TOPICAL REVIEW

Contact electrification of insulating materials

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TOPICAL REVIEW

Contact electrification of insulating materials

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Abstract
The electrostatic charge that is generated when two materials are contacted or rubbed and then separated is a well-known physical process that has been studied for more than 2500 years. Contact electrification occurs in many contexts, both natural and technological. For example, in dust storms the collisions between particles lead to electrostatic charging and in extreme cases, extraordinary lightning displays. In electrophotography, toner particles are intentionally charged to guide their deposition in well-defined patterns. Despite such a long history and so many important consequences, a fundamental understanding of the mechanism behind contact electrification remains elusive. An open question is what type of species are transferred between the surfaces to generate charge—experiments suggest various species ranging from electrons to ions to nanoscopic bits of material, and theoretical work suggests that non-equilibrium states may play an important role. Another open question is the contact electrification that occurs when two insulating materials with identical physical properties touch—since there is no apparent driving force, it is not clear why charge transfer occurs. A third open question involves granular systems—models and experiments have shown that a particle-size dependence for the charging often exists. In this review, we discuss the fundamental aspects of contact electrification and highlight recent research efforts aimed at understanding these open questions.

(Some figures may appear in colour only in the online journal)

1. Introduction

Everyone has had the experience of walking across a rug and then feeling a sudden shock when they touch a doorknob, and has observed that a balloon rubbed on hair will stick to the hair. These are just two examples of contact electrification, which is the process by which material surfaces become electrically charged as a result of rubbing or contact with another surface. Contact electrification is one of the oldest areas of scientific study, originating more than 2500 years ago when Thales of Miletus carried out experiments showing that rubbing amber against wool leads to electrostatic charging [1]. Contact electrification is also known as triboelectric charging; the term 'triboelectric' literally translates in Greek to 'rubbing amber'. As we describe below, contact electrification is among the most ubiquitous scientific phenomena, and has important consequences in many natural and technological areas.

Surprisingly, despite being so well known, contact electrification remains poorly understood and even the most basic questions are still being debated [2–8]. What causes surfaces to charge? What species are transferred between surfaces to generate the net charge? What is the driving force for charge transfer, particularly in the case of materials with identical physical properties (e.g. chemical composition, electronic structure)? Does humidity (i.e. water) or other adsorbed species play a role in the charging? Are chemical bonds on the surface broken as a result of the contact or rubbing, and does this play a role in the charging? How do insulators, which have very low electron mobilities, transfer charge?

Scientific progress towards a fundamental understanding of contact electrification has been slow because while appearing simple (so simple that even children are aware of it!), the underlying physics behind contact electrification is

actually very complex. For example:

- *Large effects are caused by relatively rare occurrences.* Even in the case of a highly charged surface ($\sim 1\,\mathrm{mC\,m^{-2}}$), the charge is a result of a net surplus/deficiency of only 1 electron unit per $\sim 10^5$ surface atoms. This implies that rare defects or contaminants on a material surface, which are beyond the realm of rigorous atomic level simulations, can dominate the charging behaviour. Also, this makes it difficult to achieve reproducible experimental results.

- *Contact electrification is a non-equilibrium phenomenon.* Separated surfaces are neutral at equilibrium (aside from small statistical variations). When two neutral surfaces are brought into contact, charge will tend to transfer until a new thermodynamic equilibrium is reached—i.e. at equilibrium for contacted surfaces, the Coulombic attraction between positive and negative surfaces overcomes the energy needed to separate charge, and causes charged surfaces to be thermodynamically favourable over neutral surfaces. As the surfaces are separated, this Coulombic attraction becomes small and the surfaces should again become neutral at equilibrium—however, the rate of charge transfer between the surfaces is negligible when the surfaces are separated, allowing the non-equilibrium situation of charged surfaces to persist after the surfaces are separated. Furthermore, after the surfaces are separated, charge slowly leaks away to the environment. Non-equilibrium phenomena are much more difficult to address than equilibrium phenomena, both theoretically and experimentally.

- *A wide range of length scales are important.* It is clear that the atomic scale ($<10\,\mathrm{nm}$) structure of a material surface plays a role in contact electrification, as it controls the chemical affinity for charge. The mesoscale ($10\,\mathrm{nm}$–$1\,\mu\mathrm{m}$) is also important; for example, surface roughness controls the extent of contact between two surfaces and can also significantly alter their electronic properties [9]. This has been illustrated by recent work that showed patterns of bipolar charge distributed on a surface at these length scales [8]. And, surprisingly, the macroscale ($>1\,\mu\mathrm{m}$) is important, as studies have shown that particle size in the range 10–$1000\,\mu\mathrm{m}$ influences the direction of charge transfer [10]. The wide range of length scales makes rigorous theoretical treatments impossible.

- *A wide range of time scales are important.* The timescales for atomic motion and electron tunnelling are very short ($<1\,\mathrm{ns}$); these timescales are important as these dynamics control the transfer of individual charges. The time scales of bulk material motion are much longer ($\sim 1\,\mathrm{s}$), but these timescales are important as well—as described above, contact charging is a non-equilibrium phenomenon and it occurs because the time scale for the separation of surfaces is faster than the time scale for the 'back-flow' of charge towards an equilibrium state of neutral surfaces. Again, the wide range of time scales makes rigorous theoretical treatments impossible.

There have been significant efforts to understand contact electrification in the context of these fundamental questions. Comprehensive and highly regarded reviews were published by Harper in 1967 [11] and Lowell and Rose-Innes in 1980 [12]—these reviews remain relevant. Of course, further work has been carried out in the intervening 30 years. The purpose of this topical review is to summarize and highlight recent progress that has been made towards a mechanistic understanding of contact electrification. We begin the review with some examples of contact electrification that motivate interest in this field (section 2). Next, we provide an overview of contact electrification and the important issues that must be addressed (section 3). We then describe mechanisms that have been proposed to explain contact electrification processes (section 4). Finally, we examine two especially interesting and poorly understood cases of contact electrification—charging of surfaces composed of the same material (section 5) and charging of granular materials (section 6).

2. Examples of contact electrification

Studies of contact electrification are motivated by both scientific curiosity, as in the case of how a balloon rubbed against hair picks up charge, and technologies such as electrophotography that depend on contact charging of materials. So many examples of contact electrification exist that it would be impossible to discuss them all. Here, we describe a few areas where contact electrification has important consequences.

Explosion hazards. Contact electrification can result in the build-up of significant electrical charge on a material surface. When this charge becomes sufficiently high, gas breakdown occurs, resulting in a spark. In the presence of a flammable material, the spark can lead to an explosion. Explosions are a major concern in granular systems [13, 14]—highly dispersed fine particles are sensitive to ignition because their large surface-to-volume ratio enhances surface contact and charge accumulation, and their dispersal in air provides the oxygen necessary for combustion.

Industrial granular flow processes. Contact charging occurs in industrial processes involving flowing granular materials, such as fluidized bed [15] and pneumatic conveying [16, 17] processes. For example, in polyolefin synthesis, polymer particles often become charged during fluidization, and the charge causes them to adhere to the reactor walls. At the reactor wall, the particles are not sufficiently cooled by the gas streams, and the heat from the continuing exothermic polymerization reactions causes the temperature of the polymer particles to increase. Eventually the temperature approaches the melting temperature and causes polymer particles to fuse together to form sheets on the reactor wall, which necessitates a costly reactor shut-down for cleaning [18].

