in a similar manner to Rayleigh-Bènard convection vortices [51]. More complex three-dimensional surface waves have been reported in inclined channels near frictional boundaries [52]. As shown in Figure 1.2(b), a granular bed flowing on a smooth surface with roughened sidewalls develops chevron-shaped free surface waves. These may constitute an analogy with fluid boundary layer flows, in which phenomena such as hairpin vortices develop near boundaries, signifying the onset of turbulence [53].

Electrostatic effects can also result in flow instabilities and can significantly affect the flow of granular materials. Charges can cause agglomeration or can force particles to adhere to surfaces, changing the behavior of the flow. Examples of electrostatic agglomeration and adhesion are shown in Figures 1.2(c) and (d). Flow of materials within pipes has been observed to form patterns of adhered particles to the pipe walls as the particles charge [54]. Electrostatics can seriously affect the operation of fluidized beds. Sticking and sheeting have been attributed to electrostatic effects and material segregation [55]. When external electric fields are applied, the charged grains have an even larger impact. The "freezing" of fluidized beds when subjected to large electric fields has been examined [9]. Snezhko et al. documented the patterns created by conducting particles contained in an oscillating electric field [56]. Hou et al. examined the ability of electric fields to influence the flow of particles falling through a pipe [3]. Hou et al.'s work showed that sufficient applied voltages could qualitatively change granular flows from rapid to dense.

1.1.4 Scale up

An understating of these flow instabilities is critical if true scale up criteria are to be developed. Currently there has been little consideration of the effects of scale on granular behavior. The examination of the rate of segregation and the mechanisms of mixing are yielding some insight into scaleup of granular materials [57, 58]. However, most scaleup decisions are left to heuristic models and rules of thumb [2, 59]. The prediction of electrostatic effects on the large scale has yet to receive significant attention. There are currently no methods for predicting the charge generation by large particle handling equipment. As process equipment is scaled up the amount of surface area for particle contacts increases, which may result in larger charges generated over the course of the process. Equipment design can affect everything from charging rate, to charge separation, which can lead to discharges, to particle adhesion and agglomeration [60]. In addition, there is little reason to believe that the most commonly used methods for preventing charging, such as grounding process equipment, will operate as expected on large scales. Indeed there is already evidence on the lab scale suggesting that these methods may not be effective in all situations [12, 13, 15]. Moreover, grounding equipment does not prevent particles inside the equipment from acquiring a charge through triboelectrification.

1.1.5 Outstanding issues and the path forward

The segregation and flow instabilities inherent in particulate behavior must be controlled in order to improve the low efficiencies industries often encounter when operating with particulate processes. This knowledge is especially valuable for the pharmaceutical industry, which is highly dependent on granular materials. The electrostatic mechanisms that often result in process problems are not well characterized. Commonly used "fixes" for charging problems, such as grounding or increasing the relative humidity are debated, and indeed, may be counter productive [12, 13, 15]. Meanwhile electrostatic discharges continue to cause deaths due to dust explosions every year.

There are several directions of study which must be examined if these electrostatic effects are to be better understood. Firstly, the effects of electrostatic forces and secondary electrostatic effects (such as particle polarization) on the flow of grains must be determined. That, however, simply identifies the problems caused by electrostatic charging. To truly control these behaviors there must be some knowledge of how particles charge, and how these charges are distributed amongst the particles. The parameters, if any exist, that may be useful for predicting the charge generated during scale up of processes must be determined as well.

At the very least, determining a method to remove charges or prevent charging altogether may prevent segregation and flow problems caused by electrostatic forces. However, as some industries have successfully demonstrated, the true power of a greater knowledge of electrostatic effects may lie in the control of granular materials. Several industries already mentioned have developed methods that utilize electrostatics to controllably separate materials or control the motions of individual grains on large scales. These methods have been refined to such an extent that objects smaller than the text on this page can be quickly and reliably printed in large quantities by controlling the deposition of toner particles using electrostatic forces. Electrostatics could potentially be used to improve other particle processes. Control has been demonstrated over fluidization velocity [9], flow rates [3] and agglomeration [8, 9, 61]. There is even the possibility that electrostatic forces may be used to "freeze," mixtures of granular materials together after blending to prevent segregation during further handling [61]. The solutions to many of the granular process problems encountered in industry may be found by developing electrostatic control technologies.

In sections 1.2 and 1.3 of this chapter the theories of triboelectrification and electrostatic forces, as well as the forces created by secondary electrostatic effects will be described. Chapter 2 examines the effects of flow instabilities, both caused by electrostatics and other mechanisms, on the free surface flow of grains down inclined planes. The relationship between the charges generated during the flow of grains and the surface area of contact between the grains and the walls of the apparatus is examined in

chapter 3. Chapter 4 investigates the effects of secondary electrostatic forces, also known as dielectrophoretic forces, on granular materials, as well as the conditions under which these forces can dominate the forces created by triboelectrification.

1.2 Triboelectrification

The process by which charges are transferred between materials when they come into contact is commonly referred to as triboelectrification. The triboelectrification process itself is somewhat counterintuitive. For triboelectrification to take place, charge carriers of some kind (such as electrons, protons or ions) must transfer from one material to another in significant quantities. This places many charges of like sign near one another on both materials. One would not necessarily expect these charge carriers to resist the repulsion of their neighbors and to remain adhered to a material. Yet electrostatic charging is commonplace and almost all materials, even those with large resistivities, will become charged when brought into contact with other materials. Even more surprising is the observation that objects will sometimes become charged after contact with another object of the same material [62, 63].

Triboelectrification experiments are famously difficult to reproduce. The charge produced by contacts can vary widely or even reverse sign altogether [62]. This difficulty is compounded by the lack of understanding of material surface structures and surface chemistry, which determines electrostatic charging behavior. Even minute amounts of contamination are enough to completely alter even the most careful experiments, making the identification of tribocharging mechanisms extraordinarily difficult [62]. The last 100 years of research has produced a well understood theory of contact charging between conducting surfaces. However, the charging of non-conductors is still not fully understood [62, 64, 65]. Here we will review the basic theories of electrostatics as well as the current theories of triboelectrification.

1.2.1 Electrostatic forces

The force acting on a charged particle is given by Coulomb's law. Given two point charges q_1 and q_2 and separated by distance r_{21} , the force acting on charge 1 is:

$$F = k \frac{\mathbf{q}_1 \mathbf{q}_2}{\mathbf{r}_{_{21}}^2} \hat{r}_{_{21}}$$
 Eq. 1.1

Here \check{r}_{21} is a unit vector pointing from charge 2 to 1 and k is a constant. The amount of charge, in the SI system, is given in units of Coulombs, where 1 Coulomb is equal to the charge of 6.25×10^{18} electrons. Charge is also often denoted in electrostatic units (or statCoulombs), which are equivalent to 3.3×10^{-10} Coulombs. Throughout this text we will use the SI unit system.

The principle of superposition allows Coulomb's law to be extended to describe the forces between several charged particles. The electrostatic force acting on any charged particle is simply the sum of all individual interactions with other charges. This allows a vector field of forces, normalized by a test charge q_0 , to be constructed. This normalized force distribution is known as the electric field, and at a given point (x,y,z) is defined by:

$$E(x, y, z) = \frac{F}{q_0}$$
 Eq. 1.2

The electric field is commonly depicted as a set of field lines, which are used to denote the shape of the field. By convention these lines are directed so that a tangent to any point along their length lies in the direction of the force that a positive test charge would experience at that point. An example of an electric field can be seen in Figure 1.3.

Another commonly used concept in electrostatics is that of potential. Electrostatic potential is a scalar field and denotes the work required to bring a test charge from some reference point (usually defined to be infinitely far away) to any other point. The electric field is the negative of the gradient of the potential:

$$E = -\nabla \varphi$$
 Eq. 1.3

Potential is measured in volts which are defined by the potential difference necessary for 1 joule of work to be expended while moving a 1 Coulomb charge through an electric field. The potential is a convenient concept and is often used to simplify electrostatic calculations [66].

There are several important implications of these physical relations to electrostatic behavior that will be summarized here. Firstly the electric field must be perpendicular to any line of constant potential. For static systems this means that the surface of any conductor must be at a constant potential everywhere, and the electric field must be perpendicular to the surface. If the electric field were not perpendicular to the surface, charges, which are free to move in a conductor, would reposition themselves so that their forces would be equalized and all charges would be at the same potential [67].

The other important result of electrostatics is that the electric field inside any conductor is always zero. Any charges in a conductor can only be stable if they are spaced as far apart from each other as possible, which can only occur at the surface of the conductor. Any static electric field inside a conductor would cause charges to move until that field was cancelled. This means that in any conductor, no matter if that conductor is hollow, there can exist no electric field (assuming no charges are placed inside the conductor). This result is important as it allows us to both shield an experiment from external electric fields, often called a Faraday cage, and measure the electrostatic charge of an object placed inside a hollow conductor, referred to as a Faraday cup [68].

1.2.2 The charging process

The tribocharging process is actually characterized by two distinct behaviors [69]. Contact charging occurs when two materials are brought into intimate contact with no relative motion between them. Frictional charging occurs when materials are rubbed against each other [62]. The term triboelectrification is commonly applied to both contact charging and to frictional charging [69]. Here we will adopt the term to denote both charging mechanisms and reserve frictional charging to describe the case of rubbed materials alone.

While the mechanisms of contact electrification of conductors are well understood the mechanisms that cause insulators to charge are still unknown [62]. There are several theories that conform to the experimentally observed charging behavior of nonconductors, which range from the transfer of electrons, to surface contaminates, to adhered ions. In all likelihood most of the proposed mechanisms probably account for at least part of the contact charging observed.

Most of the difficulties in determining the mechanisms behind charging stem from a lack of knowledge of the surface chemistry and surface features of a material even under carefully controlled laboratory conditions. Surfaces are almost always covered in layers of contaminants or water and ions from the atmosphere [62]. These problems can persist even after stringent clearing procedures. In an attempt to clean the surface of a quartz ball, for electrostatic research, one researcher went through a drawn-out cleaning procedure:

"The quartz ball was first given a preliminary wash in several solvents so that visible dirt could be removed without difficulty by rubbing hard on chamois leather, rubbing lightly on clean cotton cloth, and then dusting under the microscope with a stereoscopic magnification of 25x, using a camel-hair brush. The balls were then washed for a few minutes in each liquid of the flowing sequence: anhydrous ether, absolute alcohol; a mixture of ether, alcohol, and concentrated ammonia; conductivity water, alcohol, and anhydrous ether. ... After 20 min in a mixture of 50 per cent conc. A.R. nitric acid and 50 per cent conc. A.R. sulphuric acid, it was rinsed for a few minutes in four changes of conductivity water. It was then refluxed for several days with conductivity water" [62, p. 78].

Even after this thorough cleaning process, contaminates were still found on the surface (on the order 10^6 particles per cm²), although to a lesser degree than before cleaning [62].

To prepare a surface that is free from contamination is exceedingly difficult, and in fact, the cleaning procedure used can itself affect charging mechanisms. Shaw and Jex performed tribocharging experiments with glass that was washed with either an acid or base [70]. The polarity of the charge generated by the glass was reversed when the wash was changed from acidic to basic. This is most likely due to a change in the ions bound to the unsatisfied bonds at the surface of the glass from H^+ to OH^- .

The importance of surface chemistry was also demonstrated by Harper when experimenting with the charge generated by different quartz crystal faces [71]. He found that dissimilar faces of the crystal, and therefore different dangling bonds, charged when the faces were brought into contact, but did not charge when similar faces were brought into contact.

Both these results demonstrate the difficulty in understating and predicting the charges transferred during material contact. The charge generated by both crystalline and amorphous materials depends strongly on the current state of the surface and the functional groups attached to the dangling bonds. Without a detailed knowledge of the history or crystal structure of a material, understanding its charging behavior is extremely difficult.

The theories of contact charging, while difficult to apply in all but the most controlled situations, are illuminating in their description of the range of possible electrostatic behavior. We will first discuss the charging behavior of conductors and then the theories of contact charging of insulators. Finally we will describe the theories of frictional charging and how they may differ from contact charging mechanisms.

1.2.3 Contact charging

According to the band theory of electronic structure, the bonding electrons for most materials reside within energy levels that are shared throughout the material. In conductors, unfilled energy levels are easily accessible to electrons [62]. These partially empty energy levels are the material's conduction band.

The Fermi level is the energy level that electrons would fill up to if the material was cooled to absolute zero (the energy needed to move an electron from the Fermi level out of the material altogether is known as the "work function"). At temperatures higher than absolute zero some electrons are raised into levels higher than the Fermi level by thermal excitation. It is these electrons, along with those in the now only partially filled levels below the Fermi level, which can conduct electricity. Different materials have Fermi levels at different potential energies. When two conductors are brought into contact, the electrons that are higher in potential energy move from their initial material into the conductor with the lower Fermi level. As the electrons transfer they create an electric field, which raises the potential energy of the electrons already in the lower Fermi

level material. When the potential energy of the Fermi levels of the two materials become equal charge transfer stops [62]. This process is depicted in Figure 1.4.

When the conductors are separated, the electric field set up by the initial charging forces some electrons back to the original material. This means that the full charge transferred by contact is not the charge measured after the conductors are separated. This charge is the separation charge and is usually much smaller [62].

Insulators do not have easily accessible empty energy levels. There is a large gap between the Fermi level and the next possible energy level. Electrons cannot easily reach these energy levels (such as by thermal excitation) and therefore cannot conduct electricity. A conductor with a high enough Fermi level could, conceivably, put electrons directly into a conduction band of an insulator. This would not only charge the insulator but also make it conductive. However, this behavior has not yet been experimentally observed [62]. It is possible that impurities (such as oxygen) in the insulator could create new energy levels in the material, which would be lower in potential energy than the conduction band and would localize free electrons so that they could not conduct. Even a very small amount of impurities, on the order of 1 part in a billion, could account for the charges usually observed during contact charging experiments [62].

The electrons trapped near the surface of insulators, which are localized and unable to conduct, could be transferred between insulating materials in a mechanism similar to that of charge transfer between conductors. Depending on whether or not there is a high or low density of surface states on the insulators, the number of electrons transferred could be limited by either the small numbers of electrons available in the low density case or the flow of electrons may cease when the Fermi levels of the materials are equalized, similar to the behavior of conductors, for the high density case [69, 64, 65]. The electronic structure of insulators is difficult to probe experimentally, although most experiments so far seem to suggest that insulators have a high density of electron states at their surface [64].

Other possibilities for the charging of insulators have been proposed. Ions loosely adhered to the surface of insulators could also be transferred. These ions may be present as contamination or they may be adhered to the surface due to the chemical structure of the surface of the material [62, 64]. If dangling bonds at the surface of an insulator are bonded to charged functional groups (OH⁻ ions for example) atmospheric ions will be attracted to the surface. When another insulator is brought into contact, these ions can be easily transferred.

Electrolytic ions dissolved in a thin layer of water on the surface of insulators could also be transferred and lead to charging, especially if a potential difference existed between the materials. The potential difference would separate the ions of opposite charge. Charging still occurs between extensively cleaned insulators and insulators in dry environments. So it is unlikely that this mechanism is solely responsible for the contact charging of insulators, however, under atmospheric conditions it may play a considerable role in observed charges [62].

1.2.4 Frictional charging

Charging during rubbing often produces different charge amounts, and sometimes different polarities, than contact charging alone [62]. The nature of surface contacts during the rubbing or sliding of one material over another can be quite different from the contacts that occur when materials are simply brought together with no lateral motion.

One possible contribution to charging during sliding could be caused by the increase in the number of points of contact between the materials and therefore an increase in the amount of contact charging that can take place. This mechanism, known as the Volta-Helmholtz hypothesis, may play a large role in the frictional charging of materials under some circumstances; however, charging has also been observed to depend on the method of rubbing. It has been observed that when two objects, made of the same material, are rubbed against each other asymmetrically they can become charged, while no charging results if they are rubbed symmetrically [62, 63]. None of the contact charging mechanisms can account for the like-material charging observed in these experiments, which suggests that the Volta-Helmholtz hypothesis cannot be the only mechanism of charging in rubbed materials.

Local heating of a material during rubbing may be responsible for the charge generated during asymmetric rubbing. For example, if two rods of the same material are rubbed, one stationary, the other moving in a saw-like manner, charging can result [62]. The rubbing will heat the materials differently. On the stationary rod all of the friction is concentrated on one area while the moving rod spreads out the heat over a longer contact area. This heating may increase the mobility of electrons or ions on the stationary rod and deposit them on the cooler moving rod or it may deposit hot material, which has lost electrons to cooler areas around it, on the moving rod [62]. This mechanism could take place whenever materials are rubbed. Friction can increase the temperature of the small areas that are in actual contact and these hot spots can then lead to the transfer of charge.

A mechanism which may be related to hot spots may occur if small amounts of charged material are transferred from one material to the other during rubbing. If these pieces are charged differently than the bulk of the material, either due to differences in temperature or composition between the pieces and the bulk, their movement can result in charge transfer [62]. These small pieces may be made up of the top layers of a material or they could consist of contaminates adhered to the surface of the material.

1.2.5 Electrostatic discharges

Charge amounts are limited by the small concentration of ever-present atmospheric ions. Ions are constantly produced by radioactivity and cosmic rays. When an electric field becomes strong enough these ions are accelerated, either towards the charged surface or away, fast enough that collisions with other molecules produce more ions, which are also accelerated and collide, producing yet more ions. This process leads to a cascade of ions, which can act to transport charge from the surface of a charged material [62].

There are several types of electrostatic discharge. The most commonly observed discharge is a spark discharge. These discharges occur between conductors with large

differences in voltage and are characterized by a bright arc between the conductors. Brush discharges are more commonly seen on charged non-conducting surfaces. These discharges are similar to those one might see between sheets or blankets in the winter, and are often responsible for igniting dust explosions [72]. Corona discharges, which are also known as St. Elmo's fire, are also a commonly seen type of discharge. They appear as a blueish-white glow around areas with high electric fields and can limit the voltage of high voltage equipment or appear due to atmospheric effects.

