Nonequilibrium Accumulation of Surface Species and Triboelectric Charging in Single Component Particulate Systems

Daniel J. Lacks* and Nathan Duff
Department of Chemical Engineering, Case Western Reserve University, Cleveland, Ohio 44106, USA

Sanat K. Kumar
Department of Chemical Engineering, Columbia University, New York, New York, USA
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Triboelectric charging occurs in granular systems composed of chemically identical particles even though there is no apparent driving force for charge transfer. We show that such charging can result from nonequilibrium dynamics in which collision-induced electron transfer generates electron accumulation on a particle-size-dependent subset of the system. This idea rationalizes experimental results that suggest that smaller particles charge negatively while the large ones charge positively. This effect occurs generally when there are high energy electrons on a surface that cannot equilibrate to lower energy states on the same surface, but can transfer to lower energy states on other particles during collisions.

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A perplexing phenomenon is the triboelectric charging of granular systems of chemically identical particles. In mixtures with different types of particles, e.g., carrier-toner mixtures used in electrophotography, net charge transfer is driven by differences in material properties [1]. While this driving force for charge transfer does not exist with chemically identical particles, it is well known that they nonetheless undergo substantial triboelectric charging [2–6]. The charging in such systems is bipolar, with a specific particle-size dependence of the polarity: Electric fields in dust storms [7–11] and volcanic plumes [12] (and results from controlled lab experiments [13–18]) uniformly suggest that the smaller particles charge negatively and larger particles charge positively, with gravity separating the particles by size. Further, experiments show that the magnitude of charging is greater when there is a broad particle-size distribution [19,20]. The driving force cannot be due to a particle-size dependence of the electronic states, since this effect is negligible for the macroscopic particles under consideration [21]. We propose that these results follow from the nonequilibrium dynamics of surface electrons trapped in defect states, following ideas put forth by Lowell and Truscott for asymmetrically rubbed bulk materials [22].

To quantitatively describe this phenomenon we consider a particulate system with a size distribution (PSD) described by particles of radius R_i and corresponding number densities x_i. The population of surface species in state α on particles of radius R_i at time t is $n_{i,\alpha}(t)$. Following Lowell and Truscott [22], we assume that the species cannot equilibrate between the various states on a single surface, but can be transferred by surface contact to states on other surfaces. The rate of transfer from state α on a particle of type i to state β on a particle of type j is proportional to (1) the rate of collision for particles of type i with particles of type j, which is proportional to the collision cross section $(R_i + R_j)^2$, (2) the surface density of the species in the donor state of the donor particle, $\frac{n_{i\alpha}(t)}{4\pi R_i^2}$, and (3) the probability, $c_{\alpha\beta}$, that the species will be transferred from state α to state β in a collision (this probability of transfer is independent of particle size because the particles are macroscopic). We then derive a population balance,

$$\frac{dn_{i\alpha}(t)}{dt} = k_0 \sum_j x_j (R_i + R_j)^2 \sum_\beta \left(c_{\beta\alpha} \frac{n_{j\beta}}{4\pi R_j^2} - c_{\alpha\beta} \frac{n_{i\alpha}}{4\pi R_i^2} \right), \tag{1}$$

where k_0 takes into account all constants of proportionality. The total number of the surface species on particles of type i at time t, $N_i(t)$, is obtained by summing the number of species in each state, $N_i(t) = \sum_\alpha n_{i\alpha}(t)$. We address systems in which each particle initially has the same surface densities of species in each state α, $\rho_{\alpha,0}$, so that $n_{i\alpha}(0) = 4\pi R_i^2 \rho_{\alpha,0}$ for all types of particles.

We first demonstrate that the general behavior that follows from this model is independent of the model parameters, by examining it with randomly chosen parameters: the particle sizes R_i, number fractions x_i, transition probabilities $c_{\alpha\beta}$, and initial state surface densities $\rho_{\alpha,0}$ are all assigned random values between 0 and 1 (the number fractions are subsequently normalized). For this model, as shown in Fig. 1, the surface densities depart from their equilibrium values and ''charging'' occurs such that the species accumulate on the smaller particles, but at longer times the surface densities ultimately return to equilibrium as ''charge'' neutrality prevails. The behavior that occurs generally for all randomly chosen values of the model parameters is that the species accumulates on a particle-size dependent subset of the system; the accumulation can either be on the smaller or larger particles, depending on the initial species distribution among states, as described