Pharmaceuticals. Many pharmaceuticals are processed in powder form, and contact charging occurs as the particles flow during processing. The resulting electrostatic charge

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Figure 1. Our colleague, Dr Mamadou Sow, shown near a dust storm in Niamey, Niger during their annual monsoon period (June 2010).

can lead to non-uniform blending (agglomeration, segregation) [19–21], and thus non-uniform dosages in the products [22]. Additionally, contact charging can occur in pharmaceutical dispersal devices such as dry powder inhalers, and the resulting electrostatic charge can negatively impact how the particles are introduced in the body [23].

Electrophotography. All electrophotographic processes (e.g. photocopying, laser printing) rely on contact charging. Toner particles become charged by rubbing against metal beads, and the toner particles are subsequently attracted to a corona-charged drum [24]. Recent research has aimed to reduce the length scales for this process to enable nanoscale patterning [25].

Dust storms/dust devils. Contact charging occurs in sand/dust storms [26] and dust devils [27, 28] when soil particles are lifted by the wind; an example of a dust storm in Niger is shown in figure 1. As a result of particle collisions, electrostatic charge is generated on particles, which in turn affects how easily dust is lifted and moved [29] and thus the size of the storm. Dust storms have a number of implications including (i) climate change, through the interaction of particles with solar and terrestrial radiation [30] and cloud formation [31]; (ii) desertification, since semi-arid areas that are already poor in soil nutrients lose fine dust enriched in nutrients [32]; and (iii) disease, as airborne dusts can spread meningitis [33].

Space applications. Contact charging is a serious issue for space exploration including missions to the Moon and Mars [34–36]. Contact charging of lunar dust causes dust to adhere to the astronauts' spacesuits, which can be tracked into the spaceship. On Mars, dust storms and dust devils are much larger than those on Earth [37, 38], and the resulting electric fields can damage equipment. The electrostatic charge on Mars soil particles can also affect the climate (see above discussion on dust storms) and may lead to unusual geological features [39].
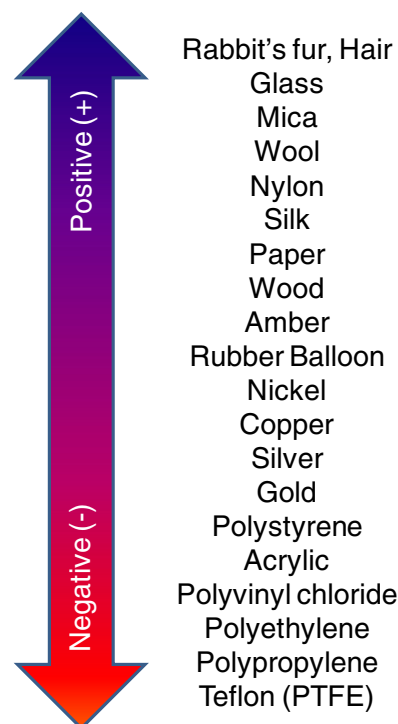

Figure 2. Example of a triboelectric series that shows an ordering of materials based on their empirically derived direction of charge transfer. A material closer to the top of the list contacted with a material closer to the bottom of the list will charge positively (while the other material charges negatively). Adapted from [12, 49].

Damage to electronics. Electronic components are easily damaged by electrical discharges caused by contact charging. Therefore, in the manufacturing of electronic components, extreme care must be taken to minimize contact charging. For example, the Intel packaging guide states that 'the simple act of walking across a vinyl floor can generate up to 12 000 V of static electricity. This is many times larger than the charge needed to damage a standard Schottky TTL component' [40].

Origin of life. Contact electrification may have played a key role in the origin of life. The seminal study by Miller in 1953 [41] demonstrated that amino acids can be synthesized from an electrical discharge in an appropriate gas mixture. A recent report suggests that this scenario is most likely realized during volcanic eruptions [42]. Volcanic plumes contain a rich variety of gases that could serve as precursors to amino acids, and the violent agitation of ash in the plumes leads to contact charging of the ash particles [43], which in turn leads to electrical discharges (i.e. lightning) [44–48].

3. An overview of contact electrification

3.1. Direction of charge transfer

Contact between a pair of different materials will *usually* result in the transfer of charge from one material to the other in a predictable direction; the ordering of materials in terms of the direction they transfer charge is known as the 'triboelectric series'. The term 'triboelectric series' was coined by Shaw

in 1917 [49], but the idea has roots at least as far back as 1759, with the studies of Swedish physicist Johan Wilcke (see [49]). This empirical approach orders materials (metals and insulators) in terms of the direction of charge transfer when they are touched by another material (see figure 2). When two surfaces are contacted, the material that is closer to the '−' end of the series will charge negatively while the material that is closer to the '+' end will charge positively. As an example, Teflon is near the '−' end of the series, and Nylon is near the '+' end; when they contact, Teflon charges negatively and Nylon charges positively. The triboelectric series is not fully reproducible, and different experiments lead to different orderings of materials—these variations are likely due to small differences in the material, environment, or measurement technique [12, 49].

Many studies have been performed to relate the triboelectric series to some intrinsic property of the material. For metals, the work function (the energy required to remove an electron from the surface) has been used to explain the position in the triboelectric series. Some investigators have extended this idea to insulators, in terms of effective work functions either determined empirically by fitting to experimental results [50–52] or directly from ultraviolet photoelectron experiments [53, 54].

Reports have also linked the triboelectric series to the wetting behaviour of insulators [55]. The rationale behind this idea is that the wetting behaviour is determined by the Lewis acid–base properties of an insulating material, which can control charge transfer (for more complete discussion see [4]). The wetting property of an insulator is easily measured, and Horn *et al* suggest that 'wetting experiments . . . may serve as useful predictors of the sign and magnitude of contact electrification between insulators' [55]. This idea that wetting and contact charging behaviour are related has been supported by experiments. For example, the electron-donor surface tension parameter obtained from wetting experiments correlates well with the position of the materials in the triboelectric series [56]. Also, a comparison of contact angle and contact charging results for polystyrene prepared with different levels of oxidation shows that increased oxidation acts both to decrease the contact angle and increase the rate of charging [57]. And, very recently, photochromic polymers that can undergo reversible chemical transformations by absorbing light were shown to exhibit contact charging behaviour that correlates with the hydrophobicity of their surface [58].

A similar theory has been proposed for polymers, relating contact charging to acid–base properties of molecular analogues of the polymers [59]. The position of the polymer in the triboelectric series was shown to be related to the equilibrium constant for the dissociation of a proton (pK_b) of the molecular analogue of the polymer.

While the approaches described here seem to have validity for some materials, a general physical basis underlying the complete triboelectric series is still not known.

3.2. Magnitude of charge transfer

The magnitude of net charge on a surface caused by contact electrification can be up to $\sim 10^{-3}\,C\,m^{-2}$ [26]. Since 1 C

corresponds to $\sim 10^{19}$ electron units, the surface charge density corresponds to 1 electron unit per 100 nm^2. We address here the factors that determine this magnitude of charge.