Electrostatic discharges occur at high electric fields but the exact field strength depends on the size of the region of high charge [62, 73]. The smaller a charged particle, the higher the electric field must be to produce enough ions to lead to breakdown. This dependence of the breakdown field on particle radius allows small particles to build up much higher charges than are possible for larger particles. This suggests that electrostatic forces created by triboelectrification play a much larger role for small particles (<100µm) not only because of their large surface to mass ratio but also because they can potentially retain much higher levels of charge than larger particles. However, it should be noted that while the breakdown potential represents a theoretical upper limit to the charge a particle can develop, the charge produced by a tribocharging mechanism may saturate at a level well below this limit.
1.3 Dielectrophoresis

For point charges, Coulomb's law completely describes the electrostatic forces, but for particles of finite size, higher order electrostatic forces need to be considered. When materials are placed in an electric field their electronic structure is disturbed and they become polarized. It is the interaction of the electric field with polarized particles that creates higher order forces. In conductors, charges transfer around the surface until the electric field within the conductor is brought to zero, polarizing the particle in the process. In insulating materials, charges, either on the atomic or molecular scale, move from their equilibrium positions and give the material positive and negative regions along its surface, however the particle's overall charge remains neutral.

The response of a nonconductor (also referred to as a dielectric) to an electric field is given by its dielectric constant, which is the ratio of a material's permeability to electric fields to the permeability of a vacuum. This is a measure of a material's ability to reduce the strength of an applied electric field, relative to that field's strength in a vacuum, by storing the field's energy in distorting its own electronic structure. This energy storage property of dielectrics has long been used to produce capacitors in electrical circuits.

An electric field can disturb the shape of electron orbitals around atoms, or reorient molecules with permanent dipole moments, which can produce a dipole moment within a material. Other mechanisms can produce dipole moments and several of these are depicted in Figure 1.5 and can produce a wide range of dielectric properties [74]. A material's dielectric constant can range from about 1 for air to about 80 for pure water, to

over 1000 for high dielectric constant materials. These mechanisms cannot react instantaneously to changes in the electric field. In high frequency electric fields most material's dielectric constant becomes frequency dependent.

The force acting on dielectric particles is given by:

$$F_d = q E + (\bar{m}\nabla)E + \frac{1}{6}\nabla(\bar{Q}:\nabla E) + \dots$$
Eq. 1.4

Where the first term is Coulombs law. The motion of charged particles due to an electric field is described as electrophoretic, while dielectrophoresis (DEP) describes the movement of polarized particles [75, 76]. The higher order terms are known as DEP forces and include the interactions of a particle's dipole (second term) and quadrapole (third term) in nonuniform electric fields. In some applications it is necessary to consider the quadrapole interactions, however, in most cases assuming only dipolar interactions is sufficient [77].

The force exerted on a polarized particle in an electric field is analogous to the forces acting on magnets (which are always dipolar) in a magnetic field. In a nonuniform field one side of a particle is subjected to a more intense electric field than the other, as shown in Figure 1.6, and therefore feels a force in the direction of the converging field. The direction of the field (whether positive or negative charges are present) does not affect the motion of the particles; only the direction of increasing field intensity determines the direction of the DEP force. This allows both AC and DC fields to be used to control the motion of particles [75].

A material's dielectric response to an electric field can be time dependent and varies with the frequency of an applied electric field, especially so at high frequencies. The time averaged force acting on a particle due to dipole interactions was first described by Pohl [75]:

$$\langle F_d \rangle = 2\pi \varepsilon_m r^3 [\operatorname{Re}(K(\omega)) \nabla E^2]$$
 Eq. 1.5

Here ε_m is the dielectric constant of the medium surrounding the particle, ω is the frequency at which the electric field oscillates and K(ω) is the Clausius-Mossotti factor, which in turn is given by:

$$K(\omega) = \frac{\varepsilon_p^*(\omega) - \varepsilon_m^*(\omega)}{\varepsilon_p^*(\omega) + 2\varepsilon_m^*(\omega)}$$
Eq. 1.6

And here ε_p^* and ε_m^* are the complex dielectric constants of the particle and medium respectively. It should be noted that if the surrounding medium's dielectric constant is larger that of a particle's suspended within it, then that particle will be repelled from converging electric fields instead of attracted. By varying the electric field frequency the DEP force can be made positive or negative allowing particles to be attracted to electrodes or repelled.

This frequency dependence on the direction of DEP forces has been utilized to both manipulate and separate particles, especially biological particles such as cells [78, 79]. It has been used for both the separation of living and dead cells, as well as cancerous cells from healthy ones [80, 81]. DEP is also being studied for its ability to separate micro and nano-sized particles [78]. The ability to manipulate individual particles on these small scales has also attracted attention. These forces can be used to stretch, squeeze, rupture cell walls, or fuse cells together by applying sufficient force [82]. DEP has also been used to manipulate individual DNA molecules allowing them to be anchored to an electrode surface, stretched and then severed at specific locations [83]. While most applications of DEP have occurred on the small scale, Pohl and others have used DEP to separate large particles from suspensions in nonconducting fluids [84, 85, 86].

Strong, constant electric fields can be commonly found around many particle handling processes, especially when plastic equipment or containers are involved [44, 87]. It is entirely likely that particles in these situations will be affected by DEP forces, and DEP, much like other electrostatic effects, can lead to segregation and flow problems. Several reports in literature have described the agglomeration of particles while being subjected to high electric fields [3, 9, 61, 88], but thus far it is unclear what forces have caused these behaviors. Johnson and Melcher reported that chains of particles formed in a fluidized bed after a large electric field was applied [9]. Using this electric field they were able to "freeze" the fluidized bed. Others have used high electric fields to control particle flows [3, 88] and prevent particle segregation [61]. There has been surprisingly little research performed on the effect of these forces on macroscopic granular behavior, in spite of the flow problems and segregation that could be produced by DEP near charged surfaces and the possible applications of DEP for controlling particle behavior. The effect of DEP on particle flows is examined in more detail in chapter 4 with the hope that flow problems caused by DEP can be more easily identified and that DEP may eventually prove itself useful for bulk particle handling applications.

1.4 Figures for Chapter 1



Figure 1.1 a) An example of the Brazil nut effect. After vibration the larger particles rise to the surface. (Source: Breau et al, Phys. Rev. Lett., 2003.) b) The segregation of materials after pouring. The red particles are able to roll farther than the blue particles and form these stripes. (Source: Makse et al., Nature, 1995.) c) The segregation of red and blue art sand due to electrostatics after charging by flowing down a Teflon sheet.



Figure 1.2 Flow instabilities. a) A regular pattern of bumps in the surface of sand flowing down an inclined plane. (picture provided by Dr. Y. Forterre.) The patterns are created by vortices in the flow. b) Chevron patterns occur in smoothed bottom chutes near the outer walls. These patterns are believed to be created by vortices induced by granular heating at the walls. c) Cellulose adhered to the end of a charged plastic rod. This is an example of the ability of electrostatics to agglomerate particles. d) Sand particles flowing from a steel hopper and onto a plastic sheet. As the sand, hopper and sheet charge the sand adheres to the hopper and affects the flow of the material.



Figure 1.3 An example of electrostatic field lines and equipotential surfaces for a system of two oppositely charged particles.



Figure 1.4 The movement of electrons during the contact charging of conductors. Here Φ is the metal's work function. The electrons in two conductor's conduction band are represented as being within energy wells surrounded by potential energy barriers. Conductor 1 has a higher Fermi level (smaller work function) than conductor 2, and therefore electrons in conductor 1 have a higher potential energy than conductor 2. When the metals come into contact electrons flow from 1 into 2, increasing the Fermi level of 2 as well as setting up an electric field, which raises the potential energy of 2. When the conductors' Fermi levels become equal the flow of electrons stop.



Figure 1.5 Polarization mechanisms. Figures on the right: no electric field, on the left: with an electric field. a) Electronic polarization, where the electrons around individual atoms or molecules are moved, on average, away from the nucleus producing a dipole moment. b) Atomic (or ionic) polarization which occurs when charged atoms are displaced relative to each other producing polarization. c) Interfacial polarization where mobile charge carriers travel through a material until they are blocked by an interface. d) Orientational polarization occurs in materials with permanent molecular dipole moments that are free to rotate. In an electric field the material's dipole moments become aligned giving the entire material a dipole moment.



Figure 1.6 In a nonuniform electric field the net force on an uncharged particle is in the direction of increasing electric field strength. One side of the particle is contacted by a higher density of field lines than the other and therefore experiences a net force.

Chapter 2 Instabilities in granular chute flow with and without electrostatics

Granular material flow instabilities, with and without electrostatics must be understood before any theory of granular behavior can be considered complete. Flow instabilities are a window into the inner physics of flowing materials. From the behaviors generated under various conditions the mechanisms behind all flowing behavior can be examined, tested and deduced [1]. In addition, most industrial granular flows are unsteady and spatially inhomogeneous and are subject to flow instabilities. Here we build on previous work [89] by studying the effect of flow instabilities on the movement of grains in a prototypical geometry, namely flow down inclined planes, and how electrostatic forces produce previously unreported instabilities.

2.1 Chute flow

Chutes and inclined planes are commonly used, both for the study of granular flow and throughout industry to transport grains. Many of the behaviors of these systems are also observed in geological avalanching flows. Convection within granular chute flows was first described by Savage [90] for chutes with roughened surfaces. Others have since widely studied the instabilities produced by flowing granular materials in chutes [50, 52] as well as other systems [49], observing many behaviors that are analogous to instabilities found in fluids [49, 50, 91], including the formation of shockwaves around obstacles [92] as well as novel instabilities [46, 47, 48] without direct analogy.

Some of the most fascinating flow behaviors observed in chute flow, already mentioned in section 1.1.4, have only been identified in the last 10 years. The longitudinal vortices and the chevrons, reported by Forterre et al. [50] and Conway et al. [52] respectively, have shown that complicated flow structures can be spontaneously created in granular flows. These convective flow patterns may have several analogous patterns observed in fluids.

The experiments and analysis of longitudinal and other vortices, which appear in wide, rough-bottomed chutes, by Forterre and Pouliquen [50], have advanced our understanding of complex internal flows. These vortices are orientated parallel to the mean flow direction and transport grains between the base of the chute and the free surface. Forterre and Pouliquen proposed that the rough surface of the chute caused particles near the bottom of the flow to be agitated by frequent collisions, and thereby to generate an increased local granular temperature and a decreased local density. Using kinetic theory modeling, Forterre and Pouliquen [51] further showed that chute flow on rough bottoms could indeed become unstable to transverse perturbations and would produce counter-rotating vortices.

Chevrons, a pattern first observed by Conway et al. [52], appear to be created by shear induced vortical flow that occurs along chute boundaries. These patterns consisting of Λ -shaped surface waves, surprisingly oriented against the flow. They occur at low inclination angles, near the angle of repose, and consist of two distinct patterns. The chevrons that appear at higher inclination angles, type A, occur with a greater frequency and a larger angle with respect to the chute walls than type B chevrons. Figure 2.1 presents examples of A and B chevrons. These patterns may represent a granular analog with boundary layer effects within fluids [53].

These instabilities, while not created by electrostatic forces, are worth further exploration before the added complexities of electrostatics are considered. In this way the effects of electrostatics can be more easily differentiated from other granular behavior. These patterns, as well as others, have been examined with a cellular automata model.

2. 2 Cellular automata for free surface granular flows

Cellular automata (CA) models are based on simple rules that govern the interactions of neighboring cells. These models have been applied to a variety of complex systems including those involved in turbulence, combustion, and bacterial growth [93, 94]. In the granular flow literature, cellular automata have also had a long history, including applications to avalanches [95, 96], sand pile creation [97], jamming [98], flow from a hopper [99, 100], the segregation of particles in rotating drums [101,

102], and other problems. Examples of simple CA models for both flow from a hopper and segregation in a rotating horizontal drum have been given by Savage [103]. As stated by Baxter and Behringer [99], cellular automata models have important advantages over the more widely used continuum and discrete element methods. Continuum models are limited to systems with both simple geometries and spherical particles. In addition to this, the constitutive relations for continuum models, which are necessary for accurate simulations, are still being developed. As for discrete element methods, they are limited by the computational cost of tracking large numbers of particles. Recent work by Bazant [104] has tried to address the computational limitations of DEM while still capturing the important physics through a "spot model". The number of particles that would be required to accurately simulate a 3-dimensional flowing chute for an extended time is, presently, too computationally expensive to be attempted with DEM. A review of the many methods for modeling granular materials was recently written by Herrmann and Luding [105]. While there are limits to the predictive capabilities of CA models, they are much faster than alternatives, allowing larger and more complex systems to be studied.

A promising development in the modeling of granular beds was introduced in 1994 by a collaboration of authors with the acronym: BCRE [106]. The BCRE model defines an interface between a flowing layer of grains and a solidified bed beneath, and permits the interface to move up or down so as to account for material transfer between the flowing and static regions. The BCRE model has great potential to permit the future analysis of flow transitions, but in its present form is limited insofar as it does not predict the rich variety of behaviors seen in flowing granular beds.

2.2.1 Model details

In this section, we describe a CA that is motivated by the BCRE model, which permits an interface between a surface flowing layer of grains and a solidified bed beneath to move up or down so as to account for material transfer between flowing and static regions. Correspondingly, we construct our CA by permitting 'material' above an interface to flow downhill, and constraining material beneath the interface to remain fixed in place. The interface itself evolves dynamically according to prescribed rules – essentially, if the free surface of the simulated granular bed is steep the interface will submerge (causing more material to flow), until the surface slope lessens, at which point the interface will rise (reducing or even halting the flow).

In detail, the chute is modeled as a discrete grid of points in X and Y, each with a continuous height, Z(X,Y). Flow of material is simulated by transferring a quantity $\Delta Z(X,Y)$ in a downhill direction, where downhill is determined by a calculation of the gradient of Z. The gradient is calculated in the X-direction at the grid locations (X_i, Y_j) so that it always points downhill:

$$\nabla_{i,j}^{X} = \left(Z_{i,j} - Z_{i-1,j} \right) \text{ if } Z_{i-1,j} < Z_{i,j}, \text{ or}$$

$$\nabla_{i,j}^{X} = \left(Z_{i,j} - Z_{i+1,j} \right) \text{ if } Z_{i+1,j} < Z_{i,j}.$$
Eq. 2.1a

Similarly in the Y-direction:

$$\nabla_{i,j}^{Y} = \left(Z_{i,j} - Z_{i,j-1} \right) \text{ if } Z_{i,j-1} < Z_{i,j}, \text{ or}$$

$$\nabla_{i,j}^{Y} = \left(Z_{i,j} - Z_{i,j+1} \right) \text{ if } Z_{i,j+1} < Z_{i,j}.$$
Eq. 2.1b

If (X_i, Y_j) is a local maximum, the larger slope is chosen; if it is a local minimum or if both slopes happen to be the same, one is chosen at random.

At each time step an amount of height, ΔZ , proportional to the slope is removed from a point and the same ΔZ is added to the height of another point downhill a distance, again, proportional to the slope. In this way, the CA explicitly conserves volume: every quantity of material removed from one location is deposited in another, downhill, location.

$$Z_{i,j} \rightarrow Z_{i,j} - \alpha \left(\nabla_{ij}^{X} + \nabla_{ij}^{Y} \right) \text{ and}$$

$$Z_{i+k^{X},j+k^{Y}} \rightarrow Z_{i+k^{X},j+k^{Y}} + \alpha \left(\nabla_{ij}^{X} + \nabla_{ij}^{Y} \right)$$

Eq. 2.2

The distances, k^X and k^Y , at which material is deposited are calculated to again be proportional to the local gradient:

$$k^{X} = k_{ij}^{X} = int(\beta \nabla_{ij}^{X})$$

$$k^{Y} = k_{ij}^{Y} = int(\beta \nabla_{ij}^{Y})^{2}$$

Eq. 2.3

In these equations, α and β are constants: α defines how thick the flowing layer will be, and β defines how far it will travel per unit time (i.e. its velocity). A schematic of this process is shown in Figure 2.2.

We note that k^X and k^Y are necessarily integers, since the model surface is only defined at discrete X and Y gridpoints, so if k^X or k^Y is less than the grid spacing, no

material will be transported in the corresponding direction. Thus the simulation provides an angle of repose, or gradient, below which flow will stop: this repose angle is defined such that whenever the total slope $\nabla_{i,j}^{X} + \nabla_{i,j}^{Y}$ decreases below 1/ β , flow stops. This is illustrated in Figure 2.3, where we show the outcome of a simulation beginning with a sum of 5 random Fourier terms (i.e. sinusoidal shapes of random amplitude) in X and Y directions. Initially, some surface gradients, ∇ , exceeded the angle of repose specified above, and so material (i.e. surface height) was transported to fill valleys downhill until the angle of repose was no longer exceeded. Consequently, in the histogram shown beneath the surface plot in Figure 2.3, surface gradients reach a maximum critical amplitude; slopes below this amplitude are also present in valleys or near peaks. Parameter values used in this example are given in the figure caption.

In summary, this model prescribes simple flow in the spirit of the BCRE model: material beneath an interface (defined by $Z_{i,j} - \alpha(\nabla_{i,j}^{x} + \nabla_{i,j}^{y})$) is solid-like, while material above the interface travels with velocity $int(\beta \nabla_{i,j})$ per unit time. The model is easily embellished by including terms to simulate diffusive, viscous, boundary, and body force effects. We describe such embellishments next.

2.2.2 Diffusion

To include diffusive motion of particles – either due to collisional effects in the moving layer or random wandering of particles near the surface – we add white noise of

maximum amplitude δ to the gradient terms [107]. For either stalled or well developed flows, this typically has little effect; for near-critical flows (i.e. surfaces on the verge of motion as prescribed by Eq. 2.3), this causes small variations similar to the motion of a single particle. These variations are observed to trigger subsequent avalanches of either small or large extent, depending on the states of nearby slopes [108].