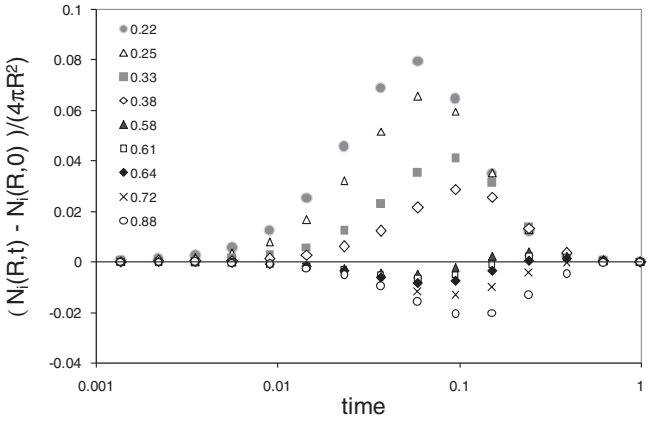

FIG. 1. Time dependence of the total surface concentrations for the model with randomly chosen parameters. Each set of data corresponds to particles of a different size, with the particle radius shown in the legend. Note that the order of the data, from top left to bottom right, follows the order in the legend. The units of time are k_0^{-1}.

below. This accumulation of species on a particle-size dependent subset occurs regardless of the particular transition probabilities and particle sizes, so long as there are distributions of these properties, and the initial occupation of surface states is not at equilibrium.

This particle-size dependent accumulation is elucidated by the analytic solution to Eq. (1) in the short-time limit, $N_i(t) - N_i(0) = (\frac{dN_i}{dt})_{t=0} t + \frac{1}{2}(\frac{d^2N_i}{dt^2})_{t=0} t^2 + \ldots$. The first order term is equal to zero because $\sum_\alpha \sum_\beta c_{\beta\alpha}\rho_{\beta,0} = \sum_\alpha \sum_\beta c_{\alpha\beta}\rho_{\alpha,0}$. Importantly, the second order term, however, is nonzero:

$$\frac{d^2N_i}{dt^2} = k_0 \sum_j x_j (R_i + R_j)^2 \sum_\alpha \sum_\beta \left(c_{\beta\alpha} \frac{1}{4\pi R_j^2} \frac{dn_{j\beta}}{dt} - c_{\alpha\beta} \frac{1}{4\pi R_i^2} \frac{dn_{i\alpha}}{dt} \right). \quad (2)$$

Thus, the net particle charging simplifies in the short time limit to

$$N_i(t) - N_i(0) = \frac{1}{2} \frac{k_0}{4\pi} C g_i t^2, \quad (3)$$

where $g_i = \sum_j x_j (R_i + R_j)^2 \sum_k x_k (\frac{R_k^2(R_i^2 - R_j^2) + 2R_i R_j R_k (R_i - R_j)}{R_i^2 R_j^2})$ and $C = \sum_\alpha \sum_\beta \sum_\gamma c_{\beta\alpha} c_{\gamma\beta} \rho_{\gamma,0} (1 - \frac{c_{\beta\gamma}}{c_{\gamma\beta}} \frac{\rho_{\beta,0}}{\rho_{\gamma,0}})$. Note that C is identical for all particle types, while g_i depends on particle size: $g_i > 0$ for larger particles, and $g_i < 0$ for smaller particles. Thus there is a systematic net transfer of species, either (a) from small particle to large particles if $C > 0$, or (b) from large particles to small particles if $C < 0$. This systematic transfer occurs regardless of the values of the rate constants.

The direction of species transfer—from small to large particles or vice versa—depends on the sign of C, which in turn depends on the nonequilibrium distribution of species in the surface states as described by the terms $\frac{c_{\beta\gamma}}{c_{\gamma\beta}} \frac{\rho_{\beta,0}}{\rho_{\gamma,0}}$. From transition state arguments, the ratio of forward and backward rates is given by $\frac{c_{\beta\gamma}}{c_{\gamma\beta}} = \exp[\frac{-(E_\gamma - E_\beta)}{kT}]$, where E_β and E_γ are the energies of the states. The contributions to C are negative when $\frac{\rho_{\beta,0}}{\rho_{\gamma,0}} > \exp[\frac{-(E_\beta - E_\gamma)}{kT}]$; this condition corresponds to an excess population in the higher energy states (compared to the equilibrium distribution). Thus, species are systematically transferred from large particles to small particles when there is excess population in the higher energy states. For the results shown in Fig. 1, the randomly chosen model parameters correspond to the case of excess population in the higher energy states; thus, as shown in Fig. 1, the species accumulate on the smaller particles.