An upper limit for surface charge density is set by the dielectric breakdown of air. When the charge density on a surface becomes sufficiently high, the voltage on the surface (with respect to another surface) can reach the threshold value for air breakdown and the surface charge is conducted through the air, away from the charged surface. This breakdown voltage depends on the distance between the charged surface and the other surface, the pressure of the surrounding gas (e.g. air), and the composition of the gas, and is described by Paschen's law [60]. Under typical conditions, the breakdown value of merit for air is approximately $30\,kV\,cm^{-1}$. Some contact charging experiments have shown direct evidence of discharges associated with dielectric breakdown, which suggests that dielectric breakdown limits the charge that develops from contact charging [55, 61–63]. Furthermore, a model based on dielectric breakdown shows good agreement with experimental results for the maximum charge obtained on particles in contact electrification [64].

The magnitude of charge on a surface could also be limited by a finite number of states available on the acceptor surface, or a finite number of charge carriers on the donor surface. However, a number of studies have concluded that the density of states is not a limiting factor. Charge injection experiments—where a voltage-biased probe is used to inject charge onto an insulator—show no saturation of charge with applied voltage, implying that there is a sufficiently high density of available states that would not limit the amount of charge that is transferred [65, 66]. Also, Castle and Schein examined the charge per mass of particle mixtures (toner and carrier), and found the experimental results were in good agreement with a surface state model where the density of states is not a limiting factor [67, 68].

Another mechanism that can limit charge transfer is that as charge builds up, it becomes more energetically unfavourable to transfer charge in the same direction due to the existence of a repelling electric field. For example, the transfer of negative charge from a positively charged surface to a negatively charged surface must move against the force of the electric field created by the charged surfaces. Castle and Schein conclude, from their study described above, that this is the factor that limits the magnitude of charge transferred [67].

Finally, leakage of charge to a grounded surface will limit the magnitude of charge observed—i.e. higher amounts of charge may be transferred from one surface to the other, but then some of this charge may be quickly conducted away before the charge can be measured. The charge leakage from insulators is likely mediated by surface layers of water that form under humid conditions. The charge leakage can have a significant temperature dependence—some studies have shown that the measured charge due to contact electrification can decrease by 50% when the temperature increases by 15 °C [69], presumably due to the charge leakage.

An additional complication is that the magnitude of charge on a surface is not uniform—i.e. when two surfaces are contacted, one surface develops a net negative charge while the
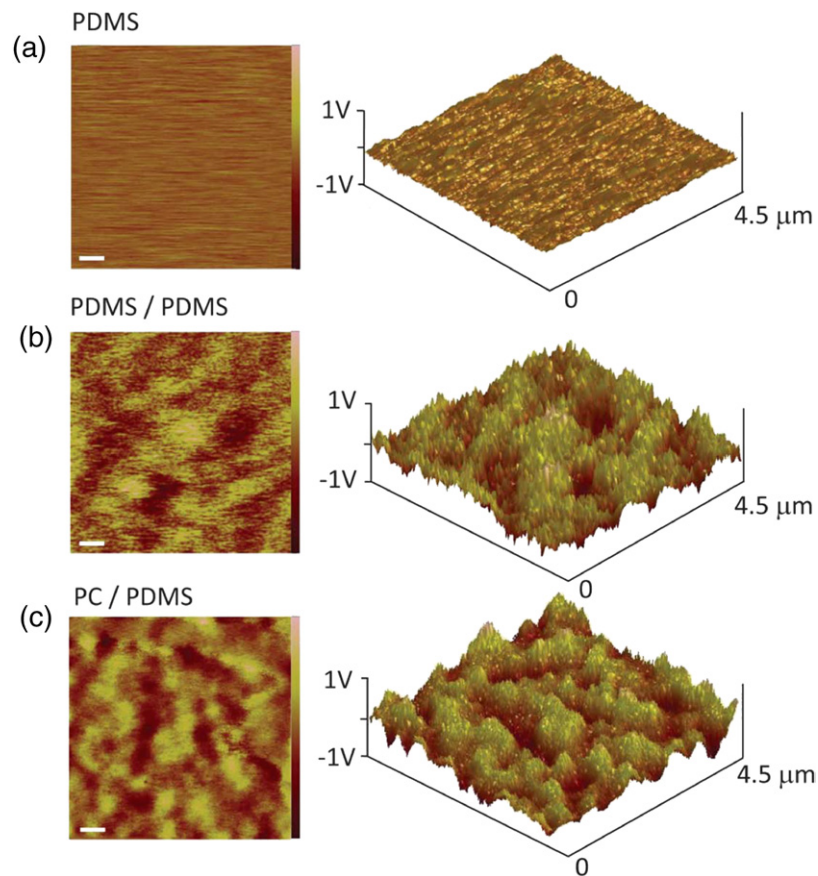
Figure 3. Surface potential maps obtained by Kelvin force microscopy. The map in (*a*) corresponds to PDMS before contact electrification. After contact, the surfaces in (*b*) and (*c*) feature a mosaic of (+) and (−) charged regions. Reprinted with permission from [8], copyright 2011 American Association for the Advancement of Science.

other develops a net positive charge, but the respective surfaces may have both positive and negative regions. This implies that the local charge can be much greater in magnitude than the net charge, and that the net charge represents a delicate balance of the contributions from the positive and negative regions. This result was first shown on the macroscopic scale by Lowell and Akande [70] who contacted a metal and a polymer over a 20×20 array of positions (separated by ~ 1 mm). The charge was found to vary significantly with position—in fact, charge of both polarities was found on a single surface. The charging patterns were similar when the polymer was contacted with different metals and cleaned with different methodologies, suggesting that the variation results from intrinsic differences in the properties of the polymer. Similar observations were also made by other groups [71, 72]. On the micrometre scale, Terris *et al* used atomic force microscopy [73] to show that charge patterns on a polymer after contact with a narrow metal tip (10 μm diameter) had both regions of positive and negative charge, with domain sizes on the order of several micrometres. Recently, the non-uniformity of charge was shown on the nanoscale by Baytekin *et al* [8]. Here, two polymer surfaces were contacted, and the charge distributions on the nanoscale were characterized by Kelvin force microscopy. The results show intricate 'mosaics' of positively and negatively charged regions across the surface (see figure 3). The mosaic is described by a random field with two spatial scales, one of apparent size ~ 400 nm and another ~ 40 nm.

3.3. The role of rubbing

It is well known that rubbing enhances contact charging—this is obvious to any child that has rubbed a balloon on his or her hair. However, it is not known *why* rubbing acts to increase charge transfer—does rubbing simply increase the contact area between the surfaces, or is the stress imparted from the rubbing important? Some results seem to suggest that the rate of rubbing can play a role in the charge transfer [11], which would suggest the significance of stress, but this is inconclusive. For monolayer surfaces, experiments suggest that stress from rubbing leads to charge transfer by generating electron–hole pairs in mid-gap states [74, 75].

There is a long history of evidence that suggests stress affects electrostatic charging [49]. For example, contact charging appears to be affected by surface damage, and these effects are reversed by annealing [76–78]. And recently, experiments showed that the polarity of charging between two materials can be reversed by varying the loading forces for contact [79].