2.2.3 Viscosity

Viscous memory can be added to the model by retaining a fraction of a point's previous velocity for the next time step. This is done by modifying Eq. 2.1 as follows:

$$\begin{split} \tilde{\nabla}_{i,j}^{X} &= \nabla_{i,j}^{X} + (1 - \nu) \nabla_{-i,j}^{X} \\ \tilde{\nabla}_{i,j}^{Y} &= \nabla_{i,j}^{Y} + (1 - \nu) \nabla_{-i,j}^{Y} \end{split}$$
 Eq. 2.4

Here, $\widetilde{\nabla}$ is the gradient corrected to include viscosity, v, and ∇ . is the slope from the previous time step. The coefficient v represents the effective viscosity and is chosen on [0,1]: for small v, the speed increases as the bed travels down hill, and when v approaches 1, the bed responds only to the current slope. These two limits approximate the behaviors seen respectively in spherical beads with few collisions that can continually accelerate as they travel down a chute [109] and in small highly dissipative grains that rapidly acquire a terminal velocity [90].

2.2.4 Boundary conditions

The simplest boundary conditions that one can apply are periodic: thus in Figure 2.3, all gradients and flows that travel off the rightmost edge of the simulation domain are calculated to continue at the leftmost edge, and similarly in front and back. Practical problems are not periodic, however, and so realistic boundary conditions are needed. Boundary conditions in granular systems are notoriously problematic [110, 111]. For the X-direction boundary condition a simple choice could be no-flux, and this can be specified by fixing gradients transverse to a wall to be zero, thus preventing any flow toward or away from a boundary. On the other hand, stress-free conditions in the cross-stream direction are approximated by reflecting any bed material leaving the domain, say in the +X direction, back an equal distance in the -X direction. The no-flux and no-stress conditions are appropriate for many cross-stream flows, but are not typically suitable in the streamwise direction, especially when convective, frictional or other influences occur near boundaries. Therefore we have included a variety of boundary alternatives in the CA (examples of some of these alternatives are shown in subsequent sections).

Taking Y to be the down-stream coordinate, we can apply a fixed frictional momentum flux at the walls by decreasing the calculated slope at the wall in the Y direction. This changes both the quantity (from Eq. 2.2) and the speed (from Eq. 2.3) at which material travels down-stream near the boundaries.

The boundary condition at the upstream and down-stream ends of the simulation can be set to several possible geometries to approximate the conditions seen in experiments. Thus a continual inflow can be specified by setting the gradient in the Ydirection at the upstream end of the geometry of interest to be a fixed positive value. Similarly, a continual outflow can be specified at the bottom of the chute by fixing the gradient in the Y-direction there to be another fixed value. Alternatively, free outflow can be chosen by setting the height at the end of the computational domain to a value such that to entire last row of the chute it will appear that the next point is at a height lower that itself. This allows material to fall off of a simulated chute or similar geometry without slowing down and impeding the flow behind it.

2.2.5 Vortices

For boundary conditions on the underside of a granular bed, we again provide alternative formulations. To model a smooth bottomed surface, the slope is calculated and the height is moved in the direction of steepest downward slope as specified in Eq.'s 2.1-2.3. Rough-bottomed chutes, on the other hand, are recognized to produce granular "heating" (an increase in mean fluctuational velocities) as grains collide with surface asperities [50], which then lead to the formation of three-dimensional (3D) vortices that transport high temperature grains to the surface while submerging lower temperature grains as the material flows down hill. In this 2-dimensional model 3D vortices cannot be captured. However, it is of interest to see if changes in the governing rules in the cross-stream direction can capture the basic features of such a circulation. In the experiments it is observed that material circulates from the base to the crests and back to

the base and adjacent vortices rotate in opposite directions. This leads to crests (troughs) where a pair of vortices forces materials away from (towards) the base. From the point of view of the surface, material seems to disappear from the troughs and reappear at the crests. It is of interest to add a rule to approximate this movement of material on the surface in the cross-stream direction. This can be accomplished by changing the signs of the gradients defined in Eq. 2.1a. While this is an oversimplification of the mechanics of the vortex process, it has the virtue of capturing the qualitative kinetics needed to provoke a cross-stream instability in an algorithmically facile manner. Using this simple change in one rule allows us to turn cross-stream instabilities on or off. This has the effect of destabilizing cross-flows in a manner that is similar to that seen in experiments [50]: we discuss this case in a later section.

2.2.6 Body forces

The CA that we have described can accommodate body forces in a straightforward manner. Simple inclines can be defined by adding a constant term to the gradient in a prescribed direction. Thus to simulate an incline in the Y-direction by an angle 9, we could add a constant proportional to $g_0 = g \cdot \sin(9)$ to Eq. 2.1b. Inclines can also be modeled by setting a base height along the chute such that a constant gradient is created in the down-stream direction. The material then simply travels downhill according to the algorithm already presented. Electrostatic forces would prove difficult

to add, however, as individual grains are not present in this model, making the form of attractive and repulsive body forces unclear.

2.2.7 Chute inclination

To compare the angle of inclination of both model and experimental chutes we define the parameter ϕ , which is the ratio of the chute inclination to the angle at which the flow stalls. This allows us to compare the chute inclinations where various phenomena are observed relative to a common endpoint (e.g. the angle at which motion stops) in both experiments and the CA model.

2.3 Flow down a smooth-bottomed incline

The simplest situation that one would want to be able to model correctly is flow down a smooth chute without boundaries. This is a problem that has been well studied both experimentally and analytically [112, 113, 114]. We begin by examining two configurations that have previously been studied experimentally: first, flow down a featureless inclined chute, and second, flow down an inclined chute past a single triangular obstacle.

2.3.1 Flow at increasing inclinations

By changing the angle of inclination in the CA model, several states can be produced, as shown in Figure 2.4. These results have been observed using both methods described in previous sections to produce an incline. All other cases reported here use only the base height to produce an incline. For small inclination angles, the flow reaches the angle of repose and stops flowing. Once the angle of the chute reaches a critical angle, material begins to flow in a nearly steady fashion, with only small height fluctuations provided by the small diffusive term described previously; parameter values used are defined in the figure caption.

As the effective inclination (i.e. g_o) is increased, ripples appear on the free surface as shown in Figure 2.4(b). These ripples are nearly stationary in the Y-direction, but at still higher g_o , the ripples grow and travel uphill (i.e. to the left, in the –Y-direction). This is in agreement with observations of granular flows [115], and the mechanism for this has been long understood to be as follows [106]. Once a small bump appears on a smooth surface, material from uphill collides with the bump and slows. When this material reaches the trailing edge of the bump, it accelerates again under the influence of gravity, but not before more material has been accreted onto the leading, uphill, edge of the bump. If the mass flow rate of grains is small enough, the slowed material will have time to accelerate before more material arrives from uphill: in this case, the bump will flow downhill and diminish. On the other hand, if the incoming mass flow is above a critical threshold, more material will arrive from above than will be depleted from below, and the bump will move uphill and grow. This behavior is known to be associated with shock formation [116] and is reproduced in our CA model as a natural consequence of the explicit mass conservation specified by Eq. 2.1 combined with the flow models of Eq. 2.1 & 2.3. We emphasize that this behavior is merely an elementary consequence of mass conservation, and does not imply that the CA model correctly approximates momentum conservation of granular flows.

2.3.2 Flow past an obstacle

Granular flow past obstacles has been studied using a variety of approaches. Rericha et al. [92] studied two-dimensional shockwaves past wedges using experiments, molecular dynamics simulations, and a continuum model. In that work, it was reported that shocks form at the leading edge of the wedge and an expansion fan forms at its base. Experimental examples of these features can be seen in Figure 2.5(a). Gray et al. [117] used pyramids to study supersonic avalanches around proposed barriers to rock slides and snow avalanches. In that work, experiments were compared with a simple hydraulic theory, using both forward- and backward-facing pyramids. Caram & Hong [118], by comparison, showed that simple random flow on a discrete lattice results in good agreement with experiments of granular flows past an obstacle.

In light of this pre-existing work, flow past an obstacle seems an appropriate candidate against which to test our CA model. Figure 2.5(b) shows the flow of material

around a triangular wedge. The flow contains both a bow wave at the top of the wedge and an expansion fan at the base. Similarly when a pyramidal shape was placed into the flow similar shockwaves to those of Gray et al. [117] were observed. These shockwaves can be seen in Figure 2.6.

As shown in Figure 2.5(b) the shock produced by the model is detached from the wedge. Waves can also be seen in the shock, which are marked with arrows in that figure. To the best of our knowledge these features have not been reported before in the literature on free surface granular flow around obstacles. However, when experiments were performed in our laboratory, similar detached shocks were observed, as can be seen in Figure 2.5(a). These shock waves are also detached from the obstacle and include internal waves propagating from the surface of the obstacle.

The experimental setup was similar to that of Conway et al. [52], consisting of an inclined acrylic sheet fed by a metal hopper. The chute was coated with an anti-static spray coating (Kensington Dust Guard) to prevent electrostatic charging. Sand with a diameter of $250\pm50 \ \mu m$ was poured down the chute from the hopper. A wooden wedge was used as the obstacle, and was fixed to the center of the chute.

The detached shock wave and the waves within the shock were only seen at transitional flow speeds. The model displays subsonic behavior at low ϕ (below 1.08), which is followed by this translational behavior as ϕ is increased. At higher ϕ (above 1.13), the shockwaves are no longer detached from the wedge. We have confirmed that this behavior is also found in experiments. Below roughly $\phi = 1.14$ the flow is subsonic; above about 1.32 the flow appears to be supersonic (e.g. has upward traveling shocks),

and between these points the behavior of the flow seems similar to the transitional behavior of the CA model.

2.4 Flow on a rough chute without sidewalls

A more complex flow recently described in wide, rough-bottomed chutes by Forterre and Pouliquen [50] consists of long streamwise undulations on the surface of the flow. The authors provide convincing evidence that the patterns they observe, which they refer to as longitudinal vortices, are created by granular heating at the rough surface. As the bed of grains travels down the chute, the velocities of those grains near the rough surface are randomized, leading to an increase in the granular temperature and a decrease in its density. This leads to a density inversion, in which a dense region sits on top of a less dense layer. This situation is unstable and causes the creation of longitudinal vortices. In order to model these 3-dimensional vortices, the CA requires a similar unstable configuration. As described previously, this is accomplished by changing the sign of the gradient in Eq. 2.1a.

When many vortices are nucleated on the chute at the same time, they produce straight regularly spaced stripes. This nucleation can be accomplished by adding a random factor to the velocities of the flowing height for a number of iterations. This is similar to the randomizing effect of a rough-bottomed chute. Indeed, adding a random factor to the minimum chute height, or a random entrance boundary condition has a similar effect. The surface shapes thus produced are shown in Figure 2.7, and seem to outwardly resemble the longitudinal vortices reported by Forterre and Pouliquen [50].

The velocity profiles of the experiments and model can be compared in greater detail. By averaging the distance material travels every timestep along each streamwise column of grid points, a velocity profile can be obtained. Like the velocity profile reported by Forterre and Pouliquen, the streamwise velocity obtained from our CA model is slowest in the crests of the vortices and fastest in the troughs (see Figure 2.7(c)). The velocity profiles are also similar in the cross-stream direction. As one expects for a vortical flow, the spanwise velocity vanishes at extrema of streamwise velocities. However, the direction of the flow is reversed in the CA model as a consequence of the algorithmic approximation, described previously, by which we generated the vortical instability. In experiments, material surfaces on the crests and is transported to the troughs where it is submerged and transferred back to the crests. In the CA model this transport is projected onto a 2-dimentional flow. Material is conveyed to the crests where it "jumps" and is carried to the troughs. This leads to a reversal in the directions of the velocity in the cross-stream direction.

2.5 Flow on a smooth chute with rough sidewalls

Chevrons have also been studied using this CA model. Like the longitudinal vortices the instabilities must be nucleated: in this case they are nucleated at the wall of the chute by creating disturbances in the amount of material near the wall. A no slip

condition is also set at the edge of the chute. These disturbances perturb the unstable bed and lead to the formation of vortices that behave, at least qualitatively, in much the same way as experimentally observed chevrons, as can be seen in Figure 2.8.

It has been proposed [52] that granular heating occurs at the walls and this creates vortices. The original chevron experiments [52] also reported streamwise circulatory flow in which grains beneath the surface flow away from the walls. We point out that the source of the orientation of experimental chevrons remains unclear. That is, if a vortical disturbance similar to that seen in Figure 2.8 were produced near the sidewalls of a chute, one would naively expect any incipient vortices to be dragged downhill by the faster flow nearer the chute center. This would produce downward, V-shaped, chevrons, rather than the upward, Λ -shaped, ones that actually appear. It is therefore somewhat surprising that CA reproduces the correct chevron orientation, against simple heuristic expectations.

The dynamic behavior of the chevrons is at least qualitatively reproduced in the simulations. It was observed that both the angle of the each chevron to the wall decreased over time and the distance between each chevron and the edge of the chute *increased* over time. The ultimate result of these combined effects is that convection rolls begin, close to the side of the chute, at a large angle, and move away from the wall, while approaching a parallel orientation to the wall. This behavior has been observed in both simulations and experiments. A comparison between time elapsed snapshots from both simulations and experiments is shown in Figure 2.9.

2.6 Other phenomena

This cellular automata model also seems to recreate other patterns observed in experiments. Forterre and Pouliquen [51] have reported "scales" which appear in roughbottomed chutes at high angles (52°). Similar structures form at high chute angles in the model. There is not a great deal of information available on these experimental structures. However, in both experiment and simulation the structures tend to align themselves in both a streamwise and cross-stream lattice as can be seen in Figure 2.10.

2.7 Model limitations

These simulations are limited by the 2-dimensional nature of the calculations and a difficulty in determining a priori values for the physical parameters used. For example, the application of too much dissipation can lead to a state with no instabilities or to a frozen state. Too little dissipation results in patterns persisting in the model that would otherwise die out or in the entire flow becoming unstable. Also as a 2D surface model, several important factors in the flow of granular materials cannot be examined. The velocity profile of the material below the surface cannot be captured. Thus the model cannot distinguish between flows down inclined planes - where the entire bed is in motion - and flows down piles of grains - where only the uppermost layers of grains are in motion. While this simple model produces features that appear similar to some of the experimental patterns seen in chute flow, there are some important shortcomings that should be emphasized. Foremost, the CA model is only an approximate treatment and cannot be used to make accurate quantitative predictions using physical parameter values. Additionally, the model only provides a 2-dimensional representation of 3-dimensional phenomena. More careful scrutiny reveals additional differences between experiment and simulation. For example, as can be seen in Figure 2.8, the chevrons in the model have sharper peaks than the experiments. This is due to issues associated with the choice of a value for dissipation in the model. This problem also plays a role in the long-term behavior of the model chevrons. In experiments, as the chevrons move toward the center of the chute they transport material and deposit it at the point at which they are subsumed. Due to the difficulties in choosing an appropriate value for the dissipation, at higher inclination angles, the vortices do not die out as they leave the edge of the chute, but instead join together and persist for long times.

In further detail still, experimentally two types of chevrons have been observed, referred to as A and B chevrons [52]. In the model only one type of chevron is created. The mechanism that produces the A and B chevrons in the experiments at different chute angles is evidently not included in the cellular automata rules chosen for this model. Also, in experiments chevrons and the longitudinal vortices of Pouliquen and Forterre are seen at very different chute angles. The chevrons are only seen for very low angles (about 25°) while the longitudinal vortices are seen at higher angles (about 40°) [51]. This discrepancy is not surprising considering the fact that the model produces vortices

regardless of the granular temperature, whereas in the experiments it is the difference in granular temperature that drives the vortices.

For each flow feature modeled, boundary conditions or flow rules must be adjusted, especially when changing from smooth flow to the unstable flow of the density inversion patterns. Ideally a model with one set of flow rules would be able to capture all of these behaviors. Perhaps a three dimensional CA model may have more success in that regard. Nevertheless, this simple 2D model seems to capture qualitative experimental features quickly and efficiently and fuel the debate on which boundary conditions and dissipation rates are appropriate for the wide range of granular behaviors currently being explored.

While granular materials have proven exceptionally difficult to model using convention methods, such as continuum methods, it is possible that models based on CA may prove effective at probing the inner workings of granular flows. If even the limited capabilities of this simple model, which is based primarily on conservation of volume, are able to, at least qualitatively, capture the behavior of granular instabilities, perhaps new and more complete methods may succeed in developing quantitative predictions. However these models will also need to take electrostatic charging into account, as we will see in the next section electrostatics can destabilize granular flow producing new and complicated patterns.

2.8 Electrostatic effects and flow instabilities

Throughout the experiments performed thus far, a metal sheet was inserted on the bottom of the acrylic chute and anti-static spray (Kensington Dust Guard), was applied to the chute to minimize particle charging and ensure the observed effects were not electrostatic in origin. It was found that when charging did occur the electrostatic effects altered the behavior of the chute flow producing new patterns. When the metal sheet was removed, along with the antistatic spray, the flow became erratic and occasionally produced odd intersecting grooves within the flow, an example of which can be seen in Figure 2.11. When the humidity was decreased the electrostatic effects on the flow of grains became much more pronounced.

2.9 Razorbacks

In lower humidity conditions (~20% rather than ~50%) the flow produces jagged clusters of grains along the edges of the flow (see Figure 2.12(a) and (b)). To view these clusters in more detail the walled chute was replaced with a flat sheet of acrylic. Art sand (mean diameter $250\pm50 \ \mu\text{m}$) was allowed to flow down the inclined acrylic sheet from a steel hopper suspended 5 cm from the surface of the sheet. As the sand grains flow down the inclined plane, they coalesce into small jagged clusters, which remain intact as they flow downstream. Large clusters collect at the edge of the flow and have been given the name "Razorbacks" for their thin and sharp appearance, as well as the similarity of their

appearance (Figure 2.13) to Martian geological features with the same name [8, 119]. Razorbacks are often created when one of the flowing clusters lodges at the edge of the flow. In Figure 2.14 clusters of grains can be seen flowing down the center of the sheet, while larger razorbacks line the edges of the flow. Razorback formation is most marked near the outlet of the hopper although as shown in Figure 2.12, they can be present all the way down the acrylic sheet. Occasionally, clusters of particles are ejected from the bed of sand at high velocities and land several meters away. In Figure 2.15(a) and (b), particles can be seen flying off of the surface of the bed. Some razorbacks are created and grow when these flying particles land and adhere by the edge of the flow. An example of a cluster of grains jumping from one razorback to another can be seen in Figure 2.16.