The particle-size dependent accumulation has a simple physical explanation. When two particles collide, each colliding particle i transfers species from state α in an amount proportional to the surface density $\frac{n_{i\alpha}(t)}{4\pi R_i^2}$ [see Eq. (1)]. Initially these surface densities are the same for all particles, $\frac{n_{i\alpha}(0)}{4\pi R_i^2} = \rho_{\alpha,0}$, so that in the first collision each particle transfers the same number of species (denoted $\delta_{\alpha\beta}$) from state α to state β on the other particle. The species transfer in this first collision is symmetric: there is no net species transfer between particles, and the net number of species transferred into a state α, $\delta_\alpha = \sum_\beta (\delta_{\beta\alpha} - \delta_{\alpha\beta})$, is the same for each particle. However, after this first collision, the surface densities depend on particle size, $\frac{n_{i\alpha}(0^+)}{4\pi R_i^2} = (\rho_{\alpha,0} + \frac{\delta_\alpha}{4\pi R_i^2})$; thus in subsequent collisions the species transfer between particles (of different sizes) is not symmetric. If $\delta_\alpha > 0$, then the surface density is greater for smaller particles than for larger particles, and so more species will be transferred out of the α state of smaller particles. Conversely, if $\delta_\alpha < 0$, then the surface density is less for smaller particles than for larger particles, and so more species will be transferred out of the α state of larger particles. In the case that there is initially an excess population in the higher energy states, $\delta_\alpha < 0$ for the high energy states and $\delta_\alpha > 0$ for the low energy states. If furthermore, the rate of transfer out of the high energy states is faster than the rate of transfer out of the low energy states (as would be expected), then the behavior for the high energy states dominates, and there is thus a net transfer of species from the large particles to small particles.

We validate this population balance model by comparing to results from computer simulations [23,24]. The comparison addresses systems with two species states (H and L) such that $c_{HL} \gg c_{LH}$, c_{HH}, c_{LL}, for the time scale regime $\frac{1}{k_0 c_{HL}} \ll t \ll \frac{1}{k_0 c_{LH}}, \frac{1}{k_0 c_{HH}}, \frac{1}{k_0 c_{LL}}$ (this situation corresponds physically to the case that "downhill" transitions from high to low energy states are much faster than other transitions, and the time scales investigated are such that the faster transitions go to completion but the slower

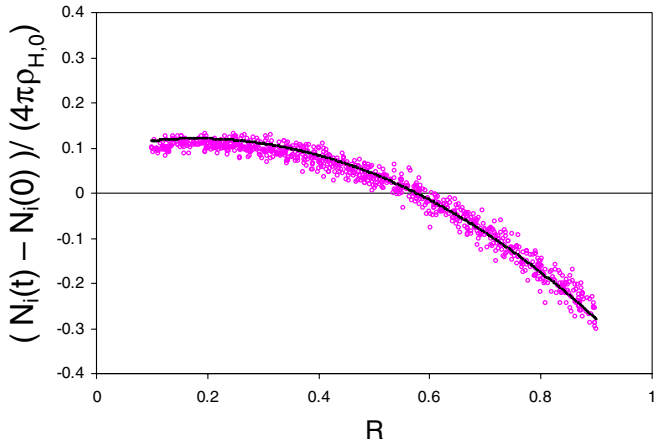

FIG. 2 (color online). Comparison of model results (line) to simulation results (points), for a particle-size distribution characterized by constant probability density between $0.1 < R < 0.9$. The simulations are carried out at a packing fraction of 0.045.

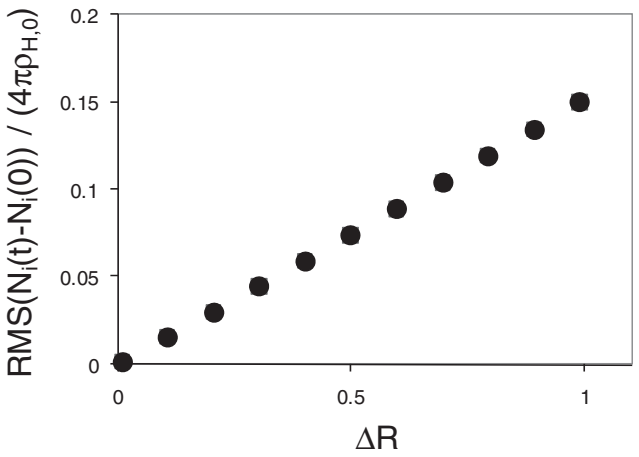

FIG. 3. Results for the magnitude of the change in the average number of species on the particles, as quantified by the root-mean-square change, for particle-size distributions with constant probability density for $(0.5 - \Delta R/2) < R < (0.5 + \Delta R/2)$.