3.4. The role of humidity

Humidity is known to play an important role in contact charging. For example, the effect of walking across a rug and then getting a shock upon touching a doorknob occurs much more frequently under drier conditions (e.g. in the winter).
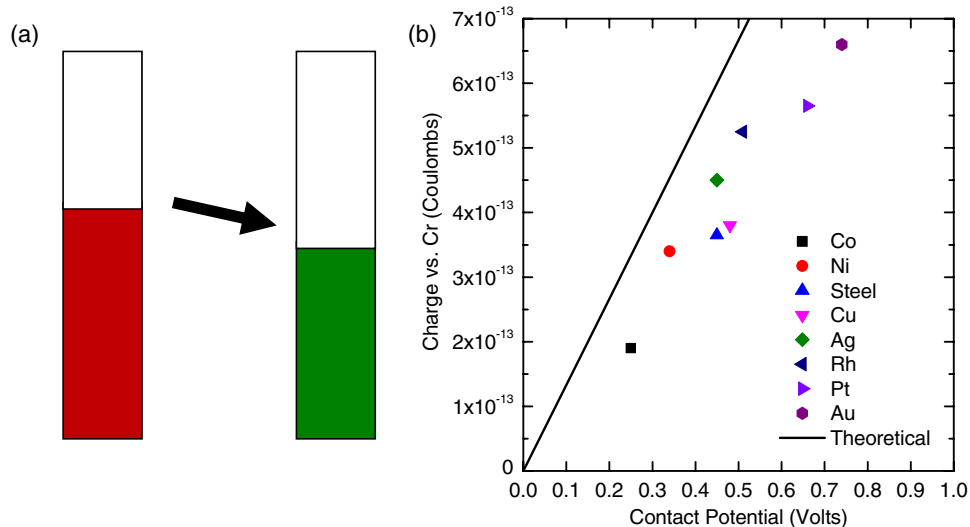
Figure 4. Electron transfer in metals. (*a*) Schematic of electron energy level diagrams for metals as it relates to charge transfer between two different metal surfaces. (*b*) Experimental results for contact charging of different metals (with respect to chromium) indicating correlation with the respective work functions. Experimental data are from [12].

However, it is not understood *why* humidity affects contact charging.

It is generally accepted that humidity creates a layer of water on a surface, which allows charge to 'leak away', thereby reducing the electrostatic charging effect. In fact, one type of 'anti-static' additive used to reduce the effects of contact charging works by this mechanism [80, 81]. Here, hydroscopic surfactant molecules partition to the polymer surface and attract water and salts from the atmosphere to form a conducting layer on the surface.

However, the role of humidity may be more complex. For example, Diaz and co-workers found in some cases that the magnitude of charge increases as the humidity increases (for humidity <30%) [82]. Other studies similarly found increases in the amount of contact charging as humidity increases [57]. It was proposed that humidity creates water layers on the surface that form 'water bridges' when the surfaces are in contact, which facilitates charge transfer between surfaces.

Recent experiments suggest that the situation is even more confounding. Galembeck and co-workers have shown that simply changing the humidity alters the charge on a surface— without any contact between the surfaces whatsoever [83, 84]. Presumably, this charging is due to reactions of the water vapour with the surfaces.

4. The mechanism behind contact electrification involving insulators

Given that contact electrification is well known to even non-scientists, it is surprising that a mechanistic understanding of contact electrification involving insulators remains elusive. For example, the type of species that carries the charge from one surface to the other is not known—different theories have proposed electrons, ions, or bits of nanoscopic material. To complicate matters, it is possible that different species are transferred in different situations.

In contrast to the situation involving insulators, contact electrification between two metal surfaces is believed to be straightforward. Metals have incompletely filled bands of electron states such that vacant conduction states are only infinitesimally higher in energy than filled valence states. The energy of the highest occupied valence state is described by the Fermi level or the work function (the energy necessary to remove an electron from the surface). When two metal surfaces come into contact, electrons are transferred from the material with the lower work function (or higher Fermi level) to the material with the higher work function (or lower Fermi level), as shown in figure 4(*a*). As shown in figure 4(*b*), experiments confirm that the amount of charge transferred is indeed proportional to the contact potential, which is related to the difference in work functions [11, 12].

In the following sections, we describe the various mechanisms that have been put forth to explain contact electrification involving insulating materials. It is entirely possible that each of these mechanisms may occur in different situations, depending on the materials and conditions involved.

4.1. Electron transfer mechanism

The electronic structure of an insulator is typically described by a filled valence band and an unfilled conduction band, with the gap separating these bands being much larger than the available thermal energy (i.e. $k_B T$, where k_B is the Boltzmann constant and T is temperature). Based on this description, electron transfer to an insulator does not seem possible. An electron cannot be transferred to a valence state because the valence states are all filled, and it cannot be transferred to a conduction state because the conduction states are much higher in energy.

The above description of insulators is idealized. More accurately, there are defect or 'trap' states in the band gap, as schematically depicted in figure 5(*a*), which are partially occupied by non-equilibrated electrons (electrons that are not in their lowest energy state). There is evidence for
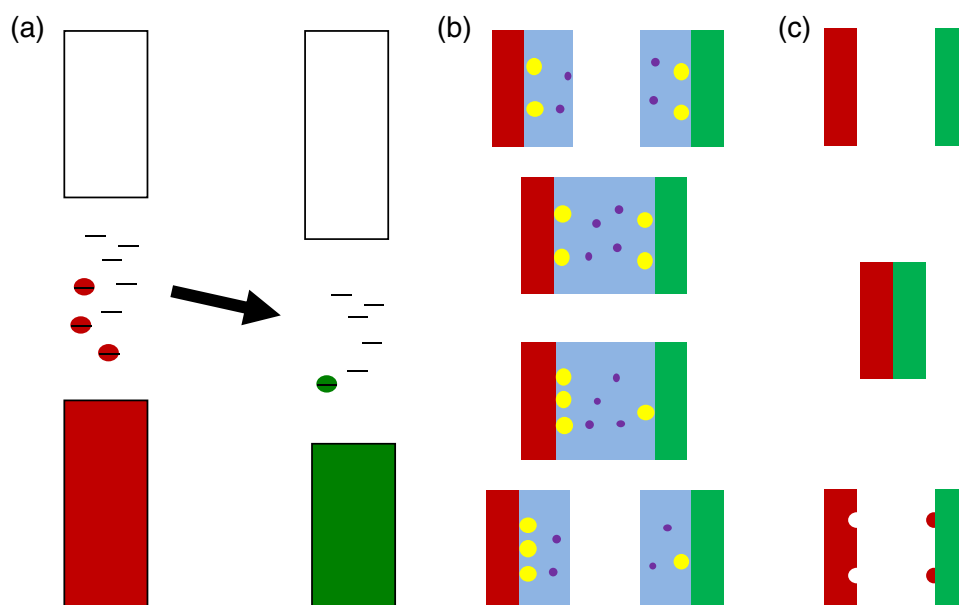
Figure 5. Proposed models for contact electrification of insulating materials. (*a*) Electron transfer model, in which charge transfer is the result of electrons trapped in mid-gap defect or surface states, transferring to lower energy states. (*b*) Ion transfer model, in which charge transfer is due to redistribution of ions in adsorbed water layers on the material surface. Note that yellow ions bind to the surface, and the oppositely charged purple ions are mobile. (Adapted from [4]) (*c*) Material transfer model, in which charge transfer is the result of material in the form of nanoscale moieties transferring during contact. The schematic shows material transfer in just one direction, but it may in fact occur in both directions.

the existence of these non-equilibrated electrons, as pointed out by Lowell and Truscott [85], from phosphorescence and thermoluminescence measurements of insulators; the electrons trapped in high energy states remain there for periods of days to centuries [86–88]. These trapped electrons are responsible for the finite conductivity of insulators, and also provide a means for contact charging to occur. The precise nature of these states is unknown, although electronic structure calculations have shown that conformational and chemical defects can give rise to such states [89–91]. It has also been suggested that these states can be formed at contact through an interaction between the two material surfaces [92, 93]. As evidence of there being surface states, it was shown that charge transferred to an insulator from a voltage-biased metal is 'stored' at the surface, and could be retrieved later when an unbiased metal is then contacted with the surface [65].