We hypothesize that these razorbacks spontaneously form due to the increase in the electric field intensity in the vicinity of the peaks. The motivation for this proposition is straightforward: once a small sharp peak of charged grains appears on a surface, the electric field intensity grows dramatically in the vicinity of the peak [120] – and consequently, charged grains passing by the peak will be locally attracted or repelled, depending on their own charge distribution [62].

To confirm the hypothesis that these razorbacks form by accretion of tribocharged grains onto the sharpest nearby points, we have performed tests in the presence of a commercial static eliminator (Westmont, Inc., Minerva, OH), consisting of fine carbon fibers attached to a grounded metal strip. Results of these tests, taken with the acrylic sheet at an incline of $31\pm1^{\circ}$ and at $15\pm2\%$ relative humidity, are shown in Figure 2.17. In the plot, we display the standard error of the local slope of razorbacks in images taken

from the side as a function of height of the eliminator. When the static eliminator is fixed in place near the flowing surface, a smooth wake forms downstream of the flow inlet, but no sharp boundaries are created. This can be seen in the lower left inset of Figure 2.17 which shows a raised wake about 15 cm downstream of the flow inlet for an eliminator fixed about 25 cm above the flowing surface. As the distance from the flowing surface to the eliminator is increased, jagged razorbacks appear, and the magnitude of the local slope at the granular surface measured from snapshots increases correspondingly. In the upper right inset, an example is shown of the sharp and jagged razorbacks that form on top of the wake, again 15 cm downstream of the flow inlet, when the eliminator is far from the flowing surface. These experiments demonstrate that both the slope at the edges of the flow and its standard error grow significantly as the static eliminator recedes.

We emphasize that it is an elementary result from electrostatics that clusters and filaments cannot be held together by a uniform charge, which would cause component particles to repel one another. Instead, charges must be strongly heterogeneously distributed. We confirm that this is in fact the case by measuring the net charge on grains that leave the chute at its downstream end. We do this in two ways. First, we wait until a steady state pattern is formed and then collect grains from the outlet of the chute in an insulating container, and pour the grains into a steel "Faraday cup" connected to a calibrated electrometer (Keithley Instruments model 610CR), which provides a charge measurement. By weighing the cup (minus tare), we obtain the mean charge per unit mass on the grains. We repeat these experiments at least 3 times with the static eliminator held at each of several fixed distances from the flowing grains, and we have confirmed separately that measured charges do not change significantly if the collecting

cup is located at the lateral center of the outflow or is moved spanwise to the edges of the flow. This first method of measurement could potentially introduce spurious charges during transfer of grains from the collecting cup to the Faraday cup, so in a second set of experiments, we collect all of the grains that fall from the chute in a large steel Faraday cup after the razorbacks have reached steady state, emptying and discharging the cup between each trial. Again, we reproduce the experiments at least 3 times for each of multiple positions of the static eliminator. The order in which the experiments were carried out was randomized, so that effects due to the order in which the height of the static eliminator was set could be discounted. The results of both methods are shown in Figure 2.18.

From this plot, we find that the net charge per unit mass ranges up to about $\sigma_{max} =$ 13 nC/g. We can estimate the order of the electrostatic force associated with this charge by approximating grains as being spherical with radius r = 0.01 cm (the mean radius of our grains), of density $\rho = 2.5$ g/cc (their approximate material density). Therefore the particles have a charge of approximately q = $(4\pi/3r^3\rho\cdot\sigma_{max} = 1.4x10^{-4} \text{ nC})$. Two such grains in contact with identical charges concentrated at their centers would be mutually repelled with force F₁ = $4x10^{-9}$ N. This force is to be compared with the weight of a grain, which is about 10^{-7} N. Evidently in our experiments homogeneously distributed charges generate about two orders of magnitude too little force to significantly perturb the inertial motions of grains.

While our flowing bed of grains undoubtedly generates higher fields collectively, this first order calculation suggests that something more than naïve considerations must be at work. Also in support of this conclusion, Figure 2.18 shows that the presence of a static eliminator actually *increases* the charge of the grains; furthermore the observed fact is that clusters of grains levitate and cling tenaciously together in the absence of a static eliminator, yet flow smoothly in its presence. These facts are all inconsistent with a hypothesis that grains in our simple experiments homogeneously charge. Rather, the experimental observations support the conclusion that grains predominantly charge heterogeneously, likely in dipolar or higher multipolar arrangements. We conclude that charge measurements, though superficially paradoxical in that net charges on grains <u>increase</u> in the presence of a static eliminator, are actually consistent with the observations that grains cluster together – which they manifestly would not do if they were identically and uniformly charged.

2.10 Charge distribution

A heterogeneous charge distribution amongst the grains may have profound implications for granular behaviors. Several experimenters have found that materials develop broad heterogeneous charge distributions when fluidized or transported pneumatically [121, 122]. Polydisperse mixtures of particles are especially known for their tendency to develop different charge polarities on particles of different sizes. The ability of even a simple flow of grains to produce a complicated charge distribution, and its implications for granular behavior, is investigated in more detail in chapter 3.
2.11 Effect of the electric field

During the razorback experiments just described, the acrylic sheet itself builds up a considerable charge. This can be confirmed by passing a metal rod a few inches above the sheet following an experiment: the rod provokes the production of audible pops as the sheet discharges to the rod. The electric field produced by the highly charged acrylic sheet may be responsible for polarizing the sand particles and dielectrophoretic (DEP) forces could result in the attraction between grains producing the clusters. Mutual attraction between particles has been attributed to DEP even in uniform electric fields due to the warping of the electric field caused by the presences of the particles themselves [123]. However, we believe this is the first time DEP agglomeration has been suspected of causing flow instabilities in a commonly used granular transport method.

Some evidence pointing to one of the electrostatic mechanisms leading to the heterogeneous particle charges, whether bipolar charge distribution developed by tribocharging or induced polarization caused by the highly charged plastic sheet, can be obtained with a simple experiment. The same art sand used in the razorbacks experiments was placed on a Van de Graaff (VDG) static electricity generator. These simple generators produce extremely high voltages (~10⁵ V) by transferring charges from a brush at the generators base to a spherical shell using a rubber belt. While being somewhat more difficult to accurately control than other high voltage equipment the VDG has the advantage in that it can be used to produce high voltages with complete safety. The current generated by a VDG is limited, preventing serous injuries from occurring during an accidental contact with the generator. The voltage of the VDG was controlled by fixing a fine, grounded wire nearby the VDG. The wire acts as a corona

source, producing a current of ions that limits the voltage of the VDG. By moving the wire closer to or further from the VDG, its surface charge – and hence its voltage – can be regulated. The method for measuring the voltage of the VDG, utilizing several large resistors and an amp meter, is described in detail in chapter 4.

When the sand was placed in a pile on the VDG and the voltage was allowed to rise, the grains began to cluster and jump from the surface of the pile in large numbers. Examples of this process can be seen in Figure 2.19. The appearance of these clusters and their behavior is quite similar to that of the clusters observed alongside the flow down the acrylic sheet. Apparently tribocharging is not necessary to cause aligned clusters to form. This supports the proposition that the induced polarization of the sand grains by the strong electric fields of both the tribocharged acrylic sheet and the VDG results in the clustering and ejection of sand grains.

These experiments, while illuminating, are far from conclusive. However, it seems that DEP may play a larger role in granular behavior, at least under certain conditions, than has been previously recognized. The magnitude of DEP effects on granular flows compared to other electrostatic effects are investigated further in chapter 4.

2.12 Other patterns: running clusters

Other patterns related to electrostatics are also observed during and after the flow of sand down the chute. After the flow has come to a rest, clusters of grains are sometimes observed "running" down the chute. As can be seen in Figure 2.20, the clusters appear to be hopping from one protruding cluster of grains to the next as it travels downhill. Occasionally these runners come to a rest intact some distance from their starting point. Other times they "trip" and break apart as they hit the surface of the chute.

2.12.1 Indented circles and grooves

Occasionally features appear in the flow near the outlet of the hopper. Indented circles, which can be seen in Figure 2.21(a) and (b) appear suddenly and quickly flow down hill. They can appear alone or multiple circles can form in the same area in quick succession. The formation of the circles are often accompanied by audible pops. Another feature also forms near the outlet of the hopper can be seen in Figure 2.21(c) and (d). These grooves appear in the flow and tend to persist until the flow has ceased. The fact that these grooves and circles tend to form in the same area of the flow and both involve indentations in the flowing surface suggests that they are related phenomena, however, at this point in time we have not investigated the mechanism for their creation.

2.12.2 Segregation

Along with these new patterns, segregation of the flowing material was also observed. Blue art sand, which had been mixed with the white in small concentrations to act as tracer particles, began to segregate from the white by preferentially adhering to the outlet of the hopper. The segregated sand can be seen near the outlet of the hopper after the flow has come to a rest in Figure 2.22. The grains of both colors of sand are similar in size and shape and differ mainly in the compound used to color them. Evidently this is enough to allow the two types of particles to be segregated by electrostatic forces.

2.13 Conclusions for instabilities in granular flow

Instabilities in the flow of grains down an inclined plane, created by both electrostatic and non-electrostatic mechanisms, have been examined. A cellular automata model was created to investigate the behaviors of non-electrostatic instabilities. While only able to produce qualitative data the model was able to reproduce several features commonly observed in chute flow as well as patterns created by vortices within the flow. The simplicity and low computational cost of CA models, while currently lacking the predictive abilities of other modeling methods, make CA a potentially useful method for describing granular flow behavior, although more complex effects, such as electrostatics, must be incorporated before CA can be used in other applications.

The behaviors of the granular flow change dramatically when electrostatic effects are present. At higher humidities they cause the flow to become erratic and interrupt the behavior of other instabilities, such as chevrons. At lower humidities jagged clusters of sand grains were observed to spontaneously form during the flow of sand down an inclined acrylic sheet. Small clusters formed in the flow and traveled downhill. Other larger clusters formed at the sides of the flow, and then continued to increase in size during the flow of grains. These clusters did not form in the presence of a static eliminator even though the measurement of the net charge on the particle increased as the static eliminator was brought closer to the flowing surface.

In addition to razorbacks, we also observed several unexpected behaviors in our experiments. For example we observe clusters of grains hop or gyrate in complicated motions as they travel *[124]*. Moreover, even within the steady granular stream, idiosyncratic patterns appear including streamwise grooves and indented circles. The grains were also observed to form clusters when placed in a strong electric field in a similar manner as when in the presence of the charged acrylic sheet.

The ability to model and predict flow instabilities will be necessary for the development of a successful theory of granular flow. Here we have investigated the underlying principles of the formation of instabilities and described new instabilities, which spontaneously form due to electrostatic effects. These investigations will hopefully provide new insight into the creation of more detailed theories of granular behavior.

2.14 Figures for Chapter 2



Figure 2.1 Type A and B chevrons. These pictures are arranged in order of decreasing angle. On the left type A chevrons can be seen and on the right type B exist alone. In the center both types of chevrons coexist.



Figure 2.2 Schematic of the flow of height in the CA model. The amount of height moved downhill and the distance that it is moved both depend on the slope, ∇^X . Here the case for the calculation in the x-direction is shown; a similar process is used for flow in the y-direction.



Figure 2.3 Top: Surface shape simulated by cellular automata code beginning with 5 random amplitude Fourier modes in X and Y directions. Boundary conditions are periodic in X and Y, and the plot shown is a surface using a 50X50 grid, $\alpha = 0.01$, $\beta = 0.2$, and diffusion = 0.01. Bottom: histogram of slopes for the surface shown above.



Figure 2.4 Surface flows as the simulated angle of a smooth inclined chute is increased. (a) Smooth surface flow on a gently inclined chute $(g_o = 1)$: here disturbances have time to disperse before additional material from uphill accumulates. (b) At a larger inclination $(g_o = 3)$, small bumps grow because material cannot flow away downhill before new material arrives from uphill. (c) At still larger inclination $(g_o = 5)$, bumps grow more rapidly, and travel upstream. In all cases, flow is from left to right, and periodic boundary conditions are applied in both X and Y. To add verisimilitude, an average inclination is added to the plot; in reality there is a constant gradient added in the +Y direction, but to make the computational domain periodic, the left side of the plot is at the same height as the right side. Parameter values used are: $\alpha = 0.1$; $\nu = 0.8$; $\beta = 0.5$; $\delta = 0.1$.



Figure 2.5 Shockwaves produced (a) experimentally and (b) in CA in flow past a wedge. Experimentally and in the model, we identify the shock as the location where the bed depth increases abruptly. The expansion fan location is approximate. The experiments were carried out at $\phi = 1.24 \pm 0.01$ while the simulation angle was set to $\phi = 1.09$. As can be seen in both figures the shock waves are detached from the wedges and the waves between the shock and the wedge have been marked with arrows. The experimental figure has been digitally enhanced to accentuate the waves. The black triangle denotes the position of the triangular wedge. This simulation was carried out on a 200 by 200 grid for 5000 iterations with $\alpha = 0.04$, $\beta = 0.07$, $\nu = 0.565$ and no diffusion. The inlet boundary condition was set to a constant depth of 10.



Figure 2.6 Shockwaves produced by CA model around a pyramidal object in the flow a) placed facing forward and b) facing backward. These shockwaves appear similar to those produced during experiments by Gray et al [117]. Here the grid size is 75 by 75 and with $\phi = 1.09 \ \alpha = 0.04$, $\beta = 0.07$, v = 0.565 and no diffusion.



Figure 2.7 Comparison of experimental longitudinal vortices (above) from Forterre and Pouliquen, and model CA vortices (below). a) Picture of experimental stripes seen in a flow down a rough bed by Forterre and Pouliquen [50]. Experimental snapshot provided by Dr. Yoël Forterre. b) Stripes produced by model with $\phi = 1.01$ on a 141 by 100 grid with $\alpha = 0.04$, $\beta = 0.07$, v = 0.565 for 1500 iterations. Noise in the system caused by the rough bed was modeled using a high level of diffusion ($\delta = 10$). Other randomizing mechanisms were tested and produced similar results. c) Typical Streamwise (top) and spanwise (bottom) velocities from CA. Solid lines denote velocities at the crests while dashed lines denote velocities at the troughs. To produce the velocity profiles of the simulation the change in positions was averaged at each time step for each column of gridpoints along the longitudinal direction of the chute at $\phi = 1.01$. Simulations used for the velocity profiles were carried out on a 75 by 75 grid for 2000 iterations while averaging for the final 500 iterations and with $\alpha = 0.04$, $\beta = 0.07$, v = 0.565 and $\delta = 10$.



Figure 2.8 Comparison of experimental and model chevrons. a) Experimentally observed chevrons for $\phi = 1.04 \pm 0.01$. b) Chevrons produced in model for $\phi = 1.05$ with no slip boundary conditions. The simulation was performed with a gridsize of 310 by 200 for 500 iterations. Here $\alpha = 0.04$, $\beta = 0.07$, v = 0.565, with no diffusion. The inlet boundary condition was set to a constant height of 10 while the depth of the bed was set to 50 for the initial condition except for 3 initially reduced height sections along each wall to perturb the bed.



Figure 2.9 Chevron angle change in both experiments and model: elapsed time is from top to bottom. a) Time progression of a chevron from computational simulations at 7500, 12300 and 17300 iterations. The angle of the chevron with the edge of the chute (dashed lines) is 9.5°, 6.0°, and 2.8° \pm 0.3° respectively. Here $\phi = 1.01$, $\alpha = 0.04$, $\beta = 0.07$ and v = 0.565. (b) Experimental chevron at 1.3, 1.93, and 2.8 seconds with $\phi = 1.06\pm0.01$. The chevron's angle with the wall is 7.3°, 5.0° and 3.8° \pm 0.3° respectively. Crosshatched areas indicate locations of side-wall in both simulations and experiments.



Figure 2.10 Other phenomena: model scales. Both the experimental scales and these patterns are created at high chute angles. The experiments were reported at θ =52° (see Forterre and Pouliquen [51] Figure 13) where the model produced these features at ϕ = 1.16. Here simulations were carried out on a 75 by 75 grid with α = 0.04, β = 0.07, v = 0.565, and no diffusion.



Figure 2.11 Grooves produced near boundaries by the erratic flow of art sand when the surface of the chute has not been treated with anti-static spray. The chute inclination is about 30° here and humidity is >50%.



Figure 2.12 a) Clusters of sand grains form during the flow of sand down an acrylic sheet while large cluster form near the edges of the flow. b) This picture was taken immediately after the flow of sand had ceased. The acrylic sheet was inclined to $28\pm1^{\circ}$ as measured by a digital level. The humidity here is 16% and the temperature is 69°F.



Figure 2.13 A close up of razorbacks produced with art sand. This picture was taken a short time after the flow had ceased. Here the angle of the chute is $27\pm1^{\circ}$.



Figure 2.14 Razorbacks and flowing clusters. A photo of roughly one half of the flow. Razorbacks can be seen on the left. Note that the sand grains have formed clusters while they flow downstream. The arrow here indicates the direction of flow. The chute angle is $27\pm1^{\circ}$.



Figure 2.15 a) and b) Sand grains jumping from the surface of the chute. These photo's were taken shortly after flow had ceased. In a) the angle of the chute is 32.1° and there is no static eliminator present. In b) The chute angle is $30\pm1^{\circ}$ and the static eliminator is set about 127 cm above the surface.



Figure 2.16 The detachment and reattachment of a cluster of grains can be seen in this sequence of frames. The arrow marks the cluster that releases from one razorback and quickly attaches to another. The chute angle here is $31\pm1^{\circ}$.



Figure 2.17 Quantitative confirmation that laboratory razorbacks are produced by electrostatic influences. Main plot: average over 3 trials of the dependence of the standard error of the local slope of razorbacks taken from side view snapshots of the flow. Lower inset: a side view of the sand taken directly after flow has stopped with the static eliminator close to the surface. Upper inset: a side view of razorbacks produced when no static eliminator was present. Here the relative humidity was 14% and the temperature was 72°F.