transitions are not significant). For the population balance model, an analytic solution is obtained in this time scale regime,

$$N_i(t) - N_i(0) = \rho_{H,0}\left[\left(\sum_j x_j R_j^2 \frac{(R_i + R_j)^2}{\sum_k x_k (R_j + R_k)^2}\right) - R_i^2\right]. \tag{4}$$

For the simulations, the dynamics of 864 hard spheres are simulated through event driven molecular dynamics [25]; each particle initially has $\mathrm{int}(4\pi R_i^2 \rho_{H,0})$ species in state H at distinct positions randomly distributed over the particle surface, and when particles collide, species in state H (on either particle) that are within a cutoff distance of the point of collision are transferred to state L on the other particle (transitions out of state L, and transitions from to state H on one particle to state H on the other particle, are omitted in the simulations so that the time scale regime $\frac{1}{k_0 c_{HL}} \ll t \ll \frac{1}{k_0 c_{LH}}, \frac{1}{k_0 c_{HH}}, \frac{1}{k_0 c_{LL}}$ is addressed). The model and simulation results are compared in Fig. 2: the quantitative agreement, with no adjustable parameters, validates the population balance model.

The magnitude of the nonequilibrium accumulation of species increases with the breadth of the particle-size distribution. This result is evident from the short time solution [Eq. (3)], which shows the explicit dependence on the particle-size differences. To further demonstrate the dependence on the breadth of the particle-size distribution, results were obtained with Eq. (4) for the two state system with $c_{HL} \gg c_{LH}$, c_{HH}, c_{LL}, in the time scale regime $\frac{1}{k_0 c_{HL}} \ll t \ll \frac{1}{k_0 c_{LH}}, \frac{1}{k_0 c_{HH}}, \frac{1}{k_0 c_{LL}}$. Figure 3 shows results for the root-mean-square change in the number of species per particle, as a function of the breadth of the particle-size distribution.

We argue that the triboelectric charging of flowing granular systems composed of chemically identical particles is a consequence of the nonequilibrium dynamics of electrons trapped in defect states. To support our argument, we show that these dynamics rationalize three puzzling experimental observations that occur in systems as varied as polymers, silicate dusts and volcanic ash, and thus appear to be universal: (1) Triboelectric charging occurs in granular systems composed of a single material, even though there is no apparent driving force for charge transfer between particles of the same composition. Our results show that this charging follows the nonequilibrium accumulation and depletion of electrons on the particles, when equilibrium is not reached on the experimental time scales. (2) Bipolar triboelectric charging occurs in granular systems with smaller particles usually charging negatively and larger particles positively [7–18], as discussed above. Our results show that the nonequilibrium dynamics lead to smaller particles charging negatively by accumulating electrons, when there is an excess of electrons in the more easily transferred states. (3) The extent of triboelectric charging in granular materials is greater when there is a broad PSD [19,20]. Our results show that the nonequilibrium dynamics lead to this behavior as well.

Our conjecture requires that there be a nonequilibrium distribution characterized by an excess of electrons trapped in the more easily transferred (presumably higher energy) states, and that the equilibrium distribution of these electrons is not reached on the time scales of the experiments. Evidence of this, as pointed out by Lowell and Truscott [22], is phosphorescence and thermoluminescence phenomena in insulators, which demonstrate that electrons are trapped in high energy states for periods of days to centuries [26–28]. Further evidence comes from the dielectrical breakdown of insulators, which is attributed to the accumulation of electrons in these trapped states [29].

In addition, recent experiments have demonstrated that triboelectric charging is in fact due to the transfer of electrons [31].

While the nonequilibrium dynamics described here provides a driving force and determines the polarity for the charging of particles of identical chemical composition, additional factors will limit the magnitude. As the charging proceeds as described here, the electric field between oppositely charged particles makes it less favorable for continued electron transfer from the negative (smaller) particles to the positive (larger) particles, which limits the magnitude of the charging [30].

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*daniel.lacks@case.edu

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