Recent studies by Liu and Bard support the electron transfer model [5, 94, 95]. In their experiments, Teflon (PTFE) was contact charged and brought into solution with a reducible species to induce a chemical reaction. Unlike electronic probes (e.g. electrometers) which cannot distinguish between different charged species, the chemical reactions could only occur if the charge carriers were electrons (analogous to a Faradaic process in conventional electrochemistry). For example, charged Teflon was immersed in a solution containing $Fe(CN)_6^{3-}$ which has a well known redox couple with $Fe(CN)_6^{4-}$ [5]. Cyclic voltammograms of the initial solution showed a single steady-state current plateau corresponding to $Fe(CN)_6^{3-}$; the height of this plateau decreased after the solution contacted charged Teflon and a new plateau appeared, confirming reduction to $Fe(CN)_6^{4-}$. Liu and Bard also explored the possibility of Faradaic metal electrodeposition with charged insulators.

Charged Teflon was immersed in a solution containing $CuSO_4$ and small amounts of Cu^{2+} were reduced and deposited as Cu metal on the surface [94]. In addition to providing evidence that non-equilibrium electrons exist on the charged surfaces, these experiments made it possible to determine their density and energy. Assuming 100% reaction efficiency, they estimated an electron density of 7.7×10^{14} cm^{-2} on charged Teflon. Using different redox couples, the energy states on a polymethylmethacrylate (PMMA) surface were found to lie somewhere between the reduction potential for $Ru(bpy)_3^{2+/+}$ (-1 V versus NHE) and $H+/H_2$ (0 V versus NHE) [95].

The interpretation of some of these electrochemical reactions has been challenged by a recent report [96]. Piperno *et al* showed that rubbing Teflon with PMMA causes adsorption of Cu^{2+} and Pd^{2+} from aqueous solutions and is not clear evidence of reduction (i.e. electron transfer reactions). These results hint at the importance of material transfer and ion adsorption which are discussed in the following sections.

4.2. Ion transfer mechanism

For the special case of insulating materials with mobile ions present (ionomers or polymers with molecular salts on surface), it is well understood that ions are transferred during contact [4]. These types of materials have strongly bound ions of one charge polarity on their surface balanced by loosely bound counter ions of the other charge polarity—upon contact with another surface, the loosely bound ions may be transferred to the other surface, leaving the original surface with a net charge of the strongly bound ions. This picture for charge transfer is verified by experiments in which the strongly and loosely bound ions are systematically varied, and predictable

results for the contact charging are obtained [97, 98]. As further evidence, experiments in which a polymer doped with ions is contacted with a metal have directly detected the transfer of ions to the contacted metal surface [99].

Based on these results, ion transfer has been put forth as a general mechanism for contact charging, even for materials that do not inherently include mobile ions [4, 11]. In this case, ions present in water layers that naturally occur on material surfaces may be transferred. One particular model suggests that it is the redistribution of adsorbed hydroxide ions between two surfaces that gives rise to contact charging (see figure 5(*b*)) [4]. Evidence in support of the role of ions within a water layer on contact charging includes several recent experiments: (i) a surface can become charged simply by changing the relative humidity, presumably because this alters the exchange of ions between the water layer and the atmosphere [83]; (ii) the magnitude of electrostatic charge on a surface undergoes sudden changes as the surrounding pressure is decreased, presumably due to the desorption of ions [100, 101]; and (iii) the rate of contact charging changes abruptly as a surface is modified (by UV-induced chemistry) to become more hydrophobic, presumably due to the importance of an adsorbed water layer on the exchange of ions during contact charging [58].

4.3. Material transfer mechanism

The material transfer mechanism involves 'patches' of one surface, roughly nanometres to micrometres in area, being transferred to the other surface during contact, as shown schematically in figure 5(*c*). The patch of material is likely to carry charge, because bonds must be broken in the material transfer process. The possibility of material transfer contributing to contact charging has been discussed for some time [102]. However, it was not considered a likely candidate—as remarked by Lowell and Rose-Innes in their classic review paper, 'it seems to us that contact electrification is in general too reproducible and systematic to be attributed to so capricious a process as material transfer' [11]. Note that this characterization by Lowell and Rose-Innes is in regard to *some* reproducibility of contact electrification (i.e. the results are not random), as illustrated by the triboelectric series (section 3.1) which *usually* predicts the direction of charge transfer, and is not meant to imply that contact electrification is highly reproducible.

There has been a very recent upsurge of support for the material transfer model—in particular, two studies provide strong evidence for its importance. As previously mentioned, Baytekin *et al* [8] examined the contact charging between polymer films. The contacted surfaces were characterized by x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy, which showed clear evidence of material transfer. The mechanism put forth is that 'mosaic' patterns of charge arise due to the transfer of material, which is driven by chemical and micromechanical properties of the material surfaces that are not homogeneous at the nano/atomic scale. Separately, Piperno *et al* used XPS to show that not only does material transfer occur when surfaces contact, but that

this material transfer changes the way that surfaces adsorb ions [96]. Thus, material transfer can influence electrostatic charging in a more indirect way than simply transferring charged bits of material.

4.4. Mechanochemical mechanism

Mechanochemistry refers to a class of chemical reactions that occur as a result of bond scission by material stress [103, 104]. Any contact between material surfaces can generate stress; of course the stress can be very large if materials are vigorously rubbed, but stresses can occur even if molecules are 'gently' contacted, due to cohesive forces between surfaces that can act to 'pull on' parts of the surfaces. The stresses may be magnified over localized regions (e.g. due to surface roughness), and cause bonds to break. A broken bond produces either a pair of radicals (if the bond scission is homogeneous), or a positive and negative ion pair (if the bond scission is heterogeneous). The mechanochemical model for contact electrification suggests that it is these ions or electrons released by the radicals that are then transferred between surfaces to create net charges on the surfaces. Note that the experimental evidence for transfer of material (discussed above in section 4.3) supports the breaking of bonds during contact charging, as broken bonds are necessary for material transfer to occur. Spectroscopic experiments confirm that stress on materials does produce radicals [103, 105], ions [103, 106] and electrons [107].

5. Contact electrification between surfaces of identical materials

When surfaces of identical materials are contacted and separated, charge transfer occurs such that one surface charges net positive and the other surface charges net negative [10, 12, 49, 71, 72, 76, 108–112], as shown schematically in figure 6(*a*). To ensure that the two surfaces are truly identical materials, a single block can be broken into two pieces [112]; even when this is done, charge transfers from one surface to the other. This phenomenon is counter-intuitive—since the chemical composition, and therefore all properties of the materials are the same, there appears to be no driving force for charge transfer. Several mechanisms have been put forth to explain how the symmetry between identical surfaces is in fact broken to drive charge transfer from one surface to the other, which we summarize below; each of these mechanisms may control charge transfer behaviour in different situations.