Figure 2.18 Net charge per gram of sand grains after the sand has traveled off the acrylic sheet for several static eliminator positions. The charge has been measured using two methods. The sand was collected in an insulating cup as they flowed from the sheet (squares) and then transferred to a Faraday cup. The charge was also measured by collecting all of the sand falling from the sheet in to a large Faraday cup. Each data point was repeated at least 3 times and the error bars here are the standard error.



Figure 2.19 Art sand placed on a Van de Graaff generator produces clusters, which can then travel down the surface of the pile and jump away from the surface. a) Here the VDG is grounded and no clusters are observed. b) As the voltage of the VDG is increased (to about 200kv), clusters of grains begin to form and jump from the surface. c) At high voltages (~300kv), many clusters form and are ejected from the surface.



Figure 2.20 A "running" cluster of sand grains. The arrow points to the runner as it hops from one position to another. During this experiment the angle of the chute was set to 27.5° and there was no static eliminator present.



Figure 2.21 Indented circles and stream wise grooves. a) A single indented circle which appears in a flow at an angle of $30\pm1^{\circ}$ without a static eliminator. b) Multiple indented circles which have all formed from in the same area of the flow. This frame was taken from the same experiment as (a). c) A single streamwise groove that appears in the flow near the hopper outlet. Here the chute angle is $27\pm1^{\circ}$ with no static eliminator. d) Here two grooves can be seen in the flow. This frame is from the same footage as (c).



Figure 2.22 The segregation of blue and white art sand due to electrostatic effects. Blue sand preferentially sticks to the opening of the hopper during flow. After flow has ceased some of the art sand falls onto the chute. Here the relative humidity is 13% and the temperature is $70 \,\text{F}$.

Chapter 3 Charge distribution and the flow of grains

The behavior of flows of charged grains depends strongly on how those charges are distributed amongst the particles. Unfortunately these charges are rarely distributed uniformly and complex distributions of charge may be the norm. The charge developed by a material depends on extrinsic factors including humidity [15], surface chemistry [62], contamination [62, 125], and particle size [4, 121]. Even the determination of the charge of a particle system of only one material can be a challenge as particles often acquire nonuniform distributions of charges [4, 121, 122]. Tanoue et al. have shown that the polarity of the charge developed by a particle may depend on its impact angle with a target [122], Lacks and Levandovsky have proposed a mechanism that would allow particles of the same materials but differing sizes to tribocharge [121], and the separation of particles due to charge differences acquired while being poured has also been reported [4].

These effects become still more complex when mixtures of materials are studied. The ability of one material to coat either equipment surfaces [5, 6] or other particles [6, 126] can lead to unexpected charging behavior. Some materials, even when added to a mixture in small concentrations, have been shown to decrease the net charge produced during powder handling and prevent agglomeration [12, 126].

3.1 Nonuniform charging and flow

Most experiments thus far have focused on regimes that maximize mixing, such as fluidized systems, and hence maximize the total charge generated [10, 127]. Here we wish to observe a case where the mixing is kept to a minimum. Net particle charge is measured as particles fall from a vertically oriented cylindrical duct. This flow of particles is in many respects similar to mass flow from hoppers. While the flow through the duct is not steady, all of the material within the duct is in motion, which is similar to mass flow in hoppers [128, 129]. By using a cylindrical geometry, complexities of hopper shape and associated flow anomalies can be ignored. Further, the cylindrical geometry permits us to easily control the amount of the container's surface area that is available for contact with the particles. We examine the charge distribution developed by single materials, including pharmaceutically relevant materials, as well as mixtures. The effect of a nanoparticle coating is also examined. We also compare the charge generated in cylinders to the charge generated in a mass flow hopper. Finally, the grounding of equipment as a method for preventing charge accumulation is examined. A stainless steel (type 304) cylinder, open at both the top and bottom, is grounded and suspended above a Faraday cup, which is surrounded by a grounded Faraday cage, as indicated in Figure 3.1. The cylinder is filled to a desired fill height, using a steel funnel to minimize contact between the particles and the cylinder during filling. This allows us to specify the amount of surface area available for contact between the bed of grains and the wall of the cylinder. The contact surface area can be varied by either increasing or decreasing the fill level of a cylinder or by replacing the cylinder with another of a different inner diameter. In this way the ratio of the surface area of contact to the mass of particles can be controlled. Cylinders with inner diameters of 3.7, 4.3, 5.5, 8.3 and 10.8 cm were used in these experiments. A base plate consisting of a plastic handle with a steel plate attached is used to prevent the particles from falling out of the cylinder while filling. When the cylinder is filled to a desired level, the base plate is quickly pulled from its initial position allowing the particles to fall into the Faraday cup.

This flow of particles was examined with a high-speed camera (Redlake MASD Inc., MotionScope, PCI 1000s) for the largest diameter cylinder used in these experiments (10.8cm). It was determined that the speed with which the base can be pulled from under the cylinder is sufficient to ensure that the flow of grains is nearly uniform across the entire cylinder. A high-speed camera was again used to determine if frictional or air pressure effects slow the fall of the granular bed significantly [130]. The grains were observed to fall at near the acceleration due to gravity, suggesting that the flow of the grains was unimpeded by air or stress chain effects.

After the particles have entered the Faraday cup the net charge of the particles is then measured using an electrometer. Any charges generated by the particles after they entered the cylinder, such as when particles reach the walls during filling or slide along the walls as they released, are thus measured. We have used both a Keithley Instruments 610CR and Trek 217 electrometer and found no significant difference between the readings of the two instruments.

Reproducibility of charge measurements was found to be improved by preconditioning all powders studied by sequentially flowing them through the feed hopper and the metal cylinder into the Faraday cup ten times. The net charge produced on grains leaving the feed hopper was measured independently and found to always be an order of magnitude less than the charges produced when the cylinder was allowed to fill and then discharge. Additionally, experiments using an active static eliminator (EXAIR, Cincinatti, OH) at the outlet of the feed hopper produced no change in the charge of grains leaving the cylinder as long as the relative humidity was kept above about 20%. At low humidities the charge was found to depend on the time between filling the cylinder and emptying the cylinder into the Faraday cup. The charge would decrease over about a 10 minute period after filling the cylinder. All experiments reported here were performed in humidities higher than 20%.

It should be noted that the diameter of the outlet of the hopper used to fill the cylinder is less than that of the cylinder (See Figure 3.1). The particles therefore flow into the center of the cylinder, where they form a slight heap and flow down the heap to the surface of the cylinder. The particles come down with enough kinetic energy and are sufficiently free flowing to ensure that the top surface is almost flat at the end of the filling operation. We found that when the particles were allowed to flow directly from the feed hopper into the Faraday cup the net charge produced was always an order of

magnitude less than the charges produced when the cylinder was allowed to fill and then discharge.

White art sand $(300\pm90\mu m)$ was used in the majority of the experiments, however microcrystalline cellulose $(140\pm100\mu m)$, FMC Biopolymer, Ph102), a commonly used pharmaceutical powder, as well as mixtures of materials were also examined. The effect of the steel base plate on the charge measured was investigated by fixing a layer of particles to the surface of the steel using double-sided tape. This prevented the sand from contact charging against the surface of the metal. It was found that when the cylinders were filled to a level that was only a small distance from the base, the base material did have a noticeable effect on the net charge, however, when the cylinder was filled with a large amount of sand, this effect became negligible. In experiments where sand was examined alone, a sand coated base plate was used. However, when working with other materials or with mixtures of particles, an uncoated steel base was employed, but the quantity of grains used was increased so that the effect of the steel base could be ignored.

3.2 Charging of a single material

To determine the relationship between the charge, the surface area of the cylinder that comes in contact with the material, and the mass of the material, several cylinders of varying diameters were filled so that each contained enough sand to cover an approximately equal surface area of the cylinder. After the particles were emptied from the cylinders, the net charge was measured. The charge developed by the sand for the amount of sand added to each cylinder can be seen in Figure 3.2. Although the data is noisy, the charge remains roughly constant even though the mass of sand falling from the cylinders varies from 430g to 1270g. The charge developed by the particles depends not on the mass of the material filling the cylinders, but instead on the surface area of the cylinder in contact with the particles. This suggests that there is little mixing between those particles at the outer edge of the cylinder and those closer to the center.

When the surface area available for contact with the particles is varied, by changing the fill level of a single cylinder, the net charge generated by the sand responds linearly. The net charges generated by sand for several contact areas in a 5.5cm cylinder are shown in Figure 3.3. Here the fill level was varied between 25.4cm and 1.3cm. A schematic depicting the area of contact within the cylinder can be found in the inset to Figure 3.3. It would seem that few charges or charged grains are being transferred to the center of the flow during both filling and emptying of the cylinder, otherwise one would expect the net charge to vary non-linearly as the fill level is increased. Moreover, the results indicate that only particles in contact with the wall pick up any appreciable charge. This will be verified in the next part of this paper. Also, if the grains were not reaching a saturated charge level, the relationship between charge and fill level would, again, be non-linear. This linear relationship holds down to the smallest amounts of particles that could be added to the cylinder and still have a reasonable coverage of the cylinder surface, compared with that of the base. This corresponds to about 50g of sand, or a fill depth of about 1.3 cm, for the 5.5cm diameter cylinder. The time necessary for a single grain to fall this distance is only about 0.05 seconds. This suggests that the grains

pick up their maximum plateau charge during filling and while falling from the cylinder within this short amount of time.

Several researchers have examined the increase of charge with time in other experimental systems and found the time for charges to reach a steady value to be on the order of minutes to hours [7, 54]. In these systems, however, the particles are mixed strenuously, allowing all of the particles to eventually reach the surface and charge [7, 54]. Matsusaka et al. [131] found that the number of impacts necessary for a rubber particle to reach a charge plateau was around 20, while the final charge depended on the interval between impacts. It is not clear if the impact charge observed by Matsusaka and the longer term sliding or rolling contacts that are likely to take places in this system will result in a similar time to reach maximum charge. An estimation of the time necessary for the charge to reach a plateau may be of use in attempts to model electrostatic effects in dense flows such as tumblers where the material can buildup charges over many contacts. In our case we cannot separate the amount of charge transferred to the grains during the filling of the cylinder and the amount transferred during emptying. However, because of the carefully controlled filling and emptying operations we can conclude that the particles reach a plateau charge by tribocharging as they fill the cylinder and after only flowing past the walls on the order of a centimeter or less. When grains flow past the walls for distances on the order of tens of centimeters, as is the case for the largest fill levels, they do not pick up any more charge than when they flow down the walls for approximately a centimeter.

To test if only those grains which contact the cylinder wall become charged during the flow, the charge of grains from various areas of the flow was measured and compared. To determine the charge distribution of the falling grains, a smaller Faraday cup, also surrounded by a grounded Faraday cage, was created to measure the charge of material that empties from the center of the cylinder. The material that does not enter this smaller Faraday cup is collected in the large cup and its charge is determined. In Figure 3.4, the charge of both the center and outer material is compared to the net charge measured for the entire sample captured at once. The central material's charge (about $25\pm4nC$) is nearly an order of magnitude lower than that of the material near the cylinder's surface and is similar to the charge found on the grains after falling from the feed hopper alone ($15\pm1nC$).

While the distribution of charge on particles based on particle size, collision angle, and humidity have been investigated previously [4, 121, 122, 132], these results suggest that even a simple granular flow can develop a complicated charge distribution, which may lead to the separation of the outer charged particles from the inner and relatively uncharged particles.

To examine how the charge is distributed amongst the particles, the number of particles filling the cylinder and the number that have come into contact with the cylinder can be estimated. For the case shown in Figure 3.4, by measuring the mass of the sample and the average mass of a sand grain, ~0.1 mg, the number of particles filling the cylinder can be determined to be about 5.6×10^6 . By assuming hexagonal close packing at the walls of the cylinder, one can estimate the maximum possible number of grains that could be in contact with the cylinder surface. For close-packing the number of particles that contact the walls can be estimated to be roughly 5.5×10^5 . Taking the charge found for the

particles in the center of the flow from the experiments of Figure 3.4, the average charge of a particle that has not come into contact with the cylinder walls can be estimated to be roughly 4.3×10^{-6} nC. Similarly the charge of those particles that have contacted the walls can be estimated to be 2.3×10^{-4} nC, two orders of magnitude larger. While these calculations are only rough estimates, they do serve to suggest the difference in the magnitude of the forces that could act on the surface and bulk particles.

The charge generated by the particles at the wall was examined further by comparing the estimates of the charges generated by the particles near the cylinder walls and the charge produced by particles agitated within the cylinder. A fixed amount of sand was agitated vigorously in the cylinder, to allow as much of the sand to contact the cylinder walls as possible. In this experiment, 35g of sand was added to the cylinder, and the cylinder was sealed on both ends with sand coated tape, to limit charging between the sand and the end caps of the cylinder. The cylinder was then vigorously shaken for 5 minutes, after which time the sand was emptied from the cylinder into the Faraday cup and the charge was determined. This measurement was repeated 3 times and the average charge per particle can be found to be about 8×10^{-5} nC. This can be compared with the value of 2.3×10^{-4} nC per particle for particles that contact the cylinder walls during flow through a cylinder in Figure 3.4. As can be seen the charges obtained for both experiments are reasonably similar. It would seem that the plateau charge observed during the emptying of the cylinder is similar to the charge produced by more vigorous collisions. It would also suggest that even though the flow of grains from a cylinder produces a distribution of charge across the particles, the charge developed by any particle that comes in contact with the walls of the cylinder can be estimated with
reasonable accuracy. Further it is also possible that an apparatus such as this could be used to estimate the charge of grains in systems with larger amounts of mixing, as long as the particles reach their saturated charge level.

It is interesting to note that these saturated charge amounts are well below the theoretical maximum charge for spherical particles of a given size, which is determined by the break down strength of air [62, 73]. The maximum theoretical charge of particles of this size would be around 10^{-2} nC. This is much larger that the $\sim 10^{-5}$ nC charge observed. Charge saturation below the theoretical limit has been observed before and may be related to material properties [131]. The nonspherical shape of these sand grains may also limit the maximum charge observed.

The pharmaceutical industry is especially interested in the effects of electrostatics on the flow [5, 6], mixing [7, 12] and agglomeration [133] of powders. To ensure that our results hold for pharmaceutically relevant powders, microcrystalline cellulose (with an average diameter of $140\pm100\mu$ m) was examined and found to behave similarly to sand (see Figure 3.5), in that the charge produced depends only on the contact surface area for different fill levels. The charge developed by the inner most particles, again estimated as above, can be found to be roughly $3x10^{-5}$ nC/particle. Similarly to sand, the charge saturates at a level much lower than the theoretical maximum for particles of this size (~ 10^{-2} nC). This suggests that the development of charge distributions while handling pharmaceutical powders may readily occur during processing.

3.3 Charging of a mixture of particles

The behavior of two component mixtures of particles was also studied. Sand was mixed with larger 4mm diameter, black painted glass beads. The charge of the blend of sand and glass beads depended on the concentration of the materials, as can be seen in Figure 3.6. In Figure 3.6 the concentration (v_s) is the ratio of the untapped volume of sand, which was added to the mixture, to the untapped volume of the mixture. The charge was found to be independent of the concentration when either material made up the majority of the volume of the cylinder.

We propose that this result may be associated with segregation of the particles while filling. In the upper left corner inset to Figure 3.6, a mixture of 20% beads by volume can be seen in a plastic cylinder with a similar diameter to that of the steel cylinder. The materials were carefully added to the funnel to prevent vertical segregation, only radial segregation was observed. Even though the black glass beads make up 20% of this mixture, very few beads can be seen at the walls of the cylinder. This is associated with well known percolation effects [35, 134], i.e. when the concentration of the smaller sand grains is high (v_s >0.7), the sand can easily fill in the areas around the large particles and monopolize the area of contact with the walls (see Figure 3.6 inset). When the glass bead concentration is high (v_s <0.4), the large beads create a network of voids, into which the sand settles. This prevents the sand from leaving the center of the cylinder and allows only the beads to reach the surface [134, 135]. Since only particles that come into contact with the cylinder walls affect the net

charge of the mixture, it follows that those particles which monopolized the surface should predominate the charged population.

When a mixture of 3 mm acrylic beads and sand is passed through the cylinder (see Figure 3.7) the behavior is quite different compared to that of the glass bead/sand mixture. Here, the net charge remains similar to that of sand alone for a much wider range of volume fractions than the glass/sand mixture (Figure 3.6). The charge then quickly approaches that of the acrylic beads alone as the volume fraction of sand is decreased further. When the beads are examined, after passing through the cylinder with sand, almost all of the beads were observed to be covered with several sand grains. This coating effect was not observed for the glass beads, which suggests that particle coating is responsible for the difference in the charge to concentration relationship for the glass/sand and acrylic/sand mixtures. It seems likely that as the acrylic beads flow with the sand grains they develop a charge of opposite polarity to that of the sand. These opposite charges allow the sand grains to coat the larger beads. A picture of these beads coated with red sand grains can be seen in the inset to Figure 3.7. Red sand was used to make the sand grains easier to distinguish in the photo, however the white sand was observed to coat the acrylic beads in a similar fashion. The beads cannot contact the walls directly when they are coated with the sand, and therefore cannot contribute to the measured net charge.

The charges that allow the sand to coat the acrylic beads result from the triboelectrification of the different materials making up the mixture and cannot be determined by measuring the mixture's net charge [136, 137]. The charges developed by the beads through rubbing against the sand grains are opposite to the charges developed

by the sand. When both the sand and beads fall into the Faraday cup their opposing charges cancel out their measurements. However, charges gained from the cylinder are not balanced and can be measured. Although, the net charge is much easier to measure than the charge distribution, which requires particles to be separated or otherwise examined [136, 137], these experiments demonstrate that measuring the net charge alone provides little information for cases when the particle charge is widely distributed. It seems likely that for mixtures of materials the net charge will rarely give a complete picture of the particle behavior [5].