5.1. Asymmetric contact

Lowell and Truscott presented a theory based on asymmetric contact between the two material surfaces [85]. For example, as shown schematically in figure 6(*b*), a small area on one surface may be rubbed against a large area on the other surface, analogous to the drawing of a bow against a violin string—the bow makes contact along its entire length, but the violin string makes contact only at a single point.

A key idea behind their theory is that charge transfer is mediated by charged species in non-equilibrium surface states.
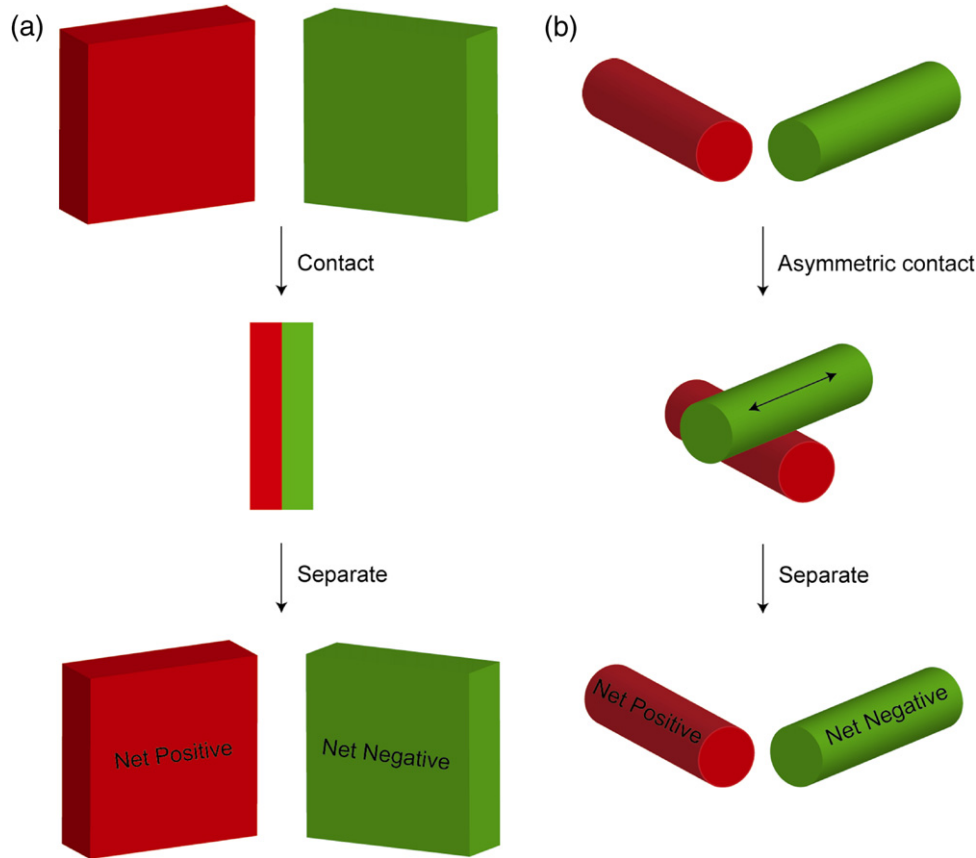
Figure 6. Contact geometry for contact charging of bulk-scale surfaces of identical insulator materials. (*a*) Contact between two material surfaces in a symmetric fashion results in a net positive charge on one surface and a net negative charge on the other [112], in an apparently random direction. (*b*) Contact between two materials' surfaces in an asymmetric fashion usually results in a net negative charge on the surface with the smaller contacting area and net positive charge on the surface with the larger contacting area [76].

At equilibrium, energy states are occupied according to the Boltzmann distribution, in which the lower energy states are predominantly occupied and the probability of a higher energy state being occupied is proportional to $\exp(-E/k_{B}T)$, where E is the energy of the state, k_{B} is the Boltzmann constant, and T is the temperature. However, equilibration can be exceedingly slow, and parts of the system can be 'trapped' in high energy states. Lowell and Truscott assumed that electrons are trapped in high energy states; experimental evidence for these non-equilibrium electrons is discussed in section 4.1. However, Castle has pointed out that the theory can be generalized, such that the charged species trapped in high energy states could be ions rather than electrons [113].

When a material surface A is contacted with another material surface B, vacant low energy states on B may be brought in close proximity to species trapped in high energy states on A, and thus provide a way for the trapped species to relax to a lower energy state. The transfer from the higher energy state to the lower energy state is a 'one-way' transfer because it moves downhill on the energy landscape (the species would not transfer from the lower energy state back to the higher energy state). Of course, the contact of surfaces also provides a way for species trapped in high energy states on surface B to relax to low energy states on surface A.

During contact, the probability that species trapped in high energy states on surface A are transferred to low energy states

on surface B is proportional to the surface density of high energy species on surface A, defined as σ_{A} = the number of high energy species on A per unit surface area of A. Similarly, species trapped in high energy states on surface B are transferred to low energy states on surface A, with probability proportional to σ_{B}. Thus the *net* charge transfer from surface A to surface B is proportional to the difference $\sigma_{A} - \sigma_{B}$. While it is possible that a finite density of acceptor states may play a role in the charge transfer, experimental evidence suggests that this is not the case (as discussed in section 3.2); thus only the donor states are considered in the analysis.

The outcome of this theory is shown schematically in figure 7 for the case that the same position of one surface is repeatedly contacted with different positions of another surface. Charged species are transferred from the high energy states of one surface to low energy states of the other surface at each contact. Initially, all positions on each surface have identical surface density of species trapped in high energy states, σ_{0}. When the first contact occurs, the transfer of species is symmetric; while there is no *net* species transfer, the number of species trapped in high energy states is depleted such that the value of σ for the positions contacted on each surface is reduced to σ_{1} ($\sigma_{1} < \sigma_{0}$). During the second contact, the same position of the green surface (with σ_{1}) contacts a new position of the red surface (with σ_{0}); since $\sigma_{1} < \sigma_{0}$, this contact causes a net species transfer from the red surface
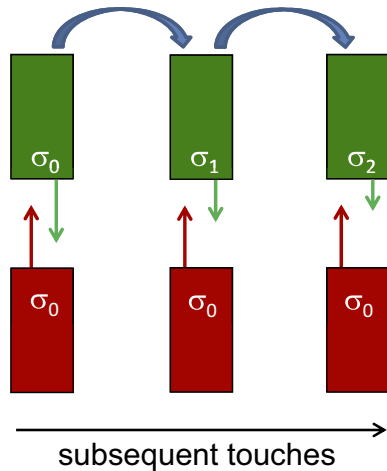
Figure 7. Schematic representation showing how the Lowell–Truscott model [85] gives rise to charge transfer when there is asymmetric contact between surfaces (section 5.1). The contact is asymmetric in that the *same* position of the green (top) surface makes multiple contacts with *different* positions on the red (bottom) surface. The surface density of charged species trapped in high energy states is denoted σ. Initially, the value of σ for both surfaces is σ_0. For the green surface, the same position repeatedly touches the red surface, and this position loses its trapped electrons with each touch—its value of σ decreases from σ_0 to σ_1 after the first touch, and from σ_1 to σ_2 after the second touch ($\sigma_0 > \sigma_1 > \sigma_2$). For the red surface, different positions are touched each time, so the contacted positions always have the value σ_0 when contact is made. At each contact, the number of species transferred away from a given surface is proportional to σ; the number of species transferred away from a surface is represented by the length of the lines in this figure. Thus, for the second and third touches, more species are transferred from the red surface to the green surface than vice versa, and the green surface accumulates species.

to the green surface. This direction of net species transfer continues with all subsequent contacts. In general, this model leads to the result that the surface with the larger contact area becomes depleted of the charged species while the surface with the smaller contact area accumulates charged species. If the charged species are negative (electrons or negative ions), then the surface with the larger area of contact will charge positively.