3.4 Scale up and charging in hoppers

The dependence of the charge on the surface area of contact suggests that it may be possible to predict the charge generated by a material on a larger scale from a benchtop experiment [138] for cylinders, and perhaps hoppers. We are able to demonstrate this in part by measuring the charge to surface area relationship in a 5.5cm diameter cylinder and then using that information to predict the charge in a larger 10.8cm diameter cylinder. In Figure 3.8, the charge generated by a 5.5cm cylinder is shown (diamonds) for several contact areas, as well as the predicted (solid line) and measured (squares) charges for the 10.8cm cylinder. Using the smaller cylinder we were able to make reasonable predictions about the charge that would be present on the sand after it flowed through the larger cylinder. We also attempted to predict the charge on sand allowed to flow through a carbon steel, conical, mass flow hopper based on the surface area of the hopper. The results of this experiment can be seen in Figure 3.9. There is reasonable agreement between the charge developed by the particles in the cylinder and the hopper; although, the charge of the hopper is offset to that of the cylinder. This could be due to the difference in the materials of construction (carbon steel versus stainless steel). Since the behavior of the charge, in relationship to the surface area, is similar for both the hopper and cylinder, it would appear that mass flow hoppers produce similar distribution of charge to that of a cylinder, with most grains uncharged and a minority with much larger charges.

3.5 Methods to prevent charging

Grounding of equipment is a common method to control electrostatic charging of materials [10, 44]. While grounding is known to minimize dangerous discharges during powder handling [44], recent experiments have suggested that grounding equipment does not necessarily decrease the charge generated by particles during handling [10]. To test this charge control method further we measured the charge generated by a 5.5cm cylinder both with the cylinder grounded and ungrounded. We found that the difference between the charges, $5.7 \times 10^{-2} \pm 0.9 \times 10^{-2}$ nC/g and $5.8 \times 10^{-2} \pm 1 \times 10^{-2}$ nC/g for the grounded and ungrounded cases respectively, was not significant. The prevention of charging by grounding, in the case of flow from a cylinder does not appear to be effective.

The effect of a nanoparticle coating on the charging generated by sand particles in this apparatus was also investigated. Sand was coated with semiconducting TiO₂ nanoparticles (Degussa, Aeroxide TiO₂ P25, ~20nm) using the magnetically assisted impaction coating method [139]. When equal amounts of coated and uncoated sand were tested using the 5.5cm diameter cylinder, it was found that the coating reduced the average charge density for five trials from $3.3x10^{-1} \pm 3x10^{-2}$ nC/g to $2.6x10^{-3} \pm 2x10^{-4}$ nC/g. The nanoparticle coating prevents the sand from contacting the cylinder walls, and because of their relatively high conductivity, the nanoparticles do not charge appreciably. The coating of a material with another changes the charging behavior of the mixture whether or not the coating was deliberate [6, 12, 126], as in this case, or accidental, as could be caused by a contaminate [122, 140]. It is possible that a change in the surface properties of a material, such as a contaminate coating, could be detected as a change in the charging properties of the material.

3.6 Conclusion for charging during flow

The tribocharging behavior of grains while flowing from both cylinders and a mass flow hopper were investigated. The net charge developed by both art sand and cellulose depended only on the amount of surface area that was in contact with the particles. This suggests that only those grains near the inner surface of the cylinder become charged leading to a significant charge on a minority of particles.

Allowing only slow, dense flows of powders, to limit the number of collision between particles and the walls of the cylinder, may be the most apparent method to prevent electrostatic charging and effects. However, this may lead to a minority of particles becoming highly charged while the rest remain relatively neutral, and could lead to an increase in the segregation or the loss of some particles from the flow altogether.

It was found that the net charge developed by a mixture of particles is dependent on the amount of each component that contacts the surface of the cylinder. For materials that are not attracted to one another, the radial segregation of the particles determines the mixture's measured charge. For materials that do attract one another, the smaller particles coat the larger and prevent them from contacting the walls of the container. Even if both materials are highly charged only the material that makes contact with the surface of the container will contribute to the net charge.

Similarly it was observed that coating the sand particles with a small amount of semiconducting particles reduced the charge developed by the sand. This could conceivably provide, by using a method similar to the one described here, an electrostatic method for quickly detecting the presence of contamination adhered to a particulate material.

By measuring the dependence of the charge developed by particles on the contact surface area in a cylinder, predictions of the charge produced in both larger cylinders and mass flow hoppers can be made with reasonable accuracy. These results suggest that it may be possible to predict the net charge generated on large-scale equipment, and provide an estimate of the distribution of charge across the dense flow of grains from cylinders and mass flow hoppers. The charging behavior of funnel flow hoppers may differ from mass flow hoppers due to their differences in flow behavior.

Finally, the ability of grounding a piece of equipment to prevent particle charging was tested. It was found that whether the cylinder was grounding or not had little affect on the net charge produced.

Even a relatively simple flow of grains, such as the one examined here, can reveal the complex tribocharging behavior granular flows can generate, and demonstrates the difficulty in measuring a material's charge and predicting its behavior. When an external electric field is applied to a granular flow the behavior can become even more complex, as will be addressed in chapter 4.



Figure 3.1 Experimental setup schematic. To fill the stainless steel cylinder, a metal funnel is used. Once the cylinder has been filled to the desired depth, the base plate is quickly removed and the particles fall into a Faraday cup where their charge is measured.



Figure 3.2 The net charge accumulated by the particles is related to the surface area of the cylinder in contact with the grains but not to the mass of the particles. The amount of sand added to each cylinder was adjusted to keep the surface area of contact constant. These experiments were repeated 5 times at 75°F and 43% relative humidity. The line displayed is the average of the points.



Figure 3.3 Net charge of white art sand generated after falling from a 5.5cm diameter stainless steel cylinder. The net charge is linearly related to the inner surface area of the cylinder that is in contact with the sand. Each data point is the average of 5 experiments and the error bars are 1 standard deviation. The temperature and humidity were 72°F and 36% Inset: Schematic showing the inner surface of the cylinder, where H is the fill level, r is the inner radius of the cylinder, and A is the surface area of contact.



Figure 3.4 Net charge of sand from different areas within the 5.5cm diameter cylinder. Schematics showing the different areas of the cylinder from which the sand was collected are shown below the abscissa. The central Faraday cup had an inner diameter of 3.7cm and an outer diameter of 4.2cm. The temperature and relative humidity during these experiments were 84°F and 20% and each experiment was repeated 5 times.



Figure 3.5 Net charge of cellulose powder after falling from a 5.5cm diameter stainless steel cylinder at 70 °F and 17% relative humidity. Here each data point is the average of 5 experiments and the error bars are 1 standard deviation.



Figure 3.6 The net charge measured for mixtures of sand and large glass beads (4mm) is independent of the concentration (v_s) when each material makes up the majority of the mixture. Upper left corner inset: a picture of an 80% sand by volume mixture in a 5.5cm diameter acrylic cylinder. As can be seen very few black glass beads are visible at the walls. Lower right corner inset: when smaller particles are present in large amounts they cover much more of the cylinder surface and charge due to contact with the walls.



Figure 3.7 The net charge of a mixture of sand and larger (3mm) acrylic beads. Here the acrylic charges oppositely with respect to the sand. The charge of the mixture remains similar to the charge of the sand alone for a wide range of concentrations. This is most likely due to the coating of the acrylic beads with adhered sand grains. An example of this coating (using red sand instead of white) can be seen in the inset. For these experiments the temperature was $72^{\circ}F$, while the humidity was 39%.



Figure 3.8 Prediction of the charge of materials in larger vessels is possible from measurements in smaller systems. Net charge accumulated by the sand after falling from a 5.5cm diameter cylinder for several contact surface area amounts were measured (diamonds). The charge developed by a 10.8cm diameter cylinder was then predicted (solid line) and compared with experiments (squares). These experiments were conducted at 75°F and 39% relative humidity.



Figure 3.9 The charge generated by a carbon steel mass flow hopper (diamonds) is similar to the charge observed from a stainless steel cylinder (squares). The difference in charge may be due to the difference in composition between the hopper and cylinder. Both charges were determined at 72°F and 37% relative humidity.

Chapter 4 The effect of dielectrophoresis on the flow of granular materials

Agglomeration and sticking cause many headaches when attempting to controllably use powders in manufacturing. It is commonly assumed that these behaviors are due to the attraction and repulsion caused by the charges on individual particles, however, the polarization of particles due to strong nonuniform electric fields can result in significant attractive forces between grains and may be responsible for a large portion of electrostatic problems. As was discussed in chapter 1.3 the forces produced by nonuniform electric fields are referred to as dielectrophoretic forces (DEP forces). We show here that these forces can create significant amounts of agglomeration and adhesion to equipment surfaces and pose possible methods for dealing with DEP attraction. But beyond the problems caused by DEP there may be new methods for particle handling, just as electrostatics has been utilized by some industries for controlling particle behavior on a large scale.

4.1 Determining DEP forces

Strong, constant electric fields can be commonly found around many particle handling processes, especially when plastic equipment or containers are involved [72]. It is likely that particles in these situations will be affected by DEP forces, and DEP, much like other electrostatic effects, can lead to segregation and flow problems. Here we wish to investigate the ability of DEP to modify the behavior of flowing granular materials, and to study whether or not this effect can be used both to characterize susceptibility to polarization and to benefit industrial particle handling operations. We do this in two ways; first we attempt to determine the strength of the DEP forces acting on grains, and second we investigate a prototypical granular flow, namely flow from a cylindrical hopper, and see whether DEP can significantly affect the flow behavior. We also wish to investigate the effects of several parameters on the adhesion of particles due to DEP forces including the effect of material, particle size and humidity. Additionally we determine the utility of two commonly used methods to control electrostatic forces and find that while coating particles with conducting substances does reduce the about of DEP adhesion, the grounding of equipment tends to exacerbate DEP adhesion. Finally, we show that DEP effects might have more general relevance than intuitively expected, by demonstrating that granular materials can spontaneously generate electric fields strong enough to cause DEP through triboelectrification.

The large, nonuniform electric fields necessary to produce significant DEP forces were created using a Van de Graaff generator (VDG). A VDG is a simple electrostatic generator capable of producing high voltages (10^5-10^6V) safely. The current produced by a VDG is limited by the rate at which it can generate charge and therefore any accidental

contact with a moderately sized generator, such as the one used in these experiments, while producing an uncomfortable shock, is completely safe. Although not as easily controlled as some other high voltage sources, it was felt that the safety attributes of the VDG more than made up for its shortcomings.

The voltage of the VDG was controlled by utilizing its limited current output (about 3μ A). By using the circuit shown in Figure 4.1, we were able to control and measure the VDG's voltage. An electrometer (either a Keithley Instruments 610CR or a Trek 217) was used in series with a very large resistor (R2 = $2x10^{10}\Omega$) and in parallel to a variable resistor (R1). A finely tipped grounded wire acting as a corona source was used as the variable resistor. By moving the wire tip nearer or farther from the VDG, could be controlled. The voltage of the VDG reaches a value large enough so that the current passing through both resistors becomes equal to the current produced by the VDG. The voltage was measured by monitoring the current running through the known large resistor. The voltage of the VDG could be controlled to within 300V when its voltage was set to 20kV or to about 1.5%. At lower voltages, the VDG's voltage could be more accurately controlled. The large resistor could also be removed and replaced with a larger or smaller resistor to investigate other voltage ranges with more accuracy.

The first experiment consisted of a metal rod (1.2cm in diameter) that was attached to a moveable jig, which allowed the rod to be smoothly moved up or down. The rod was positioned directly over the VDG and could be electrically isolated from the jig. A powder container (13 x13 x 1cm) was constructed from plastic (either Teflon or

acrylic) and filled with a powder. The container was then placed on the VDG (as depicted in Figure 4.1). Before the VDG was turned on, the rod was immersed to a depth of 6mm. The VDG was then activated and the voltage was allowed to reach a steady value, which usually occurred in about 1 second, at which time the rod was smoothly and quickly raised from the bed of grains and any material adhered to the rod was collected and weighed.

Several powders were used throughout this study and include white art sand (average diameter $300\pm90\mu$ m) and glass beads of various sizes. The pharmaceutically relevant powders lactose ($110\pm45\mu$ m, Foremost, 316/Fast-Flo) and microcrystalline cellulose ($140\pm100\mu$ m, FMC Biopolymer, Ph102) were also tested. The average diameter of the particles was determined using a Beckman Coulter LS 13 320 dynamic light scattering apparatus.

To ensure that the powder was not becoming significantly charged during the filling of the powder container or while the VDG was on, the charge of the powder was measured using a Faraday cup. The container was filled with powder, placed on the VDG for 30 seconds and then emptied into the Faraday cup and the net charge measured. The charges produced in this manner were small, and are listed in Table 4.1. The charges produced by filling the container and then emptying it after 30 seconds without using the VDG were within error of their measurements, suggesting that the VDG does not significantly charge the particles. The forces acting on these particles due to this charge are discussed in more detail in section 1.1.

In the second experiment, an electric field was applied to the flow of grains exiting a metal, cylindrical hopper to examine the ability of nonuniform electric fields to alter the flow of granular materials. The VDG was suspended horizontally near the outlet of the hopper, so that a nonuniform electric field could be produced at the outlet of the hopper. Placing the VDG directly under the hopper was not feasible; as the VDG could not be brought close enough to the outlet without interrupting the flow from the hopper. The flow was video-taped and the time necessary to empty the cylinder's reservoir was measured for different VDG voltages.

4.1.1 Agglomeration and adhesion to a rod

The amount of material adhered to a grounded rod in a large nonuniform electric field was determined for white art sand, and glass beads, as well as lactose and microcrystalline cellulose. As can be seen in Figure 4.2 the material adheres to the surface of the rod and forms large agglomerates around the rod. Cellulose, shown in Figure 4.2(a), produces a large agglomerate (about 2 grams) consisting of many jagged clusters. Similar clusters of adhered white art sand and glass beads are shown in Figures 4.2(b) and (c). These clusters are produced even if the powder is left in the container for over 48 hours before being tested.

The amount of material collected for each of the powders as the voltage of the VDG is varied is shown in Figure 4.3. Powder containers made from both acrylic and

Teflon were tested and had no effect on the amount of material collected. The amount of material adhered to the rod increases with the voltage for all materials until about 20kV. Note that when the VDG is grounded much smaller amounts of material adhere to the rod even though they had been prepared in the same manner as the materials subjected to higher voltages. For voltages higher than about 20kV, discharges occur between the rod and the powder surface. These discharges occur seemingly at random, but become more frequent as the voltage is raised and result in the reduction of the amount of material adhered to the rod, making the adhesion of material at voltages higher than 20kV substantially more erratic. The amount of material adhered to the rod is dependent on the material used. For a given voltage the mass of material increases from lactose to glass beads to white sand to cellulose. At 20kV the mass of cellulose is an order of magnitude larger than the mass of lactose adhered to the rod. The dielectric constants are fairly similar (see Figure 4 caption) so it is not obvious that a difference in dielectric constant can explain this behavior. However it is worth noting that the amount of material that sticks seems to increase for angular particles (art sand, MCC) compared to the roughly spherical particles (lactose, glass beads) as can be seen in the inset to Figure 4.3. This is not unexpected since the angular materials have a greater propensity for complex polarization, and can interact over larger surface areas than spherical particles. Several other parameters, such as particle size and humidity, as well as potential methods to prevent adhesion, are discussed in later sections.

In industrial settings, high voltage equipment may not be commonly present near powder handling operations. However, nonconducting materials such as plastics or glass would be present in some operations [44]. This begs the question of whether or not these materials, when charged, can produce electrical field of the strength necessary to cause significant DEP agglomeration. To examine this possibility we replaced both the metallic rod and the VDG with charged plastics and examined their ability to agglomerate powders.

A tribocharged acrylic rod was used to attract clusters of particles, as can be seen in the inset to Figure 4.4. This behavior was used to verify that the adhesion of particles to both the metallic and plastic rods is created by DEP forces and not other electrostatic effects. Cellulose was allowed to sit in the powder container for over 48 hours, to ensure that any electrostatic charges developed by the powder during the filling of the container were significantly dissipated, at which point an acrylic rod was tribocharged and immersed in the cellulose. The cellulose only adhered to the plastic rod when the rod was charged, indicating that the nonuniform field of the plastic rod is responsible for the observed behavior and not any charges on the powder itself.

To compare the adhesion of powder due to electric fields produced by tribocharged materials to adhesion caused by the electric field produced by the VDG, a sheet of Teflon was charged by rubbing with a paper towel until discharges could be heard, at which point the powder container, filled with cellulose, was then placed on the charged sheet and a grounded, metallic rod was brought to the surface of the powder but not immersed. The amount of adhered powder was 0.2±.1g when the sheet was charged and almost no material adhered when the sheet was left uncharged. To compare the amount of material adhered to the rod in the presence of the charged sheet to the amount collected in the presence of the VDG, the VDG experiments were repeated, only in this case the rod was brought to the surface of the powder while the VDG was active, as

opposed to immersing the rod in the powder before activating the VDG. It was found in both cases that immersing the rod after the electric field was present tended to increase the variability of the measurements, which may be due to the adhesion of the particles to each other becoming stronger than the adhesion to the rod as the particles are pushed out of the way of the rod. Both methods produced similar trends, differing mainly in magnitude. As shown in Figure 4.4 the amount of material adhered to the rod when subjected to the tribocharged Teflon field corresponds to a voltage of about 12kV on the VDG. While the actual voltage of the plastic sheet is not directly comparable to the voltage of the VDG [73], the electric fields of the two systems are strong enough to cause significant agglomeration of the powder.

4.1.2 Force calculations

By examining the mass of the powder adhered to the rod, the strength of DEP interactions can be estimated and compared to the forces commonly observed in electrostatic systems. We can compare the strength of the forces measured here to electrostatic forces in several ways. Here we choose two bracketing cases to compare to DEP forces, namely the electrostatic forces produced by charges experimentally observed by filling and emptying the powder container and the forces produced by grains charged to their theoretical maximum. The maximum surface charge a particle of a certain size can possess is limited by the discharge strength of air, and is typically about 27μ C/m² for particles 100µm and larger [73].