5.2. Statistical variations in material properties

Charge transfer can also occur when surfaces of identical materials are contacted symmetrically [71, 112]. An explanation for this effect has recently been put forth by Apodaca *et al* based on statistical distributions of material properties [112]. As background, consider first a coin flipped N times—while the *average* number of 'heads' is equal to the probability of obtaining a head multiplied by N, the actual number of 'heads' obtained will vary around this average, with the width of the variation scaling as the square root of N.

Now, consider a surface conceptually broken up into a grid, where there is a certain probability that each grid-square holds a 'donor state' (the donor states could correspond to the charged species trapped in high energy states, described in section 5.1). In analogy with the flipped coin, the *average* number of donor states on the surface is equal to the number

of grid-squares multiplied by the probability that a grid-square holds a donor state, but the actual number of donor states will vary around this average with a width of variation proportional to the square root of the number of grid-squares. Since the number of grid-squares is proportional to the surface area, the number of donor states on a surface will vary statistically, with a width of variation proportional to the square root of the surface area. Thus, when two surfaces of an identical material come in contact, the two surfaces have different numbers of donor states (due to this statistical variation) and there will be net transfer of charged species from the surface with the larger number of donor states to the surface with the smaller number of donor states. As discussed above, the magnitude of the difference in donor states scales with the square root of the surface area, so the net charge transferred is also expected to scale with the square root of the surface area. Careful experiments show, in fact, that the contact charging for two planar surfaces of identical materials has a square-root dependence on the surface area [112]; this result provides evidence in support of statistical variations driving charge transfer.

5.3. External electric fields

Pähtz *et al* have shown that external electric fields will also break the symmetry between two identical materials to cause charge transfer [114]. A material exposed to an electric field will become polarized, such that one side has a negative charge, and the other side has a positive charge of equal magnitude. Now consider two blocks of material lying on top of one another, with an electric field oriented perpendicular to their surfaces. For argument's sake, let us assume that the negative pole is up. Each block then becomes polarized, such that the top of each block is positive and the bottom of each block is negative. Since the positive surface of the bottom block is in contact with the negative surface of the top block, negative charge will be transferred from the top block to the bottom block.

6. Contact electrification of granular materials

Contact electrification is of great relevance to granular systems for two reasons: (a) when granular materials move (e.g. flow), the particles rub against each other, which generates charge; (b) the high surface-to-volume ratio makes it so that a small charge can have a large effect (e.g. the strong electrostatic forces combined with small gravitational forces due to the small particle mass can cause particles to stick to walls). Contact electrification of granular materials has consequences in many contexts, both natural and industrial—note that seven of the eight examples of contact electrification described in section 2 involve granular materials.

An interesting phenomenon that has been well documented is that charging of granular materials appears to depend on the particle-size distribution. This effect is surprising because the particles are macroscopic (diameters $>1\,\mu$m), which makes it counter-intuitive that particle size would affect charge transfer. Here, we review the research that addresses this phenomenon.
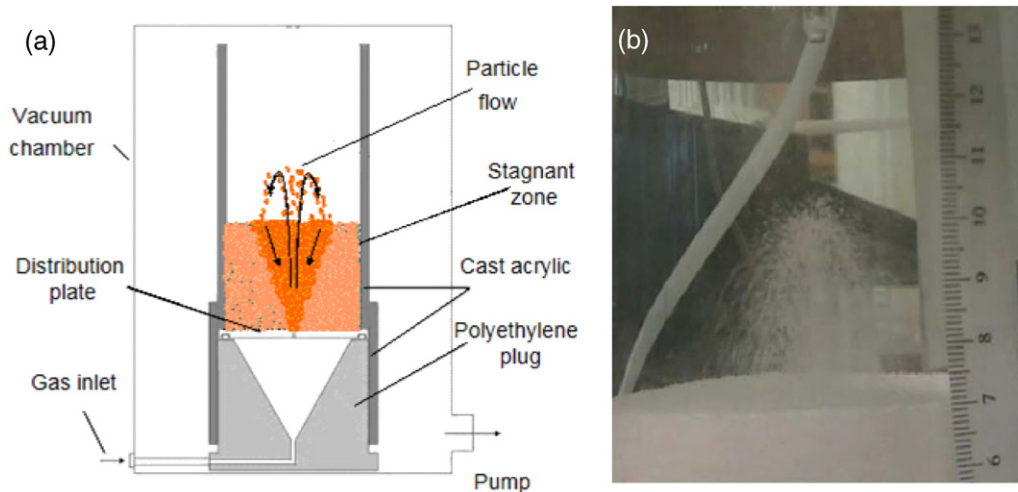
Figure 8. Single-hole particle flow apparatus used to study contact electrification of granular materials. (*a*) Schematic of apparatus with a single-hole distribution plate below a particle bed that causes particles at the top of the bed to flow and collide. The single hole ensures that only particle–particle interactions occur (no contact with the container wall). (*b*) Digital image of the 'fountain-like' flow created by the single-hole geometry. Reprinted with permission from [10], copyright 2009 American Physical Society.

6.1. Experimental investigations

The first indications of particle-size-dependent charging came from field studies of natural phenomena. The electric field has been measured in dust devils and dust storms, and the orientation of the field is found to be perpendicular to the ground with the negative pole at higher altitude [115–120]. Smaller particles are blown to higher altitudes (due to gravitational effects), so this result suggests that smaller particles charge negatively and larger particles charge positively. The particle-size dependence of charge polarity has been implemented in a number of modelling studies [29, 121–122].

Such electric fields have been observed in other situations as well. In a study of the transfer of industrial powders, Inculet *et al* showed that electric fields develop that are again consistent with smaller particles charging negative and larger particles charging positive [123]. In volcanic plumes, the rubbing of ash particles also leads to particle charging. The electric fields in volcanic plumes are more complicated due to the existence of gas and aerosol at high altitudes, but again the observed electric fields are rationalized by positively charged larger particles at the lowest altitudes and negatively charged smaller particles at higher altitudes [124].