We estimate the DEP force acting on those particles directly in contact with the rod, assuming they support the mass of all adhered grains. The assumption that all particle weight rests on those particles in contact with the rod is a simplification that would tend to overestimate the actual forces. Those particles not in contact with the rod would undoubtedly experience some attraction to the rod due to DEP, and therefore would not be supported fully by attraction to nearby grains. However, this force depends on the gradient of the electric field and most likely decays rapidly as the distance from the rod increases [123]. From Eq. 1.5 it can be shown that for a spherical geometry the DEP force varies as a function of r^{-5} and therefore drops to zero rapidly. Particles a few grain diameters away from the rod are likely to the supported almost entirely by interparticle DEP forces [123], which would be supported by the inner grains, making our assumption reasonable for an order of magnitude analysis. The maximum number of grains contacting the rod can be estimated to be about $2x10^4$, $3x10^3$, $2x10^3$, and $1x10^4$ for cellulose, sand, lactose and glass beads respectively, by assuming that the particle coverage of the rod is hexagonally close packed. Therefore, by taking the mass of typical agglomerates observed at 20kV those innermost particles of cellulose experience a force of about 6×10^{-7} N while the white sand particles experience a force of close to 5×10^{-6} N. Lactose and glass beads experience about an order of magnitude less force than the sand or cellulose; all of these forces are summarized in Table 4.1.

The electrostatic forces acting on particles of these sizes can be easily compared in two manners: the image force and the force produced by the electric field created by the VDG in these experiments. The image force, or the electrostatic force acting on a particle when in contact with an identical particle possessing an equal but opposite charge, $F = kq^2/R^2$, where k is a constant, q is the charge of the particle and R is the radius of a particle, is also the force a particle would experience in contact with a uncharged conductor. It is also interesting to compare the forces acting on particles with these charges within electric fields of a similar strength to those observed in these experiments. If the electric field is roughly estimated to be on the order of the voltage (V) divided by the distance (d) between the rod and the VDG, the forces acting on the particles can be estimated by F = qV/d. This allows us to compare the forces acting on these particles due to their own charge (image forces), as well as the electrostatic forces created by an applied electric field, to the DEP forces measured using this system and to estimate the relative importance that DEP effects may have on granular processes. These estimates are summarized in Table 4.1 for both the measured charge of the particles and their maximum possible charge.

As can be seen in Table 4.1 the results of these calculations show that the charges measured in these experiments for these materials are not large enough to account for the size of the agglomerates observed here. For both calculations the forces due to the measured charges are at least 3 orders of magnitude too small. The forces that could be created by the maximum charge acting on the particles are significantly larger and are comparable in strength to the DEP forces estimated above. It would seem that DEP forces could be larger than electrostatic interactions alone, except for particles that are highly charged. However, even this maximum possible charge may only rarely be reached, as was discussed in chapter 3, a particle's charge often reaches a saturated level at much smaller amounts [131]. In addition, the electric fields produced by highly charged grains are themselves nonuniform and could potentially be large enough to create

significant DEP forces in uncharged grains. This possibility is examined further in the next section.

4.1.3 Effect of humidity

High humidities have been long been known to reduce the effects of electrostatics. Similarly, by controlling the humidity it may also be possible to prevent significant DEP attraction. Commonly, materials become less prone to charging as the humidity is raised and adsorbed water layers on the surface of particles makes them more conductive [62, 141, 142]. However, recent electrostatic experiments have shown that some pharmaceutical powders show little response to changes in humidity [15]. We wish to determine if humidity can be used to prevent significant adhesion due to DEP. To do this we varied both the relative and absolute humidity and determined the amount of adhesion for both cellulose and white sand.

The concentration of water in the air is referred to as the absolute humidity, usually denoted in grams of water per m³ of air, while the ratio of the absolute humidity to the saturation concentration is known as the relative humidity. Under equilibrium conditions the amount of water adsorbed to a surface is controlled by the relative humidity [143, 144], making it the main factor in controlling electrostatic properties, rather than the absolute humidity. Although the absolute humidity is not believed to play a large role in electrostatic behavior it does affect the mobility of ions in the air, which

may be an important factor when working with large electric fields, such as the ones need to produce DEP.

To determine the effect of relative humidity on adhesion caused by the DEP force, we placed white sand and cellulose in a temperature and humidity controlled room for at least 16 hours before performing an experiment. When the relative humidity was varied and the absolute humidity kept constant, at around 3.7 g/m^3 , the amount of adhering cellulose decreased as the relative humidity increased, as shown in Figure 4.5. Surprisingly however, the amount of sand adhered was observed to *increase* with an *increase* of the relative humidity over the range of humidities examined.

As the relative humidity is raised the amount of water on a surface tends to increase, however, the thickness of the water layer on a surface depends greatly on the chemistry and porosity of the surface. Cellulose is well know for absorbing water readily [145] and therefore it is not surprising to observe an increase in conductivity and decrease in adhesion as the relative humidity is raised (as it is easier for the particles to become charged and repelled from the rod [146]). In fact, the amount of water absorbed to a cellulose surface need to reach a monolayer occurs at about 20% relative humidity [145]. Sand however, is well known for adsorbing only small amounts of water at low humidities and therefore sand's conductivity has a weak dependence on the relative humidity (at least at low humidities) [147, 148], which helps to explain why sand does not decrease in adhesion as cellulose does. However, water has a very large dielectric constant (80 as apposed to 2-7 for most solids) and the addition of even small amounts of water to a particle's surface has been shown to increase its dielectric constant, which in turn increases the DEP force acting on the particle [149]. This can account for sand's

ability to increase in adhesion as the relative humidity is increased. We would expect that further increasing the relative humidity, to around 50%, would lead to a decrease in the amount of sand adhered, as that is the humidity region at which significant amounts of water adhere to quartz surfaces [147]. However, we were limited in this case by the capabilities of our humidity controlled room.

As the absolute humidity does not control the thickness of water layers adsorbed to surfaces, it is somewhat surprising to find that increasing the absolute humidity can dramatically decrease the amount of adhered material. When the relative humidity was kept constant at 13% and the absolute humidity varied between 2 and 4 g/m^3 , both materials showed very little change in behavior, as can be seen in Figure 4.6. However, when the absolute humidity was increased further, the amount of adhering cellulose suddenly decreased. Similarly the adhesion of white sand also decreased suddenly after the absolute humidity was increased above about 5 g/m^3 . This surprising result is made all the more mysterious as increasing the absolute humidity, while keeping the relative humidity constant, requires that the temperature be raised (from 19 to 37°C in Figure 4.6) and increasing the temperature tends to reduce the amount of water adhered to a surface [150, 151], which should render the particles even less conductive than at low temperatures. In addition, increasing the absolute humidity tends to increase the resistively of air, preventing the conduction of a significant charge from the VDG to the particles [152]. The excess water vapor in the air decreases the mobility of airborne ions, which are responsible for conducting electricity through the air. This leads to something of a conundrum as one would expect that increasing the absolute humidity, and with it the temperature, while holding relative humidity constant, would result in less water on the

surfaces of the particles and therefore more resistive powders (which are less likely to be charged by conduction from the rod) as well as a slight decrease in the dielectric constant of the materials, due to the lack of water. Instead a very sudden, material dependent cutoff in the adhesion is observed as absolute humidity is raised.

One mechanism that could lead to observations such as this, is that the concentration of ions produced near an electrode tends to increase in higher absolute humidities [153]. This high concentration of ions is due to the capture of those ions by clusters of water, which significantly reduce their mobility preventing them from moving away from the rod quickly [153] and making them available for collision and adhesion to the particles, charging the particles [85]. This mechanism would depend on the size of the particles, with larger particles requiring larger absolute humidities, and therefore larger concentrations of ions, to become charged, which is consistent with our observations (cf. Figure 4.6).

More research is necessary to determine the mechanism for this absolute humidity dependence. However, regardless of the reasons for the decrease in the adhesion at higher absolute humidity, the results pose a potential method to prevent flow problems caused by DEP. Raising the relative humidity to a sufficiently high level should result in the decrease of DEP adhesion, however, increasing the relative humidity can also result in other unwanted powder handling problems such as agglomeration and sintering [154]. Luckily the absolute humidity does not impact these behaviors but does appear to reduce DEP adhesion. Therefore, setting the absolute humidity above some cutoff limit may prevent most DEP adhesion while allowing the process to operate at a moderate relative humidity.

4.1.4 Particle size

The effect of particle size on the DEP force acting on the particles was investigated using glass beads of various mean diameters. In general, the mass of particles adhering to the rod increases as the particle size decreases, until a maximally adhering diameter is reached, about 150 microns, at which point the amount of adhesion suddenly decreases, as is shown in Figure 4.7. Several factors vary as the particle size is changed. As can be seen from Eq. 1.5, the DEP forces should decrease as the volume of a particle is decreased for a given ∇E^2 , due to the decrease in the size of the particle's dipole moment. However, this is not observed in the data as the amount of adhesion increases as the particles size is decreased, for a certain range of particle sizes. This may be caused by the variation of ∇E^2 with distance from the rod [123]. For large particles, this results in a decrease in the DEP force, as fewer large particles are able to fit inside the high ∇E^2 region [86]. The geometry of the electric field also plays a role for smaller particles, as they may be small enough that the electric field varies slowly over the length of the particle, producing a smaller force. The combination of these factors leads to fewer of both the largest and smallest particles that are able to adhere to the rod, resulting in the creation of a particle size with a maximum response to this particular electric field. It is expected that a different electric field geometry would likewise experience maximum particle attraction at a particular particle size although not necessarily the same one observed here.

4.1.5 Conductive particles and coatings

To determine possible solutions for any flow problems caused by DEP, white sand particles coated with semiconducting TiO₂ nanoparticles (Degussa, Aeroxide TiO₂ P25, ~20nm) were tested along with uncoated sand [139]. It was found that the coated particles did not adhere to the rod at any voltage. In fact, most particles that did contact the rod jumped suddenly away from it. We believe that the relatively high conductivity of the nanoparticles allowed them to be charged as they came in contact with the rod resulting in their repulsion. To test this hypothesis further we also experimented with stainless steel powder ($100\pm20\mu$ m) and found that the powder was also repelled by the rod after contact. This suggests that coating particles with a layer of much smaller conductive particles can be used to greatly reduce their tendency to stick or agglomerate near nonuniform electric fields even when using only a small amount of coating material [139].

4.1.6 The effect of grounding

Often grounding process equipment is used as a method to control static electricity effects [12, 44]. While grounding may prevent dangerous electrostatic discharges [44], recent studies have shown that grounding may not be effective at preventing particle charging [12]. To test if grounding of equipment may be effective in reducing the adhesion produced by DEP, an experiment was conducted using grounded

and ungrounded rods. It was found that, at 20kV, grounding not only failed to decrease the amount of material that adhered to the rod but actually *increased* particle adhesion. Cellulose increased by a factor of almost 2, from 0.83 ± 0.09 g to 1.5 ± 0.2 g, when the rod was grounded, and the amount of white sand that was collected from the rod increased, by a factor of 3, from 0.34 ± 0.04 g to 1.01 ± 0.05 g. Any problems caused by DEP particle adhesion could be exacerbated by grounding process equipment rather than alleviated, as might be expected. The effect of grounding equipment on the flow of materials is investigated further in section 4.2.

4.2 The effect of DEP on flowing particles

To determine the effect of DEP on flowing granular materials white sand was allowed to flow from a metal cylindrical hopper in the presence of a strong, nonuniform electric field. As can be seen in Figure 4.8, when the VDG is placed close to the opening of the hopper, large agglomerates of grains adhere to the opening, reducing the area through which grains can flow. As the sand exits the cylinder, grains attach to the large clusters causing the clusters to grow. The particles that do not adhere to the opening are observed to form clusters as they fall, while the grains flow smoothly when no electric field is present. Occasionally a large cluster or the entire adhered mass will fall away from the cylinder opening only to quickly reform.

As the clusters obstruct the opening of the hopper, the flow rate decreases. This dependence of the flow rate on the voltage of the VDG is shown in Figure 4.9. The flow

rate was determined by measuring the time necessary to empty a given amount of sand from the cylinder. At the highest voltages, the flow rate is almost reduced by a third. The flow has also been observed to occasionally cease altogether when the agglomerates grow large enough to block the hopper's opening altogether, although this seems to occur at random. Certainly DEP forces can significantly alter the flow behavior of these grains. Figure 4.9 also shows the effect of grounding the hopper, which increased the size of the agglomerates attached to the exit of the hopper, further decreasing the flow rate from the hopper. As was observed for the adhesion of grains to the rod, grounding intensifies the impact of DEP.

When the metallic hopper is replaced with an acrylic hopper of similar dimensions and the VDG is removed, the flow is observed to behave in a similar manner (see Figure 4.10(a)). The clusters produced by the acrylic cylinder are of a similar size to those produced by the metal cylinder exposed to the VDG at high voltages. However, unlike the metallic cylinder, the flow through the plastic cylinder begins to rapidly stop and start after the flow has been active for a long enough period of time (~5mins). Often the flow stops altogether.

A similar experiment was carried out with a metal hopper placed 5cm from an inclined acrylic sheet. As the sand exited the hopper it flowed down the surface of the sheet causing the sheet to become highly charged. The hopper then developed a "beard" of agglomerated material around its exit, as can be seen in Figure 4.10(b), in a similar manner to that observed for both the metal and plastic cylinders.

Both the flow from a plastic hopper and the flow over a plastic sheet show grains can spontaneously form electric fields strong enough to induce DEP attraction simply by tribocharging with nearby equipment, and that DEP attraction can significantly reduce the rate of flow from these hoppers. It would seem that, again, an electric field produced by tribocharging can be strong enough to create significant DEP forces and affect the flow of a material, without the need for an externally applied electric field.

4.3 Agglomeration of particles

When particles become charged the electric fields produced by that charge are invariably nonuniform and therefore their field could potentially induce DEP forces strong enough to result in agglomeration of particles in the midst of the blend. This problem is of acute importance in pharmaceutical processing, where agglomeration of active substance particles can lead to overdosing as well as decreased or hindered drug bioavailability. To test this possibility acrylic beads (3mm in diameter) were charged by shaking vigorously in a plastic container and then poured onto cellulose, which had been thinly spread over a piece of felt. As can been seen in Figure 4.11, the charged acrylic beads attract cellulose particles to those areas of the beads that came into contact with the cellulose as the beads rolled. Figures 4.11(a) and (b) show cellulose particles forming spiked clusters on the surfaces of several acrylic beads similar to those observed attached to the rod and hopper exit. In Figure 4.11(c) a bead that has been completely covered in cellulose is shown.
In order to rule out electrostatic attraction of the beads and cellulose we measured the charge of the cellulose and the beads. The cellulose was poured into a Faraday cup, after being spread on a piece of felt, and the charge measured to be 1×10^{-4} nC per particle. The charge of acrylic beads was also measured and found to be -4×10^{-2} nC/particle. Using Coulomb's law it can be shown that the electrostatic forces acting on the cellulose (about 5×10^{-9} N) are 2 orders of magnitude smaller than the weight of an average cellulose particle (about 2×10^{-7} N). From Figure 4.11 it can be seen that many grains of cellulose are adhered to the surface of the beads, sometimes creating agglomerates which are almost as long as the diameter of the beads. It seems likely that DEP forces are responsible for creating these large agglomerates.

This DEP induced agglomeration could affect the mixing of two materials, with one material forming a thick coating around the other. The effect of this agglomeration between charged and relatively uncharged grains could result in changes to the flowability of even pure powders. The addition of only a relatively small number of highly charged particles could have a large impact on the behavior of the entire material. The significance of these observations is to demonstrate that DEP-induced agglomeration can occur spontaneously after materials have been "delumped" and fed to the processing equipment.

4.4 DEP and razorbacks

By comparing the results from this chapter to the results of chapter 2, it can be concluded that the agglomeration of the grains which create razorbacks is most likely due to DEP forces induced by the highly charged acrylic sheet. The razorbacks are observed to form over time as the flow of grains charges the plastic surfaces. The jagged agglomerates produced during the flow share may features with the agglomerates produced by the rod or at the exit of the cylindrical hoppers (cf. Figure 2.13, 4.2 and 4.10), in that they tend to prefer shapes that maximize the nonuniformity of the local electric field. These clusters form in the flow and interfere with the creation of other flow instabilities. This hypothesis also helps to explain the anomalous charging of the sand grains as they flow down the chute in the presence of an electrostatic eliminator (see Figure 2.18). It was observed that if the eliminator is present the clusters of grains do not form but the charge of the particles is larger than when the eliminator is removed and clustering does occur.

When the eliminator is not present the grains become agglomerated and those particles near the surface tend to remain at the surface and never contact the chute and as we observed in chapter 3 if the grains cannot reach the surface they cannot charge. If the eliminator is present, then the charge of the chute is constantly neutralized, preventing the particles from agglomerating and allowing them to mix from the surface to the base and charge in greater quantities; leading to an increase in the net charge of the particles. With our improved understanding of the forces at work on particles in electric fields we can now see that DEP forces can dominate the behavior of flowing particles and can even create new flow instabilities. While the cellular automata model presented in chapter 2 could not be modified to capture the effects of electrostatics, because not enough was known about those effects to reduce them to simple rules, it may be possible to create other cellular automata, as well as more sophisticated models, which do include electrostatic and dipole interactions. This next step in predicting and understanding the behaviors of granular materials will need to be carried out in the future and are discussed in greater detail in the next chapter.

4.5 Conclusions to DEP adhesion

The ability of DEP forces to agglomerate powders was tested using both metal and plastic rods. The adhesion and agglomeration produced either by a high voltage source or by tribocharged materials was found to be comparable, suggesting that any nonconducting surface could create DEP agglomeration if allowed to charge to significant levels. The forces acting on the particles were calculated to be much larger than the electrostatic forces acting on grains with charges produced by filling and emptying the powder container. The forces measured here were similar in scale to the electrostatic forces acting on particles charged to their maximum level. While these are only estimations, it seems clear that under the right conditions DEP forces can be as large as those acting on highly charged grains. The presence of strong nonuniform electric fields, even those produced by tribocharged materials, are enough to produce these significant forces and create sizable agglomerates. The effect of humidity on the adhesion of the grains was examined and found to eliminate adhesion after a critical absolute humidity. However, further increases in the relative humidity were found to decrease the adhesion of cellulose while increasing the adhesion of sand.