Many laboratory experiments have shown that bipolar charging occurs in granular systems composed of a single type of material—i.e. some particles are charged positive and others are charged negative [125–138]. Some of these studies examined the particle-size dependence of the particle charge—studies by Inculet, Castle and co-workers [126–128] and others [125, 130] show that the bipolar charging is usually such that larger particles charge positively and the smaller particles charge negatively, but a few studies reported the opposite polarity [137, 138]. It is unclear whether the different behaviours observed are due to different materials used, or different experimental protocols that weight various contributions differently—for example, particle–particle interactions versus particle–wall interactions.
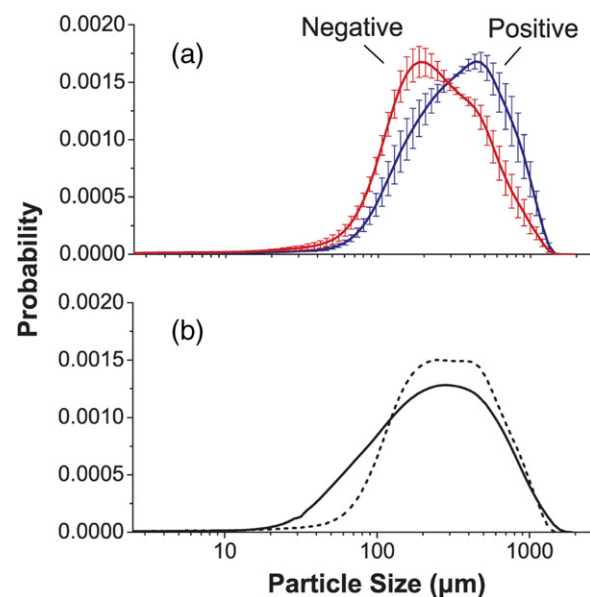

Figure 9. Particle-size distributions of JSC-1 Mars simulant after particle flow. (*a*) Negatively charged (red) and positively charged (blue) particles. (*b*) Original sample (solid) and average of collected samples (dashed). Reprinted with permission from [38], copyright 2009 American Geophysical Union.

Our group recently developed an experimental methodology to address charging of granular materials due only to particle–particle interactions, without interference arising from interactions with other material surfaces [10, 139, 140]. We fabricated an experimental apparatus consisting of a single-hole fluidized bed (figure 8(*a*)) which restricts the fluidization process to a local region at the centre of the bed, far removed from the walls of the container (figure 8(*b*)). Thus, particles only contact one another and the charge that is measured on the particles is due solely to particle–particle contact. After charging, a noncontact method was used to separate the particles by charge polarity and the particles were sized either by optical imaging or with a particle-size analyser (see figure 9).

Experiments were carried out for a range of materials, including silica glass [10], simulated Lunar [37] and Mars [38] regolith and acrylic [10]. In all cases, smaller particles tended to charge negatively while larger particles tended to charge positively. This 'charge segregation' by particle size was examined in more detail for bimodal mixtures (i.e. 2 particle sizes), and the extent of charge segregation was found to depend on the relative concentrations of the two particle sizes—charge segregation is maximized when the concentrations are such that collisions are predominantly between small and large particles (as opposed to collisions between two small or two large particles) [10].

A related result is that the magnitude of electrostatic charging seems to be larger when the particle-size distribution is broader. Krauss *et al* examined electrical discharges in agitated dust systems at low pressure [141]; the system with the broadest size distribution exhibited far more electrical discharges than other systems, suggesting that polydispersity of particle sizes enhances charge transfer. Similarly, Zheng *et al* measured electrical fields generated in wind-blown sands via wind tunnel experiments [142], and found that broader particle-size distributions increase the electric fields, presumably due to greater particle charging.

6.2. Mechanism for particle-size-dependent charging

As discussed above, the electrostatic charging in granular materials is found to depend on the particle-size distribution, with most studies suggesting that charge transfer occurs such that smaller particles tend to charge negatively and larger particles tend to charge positively. The reason for this behaviour is not clear.

Some explanations have been put forth in terms of a particle-size dependence of material properties. The effective work function of particles has been suggested to have a size dependence that drives charge transfer [128, 143]. However, the finite size correction to the work function of a sphere of radius R has been derived to be 5.4/R (eV Å) [144] and the correction for a 1 μm sphere would be $\sim$5 $\times$ 10^{-4} eV, which is negligible compared with the magnitude of the work function ($\sim$5 eV). The particle size also alters the capacitance of a pair of colliding particles, but again the magnitude of this effect in regard to contact charging is very small [145]. Other proposed explanations include a particle-size dependence for the adsorption of work function altering contaminants, and a particle-size-dependent surface roughness or shape that affects the interparticle contact [128]; however, these mechanisms would be highly system dependent and would not lead to the seemingly universal behaviour observed in a wide range of systems.

The electrostatic charging in single-component granular materials is a special case of contact electrification between identical materials, and the three mechanisms discussed in section 3 are relevant. The mechanism based on statistical variations of material properties [112] (section 5.2) would generate charging of particles, but the charging would not have a particle-size dependence. The mechanism based on an external electric field [114] (section 5.3) could lead to

particle-size-dependent charging, depending on the presence and direction of the external electric field. As previously discussed, if there is an external electric field oriented with the negative pole up, contact between two materials in this field will cause the upper material to charge positively and the lower material to charge negatively. In granular clouds, gravitational forces lead to smaller particles (on average) being higher than larger particles, and the external electric field causes a particle-size dependence for the charging where (with this orientation of the electric field) the smaller particles charge positively and the larger particles charge negatively; note that the direction of the particle-size dependence is determined by the orientation of the external electric field.

We have recently shown that particle-size-dependent charging occurs when the Lowell and Truscott model (section 5.1) is applied to the case of granular materials [146–149]. When particles of all sizes are allowed to collide, the model leads to the accumulation of charged species on the smaller particles in the system and a depletion of charged species on the larger particles. We show that this effect occurs generally when there are charged species on the particles in non-equilibrium states, i.e. charged species that cannot equilibrate to lower energy states on the same particle, but can equilibrate to lower energy states on another particle as a result of collisions.

To describe how these non-equilibrium states lead to a particle-size-dependent charging behaviour, we use a simple game as an analogy. The game involves a few hundred participants, where each participant brings 1% of their personal savings in one dollar bills; the dollars they bring are kept in their left pocket. The game is held in a large empty room. The participants are blindfolded, and walk around the room. When two participants 'collide', each gives a dollar from their *left* pocket to the other participant, and each takes the dollar they receive and put it in their *right* pocket. The game proceeds for a set amount of time (say, 1 h). No one is ever forced to leave the game—if a participant run out of bills in their left pocket, they can continue playing (they do not give away a dollar during a collision, but they would still accept dollars). Is this a good game to play? The answer depends on how wealthy you are! The game systematically transfers money from the wealthier participants to the poorer participants, because once the poorer participants run out of dollars in their left pocket subsequent collisions provide them with a net income of dollars. In contrast, wealthier participants always give dollars away, but may not always collect dollars (depending with whom they collide).

The connection between this game and charge transfer in granular systems is as follows. The dollars in the left pocket correspond to charged species trapped in high energy states and the dollars in the right pocket correspond to charged species that have been transferred to low energy states on another particle. The wealthier participants correspond to larger particles, and the poorer participants correspond to smaller particles—this is because larger particles, by virtue of their larger surface area, have a greater number of charged species trapped in high energy states (it can be assumed that all particles have the same surface density of these species, thus

the larger particle will have a greater number of them). As a result, the smaller particles will accumulate charged species while the larger particles will be depleted of charged species—if the charged species are negative (electrons or negative ions), then the small particles will charge negatively and the larger particles will charge positively, as has been empirically observed time and time again. Note that this model is treated more rigorously in our previous publications [146–149].

7. Epilogue

The first studies on contact electrification were carried out over 2500 years ago [1], when experiments showed that rubbing amber and wool caused the two materials to become oppositely charged. Our scientific understanding of contact electrification has not progressed very far in the intervening 2500 years—it is still not known what species is being transferred between the wool and amber to generate the charge, and how rubbing influences the process. A review paper such as this often concludes with a discussion of open questions, but we feel that virtually all questions involving electrostatics are in fact open questions. Hopefully, more progress will be made in the next 2500 years.

Acknowledgment

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