Adhesion first increases and then decreases as particle size increases. The particle size that resulted in the maximum particle adhesion was found to be about 150µm for glass beads. Semiconducting nanoparticle coatings were examined as a method to prevent adhesion and were found to prevent sticking almost completely. Another method commonly used to control electrostatic phenomena, grounding process equipment, was found to actually increase the amount of material that adhered to the rod by factors as high as 2 or 3.

The flow of sand from a cylindrical hopper was also subjected to nonuniform electric fields. The electric fields, whether supplied by the VDG or tribocharging, were intense enough to reduce the flow rate of grains from the hoppers by forming large agglomerates adhered to the exits. Again, grounding the equipment only exacerbated the problems caused by DEP.

It was found that charged grains were able to adhere to uncharged particles and form agglomerates due to DEP attraction. This suggests that the effect of a few highly charged grains on the agglomeration and flow of powders may be significant. These effects, which could help explain undesirable observations of drug content variability, will be studied in greater detail in future experiments. It is also important to note that many of the flow problems and effects that are commonly attributed to electrostatics, may in fact be the result of DEP. If that is the case removing the charges of the particles will do little to improve process behavior if the process equipment has become significantly charged itself. In this case improving granular flow will require that the charge of the equipment, rather than the charge of the particles, be remedied.

Finally, DEP also appears to be able to significantly affect the flow of grains down chutes. As can be seen in chapter 2, the charge developed by a plastic chute through triboelectrification is enough to create significant agglomeration and interfere with other flow instabilities. These DEP induced flow instabilities may have a significant effect on the uniformity of products under conditions which promote charging of equipment surfaces.

Hopefully this research will provide methods to limit or prevent significant DEP problems in processes where agglomeration and adhesion are not wanted. However, as will be discussed in more detail in the next chapter, it is possible that DEP forces may be utilized to improve on current particle handling techniques. These methods are more attractive than other electrostatic techniques because it does not require the particles to be uniformly charged. Only the voltage of the equipment must be controlled, which can be adjusted during a process much more easily than the charges of the powder itself.



Figure 4.1 Schematic of the Van de Graaff generator with powder container on its top surface. The rod is suspended above the powder container by a jig that allows it to be smoothly raised or lowered. The circuit used to control the voltage of the VDG is also displayed here. R1 is a variable resistor comprising a finely tipped grounded wire, which acts as a corona source. By moving the wire nearer or farther from the VDG the resistance can be raised or lowered. R2 is a large (20 G Ω) resistor, which is used to step-down the voltage as current passes through the resistor to an ammeter, where the current is determined and used to calculate the voltage of the VDG.

Material	DEP Force (N)	Charge per Particle (nC)		Measured Charge		Maximum Charge	
		Measured Charge	Maximum Charge	Image Force (N)	Electric Field (N)	Image Force (N)	Electric Field (N)
Cellulose	1×10 ⁻⁶	1.3x10 ⁻⁶	2x10 ⁻³	8x10 ⁻¹³	2x10 ⁻⁹	1x10 ⁻⁶	2x10 ⁻⁶
White Sand	5x10 ⁻⁶	5.0x10 ⁻⁵	8x10 ⁻³	3x10 ⁻¹⁰	7x10 ⁻⁸	6x10 ⁻⁶	1x10 ⁻⁵
Glass Beads (150µm)	1x10 ⁻⁷	3.2x10 ⁻⁶	1x10 ⁻³	4x10 ⁻¹²	4x10 ⁻⁹	1x10 ⁻⁶	3x10 ⁻⁶
Lactose	6x10 ⁻⁷	3.4x10 ⁻⁷	2x10 ⁻³	9x10 ⁻¹⁴	5x10 ⁻¹⁰	8x10 ⁻⁷	1x10 ⁻⁶

Table 4.1 Comparing the DEP and electrostatic forces acting on particles with either the charge that the particles developed after being placed and then emptied from the powder container or with their maximum possible charge amount.



Figure 4.2 (a) Cellulose, (b) sand and (c) $150\mu m$ glass beads adhered to a grounded metal rod above the VDG generator at 20kV. Almost no material adheres to the rod when the VDG's voltage is 0.



Figure 4.3 The mass of material adhered to a grounded rod as a function of the voltage of the VDG. As the voltage increases so does the strength of the electric field allowing more material to adhere to the rod. These data points are the average of 5 trials and the error bars are one standard deviation. In each experiment the temperature and relative humidity were held constant at about 65°F and 14% except for lactose, which was measured at 75°F and 10%. The glass beads used here are 180µm in diameter. Inset: Pictures of the materials used here, taken with a polarizing light microscope at 40x. The cellulose and white sand are the farthest from spherical while glass beads and lactose are spherical or close to spherical. The dielectric constants of the materials used here range from: 3 - 8 for cellulose [149], 5-7 for lactose [155], 3-5 for sand, and 3-7 for glass [156, 157].



Figure 4.4 Comparing the mass of powder adhered to the rod due to the VDG and a tribocharged sheet. The mass of cellulose adhered to a metallic grounded rod when the rod is brought to the surface of the powder bed and then removed, for several voltages of the VDG. The averages here are of 3 trials and the error bars are one standard deviation. The line represents the average adhered mass of particles when placed on a charged Teflon sheet and intersects the amount adhered due to the VDG at about 12kV. The dashed lines are placed one standard deviation away from the average. Inset: Cellulose adhered to the end of a tribocharged acrylic rod. Material did not adhere to the rod if it was not tribocharged. Temperature and relative humidity are 69°F and 21%, respectively.



Figure 4.5 The mass adhered to the rod at 20kV as the relative humidity is varied and the absolute humidity is kept constant at about 3.7 ± 0.3 g/m³. The adhesion of cellulose falls to almost zero as the relative humidity is increased to 20%. However, white sand tends to increase its adhesion as the humidity is raised.



Figure 4.6 The mass adhered to the rod at 20kV as the absolute humidity is varied at a constant relative humidity of about $13\pm2\%$. The amount of adhesion varies little until almost $4g/m^3$ for cellulose and $5g/m^3$ for sand.



Figure 4.7 The effect of particle size on the adhesion of spherical glass beads. The VDG here is set to 16kV and the temperature and humidity are 70°F and 13%. The size of the particles which produce the largest response to the field are about 150 μ m in diameter.



Figure 4.8 Agglomerates form at the exit of a cylindrical hopper in the presence of a strong electric field. a) The flow of sand is smooth when the voltage of the VDG is 0V. b) A view of the agglomerates that form at the exit of a cylindrical hopper at 25kV. The cylinder is about 2.86cm in diameter and the opening for flow is 1cm across.



Figure 4.9 The average flow rate of sand empting from a metal cylindrical hopper when the hopper is subjected to a nonuniform electric field. The flow rate from a grounded cylinder (diamonds) decreases to a greater extent as the voltage of the VDG is raised than the flow rate of an ungrounded cylinder (squares). Inset: Pictures from below the exit of the hopper where the voltage of the VDG varies between 0, 20kV and 24kV from left to right. More material adheres to the exit as the voltage is raised and the area available for flow decreases. Here the temperature and relative humidity are 82°F and 14%.



Figure 4.10 a) The flow of sand from an acrylic cylinder. No external electric field is present in this case. The grains exiting the cylinder form large agglomerates in a similar manner to the metallic rod in the presence of an applied electric field. b) The flow of sand from a metal hopper onto an acrylic sheet. The hopper forms agglomerates around the exit. The grains tribocharge the plastic sheet creating large electric fields.



Figure 4.11 Agglomerates of cellulose and acrylic beads. The beads in these pictures are 3mm in diameter. a) Several jagged agglomerates of cellulose formed around acrylic beads. b) A closer picture of two beads partially covered in agglomerates. c) A bead that is completely covered in agglomerated cellulose. Here the temperature and relative humidity are 80°F and 25%.

Chapter 5 Conclusions and Future Work

This work has explored some of the complex interactions that can occur between granular materials and electrostatic forces and has shown the profound impact those forces can have on the flow of particles. These forces have been shown to not only affect the already complex behavior of granular materials but that they can also be used to control the motions of even uncharged particles. We have attempted to address some of the gaps in the knowledge of how electrostatics affects particle flow, how charging occurs during flow and how electric fields can affect uncharged particles. The ability to predict and scale-up the charge produced during the flow of grains has also been examined

Many complex flow instabilities can be created by granular processes that are independent of electrostatic forces. During the flow of particles down inclined planes, several of these instabilities, such as shockwaves, longitudinal vortices and chevrons, were modeled and examined using a cellular automata model. Even though this qualitative model is very simple it was successful in reproducing many of the patterns created by experimentally observed flow instabilities. When electrostatic charging does occur, new flow instabilities arise. These new instabilities not only alter the appearance of the flow but also result in the agglomeration and the ejection of many grains from the surface of the flow and may result in significant flow problems in industrial settings. These patterns were suppressed when a static eliminator was brought close to the surface of the flow, however, it was observed that the charge of the grains increased as the static eliminator was lowered. This leads us to conclude that the agglomeration of the grains must be due to heterogeneous charges present on the particles, and as was observed in chapter 4, the polarization of the particles due to the highly charged acrylic sheet is the most likely cause of their agglomeration.

The charging of grains during a relatively simple flow was studied and found to result in complicated charge distributions, especially in the case of bi-disperse mixtures. This system allowed the underling charging behavior of granular materials to be studied and the charge distributions that can be created by a flowing material to be examined. As grains flowed through a metallic cylinder only those grains near the inner surface of the tube charged significantly. This resulted in a separation of charge between the inner and outer regions of the flow, and in the case of mixtures, the charge developed by those particles near the walls dominated the net charge of the mixture.

This dependence of the charge on the surface area available for contact between the grains and the cylinder represents a possible method for predicting the charge developed by grains flowing through much larger process equipment, which will hopefully allow the behavior of flowing particles on an industrial scale to be better understood. The charge developed during processes which result in a greater amount of mixing may also be predicted as the charge developed by those particles near the walls reached a plateau. The charge picked up by those particles that contact the cylinder walls was estimated to be about 10⁻⁵nC per sand particle. It was found that the charge developed by mixing grains strenuously produced similar charge on each particle. Methods to prevent particle charging were also tested. Grounding the cylinder did not reduce the charge produced by the grains. However, coating the grains with semiconducting nanoparticles did prevent the sand grains from charging. These results demonstrate that it may be possible to predict the amount of charge produced by granular flows.

Finally the significant role that nonuniform electric fields can play in the behavior of granular materials was also investigated. The agglomeration and adhesion caused by these fields, regardless of whether they were produced by a high voltage source or a tribocharged material, was of a sufficient strength to rival the Coulombic forces acting on highly charged particles. The amount of material that adhered to a metal rod when in the presence of a strong electric field was measured for several powders, including: white art sand, glass beads, steel powder, cellulose and lactose. It was found that the material's response to the electric field and how that response is affected by changes in absolute or relative humidity is highly dependent on the material's composition. Some materials adhered to the rod in large amounts such as sand and cellulose, while others, like lactose, adhered in smaller quantities. Increasing the absolute humidity past a material dependent critical humidity limit, almost completely prevented particles from adhering to the rod. Increasing the relative humidity, while keeping absolute humidity constant, decreased the amount of cellulose that adhered to the rod while increasing the adhesion of sand. The size of the particles also greatly affected their behavior, with particles of an intermediate size adhering to the rod in greater quantities than smaller or larger particles. While coating the particles with semiconducting nanoparticles was found to reduce adhesion, grounding the rod actually increased the amount of material which was able to adhere. This suggests that grounding process equipment may actually exacerbate problems caused by DEP. These forces were also able to significantly slow, and sometimes stop, the flow of grains from a cylindrical hopper. These higher order electrostatic effects may play a significant role in the agglomeration and flow instabilities observed under both experimental and industrial conditions, however, they also represent a possible mechanism for the control of particulate motion, even if the particles remain uncharged.

The electrostatic effects observed here in both stationary and flowing materials cannot be overlooked if a truly complete theory of granular behavior is to be developed. These effects can dominate the behavior of these materials under the right conditions, and those conditions may be unavoidable in many industrial processes. Electrostatic agglomeration can dramatically change the flow of grains down a chute. The charging processes that grains go through in common particle flows has also been investigated and a better understanding of how charging occurs and how charge distributions are created has been gained. The mechanisms that lead to agglomeration and adhesion, such as DEP, have also been examined and the parameters that control these processes have at least partially been explored. These studies have hopefully increased not only our knowledge of the effects of electrostatic but also improved our understanding of the processes that create these electrostatic effects. More knowledge of this kind will be needed if the prediction and prevention of electrostatic problems in industry is to be realized; in addition, the opportunities presented by these forces also must not be overlooked. The ideal particle handling technology would allow individual grains to be manipulated, mixed and moved, and currently electrostatic forces may represent the best method for controlling particle behavior on a fine scale. To further build upon the work presented here, projects, which may be carried out by future students, are presented below.

Future work

Two of the most problematic effects caused by electrostatics are segregation, which can cause product nonuniformities, and electrostatic discharges, which can trigger dust explosions. The distribution of charge on granular materials could be a significant factor in both of these behaviors. As was seen in chapter 3, the charge distribution in a mixture can be influenced by the concentration of the component that reaches the surface of the container. This could then lead to the segregation of the charged, outer material from the uncharged material in the center of the flow. While segregation and charge distribution have been examined previously [4, 5, 63], those studies focused on material which had been subjected to mixing and did not develop a charge distribution due to a difference in opportunity to contact equipment surfaces, as has been observed here. It may be interesting to observe the degree of segregation experimentally, perhaps by allowing particles, which have exited a cylinder, to flow through a strong uniform electric field and monitor the amount of segregation that takes place. The electric field could be supplied by either a high voltage source or a tribocharged material, which may be

commonly found in industrial situations. Observation of this segregation would confirm that the distribution of charge, which could occur in any low-mixing flow, can result in the variation of the concentration of a material in a mixture and this would also allow methods to limit this segregation to be tested, such as by uniformly charging all particles in a mixture.

Electrostatic discharges may also be created by this distribution of charge. For a discharge to occur charges of opposite polarity must be separated in considerable quantities. When the separation has created a strong enough electric field, breakdown can occur, which can then ignite dust clouds and cause an explosion. The initial separation of charge can occur in several ways, such as the charging of a powder and process equipment walls or the separation of oppositely charged particles within a flow [4, 5]. With judicious use of materials and safety procedures the charge buildup on process equipment can be limited [44]. However, the charge developed by the particles themselves can be much more difficult to control. The question can be raised as to how the separation of charged particles takes place during a flow, as the oppositely charged particles should attract one another and therefore should be unlikely to separate. A mechanism similar to that shown in chapter 3 may be responsible for this separation. If only some of the particles in a flow are charged and these particles do not mix with the particles near the center of a flow, the charges would be automatically separated. This may help to explain why so many dust explosions occur during the filling and emptying of containers and hoppers [44, 72], as these flows have already been shown to result in a large distribution of charge between the outer and inner particles. Further study could reveal methods that can reduce the likelihood of discharge during these processes.

As for the effects of dielectrophoretic forces, further study is required to observe how individual charged particles influence other particles through DEP. As was seen in chapter 4, charged particles produce nonuniform electric fields and can potentially induce DEP forces strong enough to result in agglomeration. If the charge levels necessary to cause agglomeration are easily accessible by triboelectrification, agglomerates of charged and uncharged particles may be commonly observed. As was shown in chapter 3, only some particles obtained these charges while most particles remain uncharged and could be attracted by DEP without Coulombic repulsion. To form larger agglomerates the charge of the charged particle would need to be larger and the effect of surrounding particles on the shape of the electric field may also need to be taken into account. These questions could be answered in part by a simulation of particles surrounding a charged particle and by experimental observation of the effects of adding charged grains to an uncharged material. It would be interesting to determine whether the agglomeration of a material depends on the charges of only a few grains. These simulations will also allow us to more accurately determine both the charges necessary to create agglomerates as well as their size.

Simulations of these kinds could also be used to examine granular processes that are subject to electrostatic problems. By simulating the agglomeration caused by nonuniform fields, new equipment geometries may be developed to decrease the variation of the field near the equipment and prevent agglomeration. Similarly, these models could simulate the flow of grains through a piece of equipment and be used to modify its design to minimize the contact area between the particles and its walls. This could produce equipment designed to minimize the charging of a powder during handling.

Finally, as has been mentioned previously, DEP represents a possible mechanism for controlling particle motions with relative ease and may represent the basis for new technologies for the creation of pharmaceutical tablets. To investigate these possibilities further, a device that can accurately control the voltage to a probe and simultaneously measure the amount of material adhered to the probe could be used to transfer specified amounts of material from a storage container to a small scale mixing unit and from there to the die of a tablet press. With adequate feedback control the amount of material gathered by the probe could be precisely determined and delivered to the mixer. If different components are delivered in their prescribed ratios and in amounts necessary for a single tablet, the resulting mixture could then be compressed into a tablet without the need for most of the current, large scale powder handling operations found in pharmaceutical production plants today. These methods would need to be applied at sufficient speeds to match current production rates and with adequate control and safety to be adopted by industry. However, currently there is no reason to believe that these challenges cannot be met.

In addition this process could, conceivably, increase quality control. By adjusting the ratios of material delivered to the mixer, and subsequently the press, the properties of each tablet, such as hardness, dissolution rate, and even drug concentration, could be monitored and adjusted on the fly during production. Each tablet's properties could also be recorded and then later matched to quality control tests to ensure the proper operation of the tablet formation process.

Also since each tablet would be created individually, the amounts of materials, amongst other parameters, could be varied to suit the needs of individual patients. The individualization of pharmaceuticals has long been a goal of the pharmaceutical industry and may lead to much more effective treatments for patients [158]. With the tablet specifications (drug concentration, dissolution rate, etc.) for an individual, this process could be used to create tablets specifically for that individual.

If these potential uses for DEP and electrostatic forces can be realized they may open up new horizons of granular process efficiency and product design in many industries. These processes may result in new drug delivery technologies that can potentially revolutionize the manner in which we take drugs. These techniques will require much study in the future, but will hopefully result in significant improvements for both industry and patients.

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Publications

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