



Size-dependent electron chemical potential: Effect on particle charging



John C. Angus^{a,*}, Isaac Greber^b, Kathleen Kash^c

^a Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH 44106, USA

^b Department of Mechanical and Aerospace Engineering, Case Western Reserve University, Cleveland, OH 44106, USA

^c Department of Physics, Case Western Reserve University, Cleveland, OH 44106, USA

ARTICLE INFO

Article history:

Received 3 October 2012

Received in revised form

1 October 2013

Accepted 8 October 2013

Available online 15 October 2013

Keywords:

Size dependent chemical potential

Particulate charging

Volume de-excitation

Surface de-excitation

Symmetry breaking

ABSTRACT

Electrostatic charging of particles of identical composition, but different sizes, is a poorly understood phenomenon that may be of importance in dust storms, generation of lightning, numerous technological applications involving solid particulates, and in the agglomeration of lunar dust and inter-stellar dust clouds. We show that under optical excitation, the relative magnitude of surface to volume de-excitation gives size-dependent electron and hole concentrations. The consequent differences in chemical potentials can lead to charge transfer between particles of different size. The direction of charge transfer, from large to small or vice versa, depends critically on the properties of the materials.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Electrostatic charging of insulating particles of the same composition, but different size, is believed to be of importance for electrical charging in volcanic plumes [1] and solar nebulae [2–4], in sand and dust storms [5–8], and in industrial processes involving small particles [9–11]. Despite its importance, uncertainty remains in the mechanisms leading to the charge transfer. If particles have identical composition and are in thermodynamic equilibrium, the chemical potentials of all components, including electrons and holes, are identical and therefore no charge transfer is expected. However, many experimental studies have established that charge transfer does take place. In a majority of situations the smaller particle acquires a negative charge [12–15]. However, there are reports on polymers [16] and glass beads [17] where the smaller particles become positively charged.

Lowell and Rose-Innes gave an extensive review of the work on contact electrification prior to 1980 [18]. Schein has recently emphasized how rudimentary is the understanding of electrostatic charging of insulating particles [19]. Much of the uncertainty in

mechanism likely arises because different mechanisms of charge transfer may be taking place under different circumstances. This view is reflected in several recent papers. Wiles et al. [20] showed that adsorbed water influences charge transfer between metals and polystyrene; however, their experiments did not establish whether the charge transfer took place through ion or electron transfer. Liu and Bard [21] recently showed that contact charging of polymers can occur by transfer of electrons. However, Piperno et al. [22] presented data that indicate that material transfer was the likely cause of charge transfer in this case. Recently Apodaca et al. [23] and Baytekin et al. [24] showed that local fluctuations in surface properties lead to charging of identical polymers when they are pressed together. Pähzt et al. [25] showed that a cloud of particles can charge in the presence of an electric field. Lacks and Sankaran [26] have recently given a comprehensive summary of the current state of understanding of contact electrification.

It has long been recognized that any process that breaks the symmetry between two nominally identical solids would permit electrostatic charging. For example, Henry [27] proposed that charge transfer arose from a temperature difference caused by asymmetric rubbing of two surfaces, e.g. a small spot on one surface rubbed over a large area on the second surface. Lowell and Truscott [28] assumed the presence of excited electrons in surface states and showed that the lack of geometric similarity between a sphere and a plane could lead to charging even when the concentrations of

* Corresponding author. Tel.: +1 216 368 4133; fax: +1 216 368 3016.

E-mail addresses: john.angus@case.edu (J.C. Angus), isaac.greber@case.edu (I. Greber), kathleen.kash@case.edu (K. Kash).

excited charge carriers are the same. Lacks and Levandovsky [29] proposed a model in which the symmetry was broken by assuming that the rate of charge transfer is proportional to the number of excited charge carriers on the surface rather than their concentration. Here we show that symmetry breaking by the relative magnitudes of surface and volume de-excitation leads to differences in chemical potentials of both holes and electrons and hence to particle charging.

2. Proposed model

2.1. Basic equations

Consider a spherical particle of radius, R , exposed to radiation of sufficient photon energy to excite charge carriers into a state where they are mobile. The excited carriers can recombine or become trapped by defects either in the bulk or at the surface. The concentration is described in integral form by:

$$\frac{\partial}{\partial t} \int_0^R nr^2 dr = \int_0^R (g - hn)r^2 dr - kn_s R^2 \quad (1)$$

Here n , the concentration of excited charge carriers, is a function of r . In MKS the units of n are m^{-3} ; r is the radial position and R the particle radius, m ; g is the bulk excitation rate, $\text{m}^{-3} \text{s}^{-1}$; h is the bulk recombination rate, s^{-1} (h is the reciprocal of the charge carrier lifetime, $1/\tau$); k is the surface recombination velocity, $\text{m} \text{s}^{-1}$. The subscript s denotes the surface of the particle. The excitation rate, g , is a function of radial position.

$$g(r) = I_s \alpha \exp[-\alpha(R-r)] \quad (2)$$

where I_s is the photon flux incident on the surface (photons $\text{m}^{-2} \text{s}^{-1}$) with energies above the bandgap or midgap transition energy; α is the absorption coefficient, m^{-1} . See Section 6, Methods, for a discussion of Equation (2). The simple exponential spatial decay of $g(r)$ in Equation (2) implies that R is greater than the wavelength of the radiation and Mie scattering is not a factor.

2.2. Steady state solutions for limiting cases

With steady state excitation, the concentration of excited charge carriers and its radial distribution approach steady state values. The process is most easily understood by considering two limiting cases: $\alpha R \ll 1$ and $\alpha R \gg 1$. In both limiting cases particularly simple solutions for the steady state concentration of excited charge carriers can be obtained directly from Equation (1).

For $\alpha R \ll 1$, the particle size is much less than the absorption depth, $1/\alpha$. Consequently the excitation rate, g , is essentially constant throughout the particle and from Equation (2) is equal to $I_s \alpha$. If the dimensionless parameter $k/(D\alpha) \ll 1$, diffusion is relatively rapid compared to surface de-excitation, and the concentration is relatively constant with r . In steady state, Equation (1) reduces to

$$\left(\frac{n_s k}{I_s}\right) = \frac{\alpha R}{3} \left[\frac{hR}{3k} + 1\right]^{-1} \quad (3)$$

If $hR/3k \ll 1$, surface de-excitation is dominant and n_s increases linearly with R . If $hR/3k \gg 1$, internal de-excitation dominates, and n_s is independent of R and equal to $I_s \alpha/h$.

For $\alpha R \gg 1$ the excitation occurs predominantly in a surface layer of thickness $\approx 1/\alpha$. If $k/(D\alpha) \gg 1$, diffusion to the interior of the particle is limited and the majority of bulk de-excitation occurs in the surface layer. Since all excitation and de-excitation processes

occur at the surface, n_s is independent of R and from Equation (1) is given by $I_s \alpha/(h + k\alpha)$. However, for $k/(D\alpha) \ll 1$ diffusion of excited electrons to the interior and internal de-excitation become important. Furthermore, if $k/(D\alpha)$ is sufficiently small, the concentration of excited carriers becomes relatively uniform with particle radius. In this limit the steady state equation (1) reduces to

$$\left(\frac{n_s k}{I_s}\right) = \left[\frac{hR}{3k} + 1\right]^{-1} \quad (4)$$

Here the concentration of excited charge carriers decreases with increasing R , becoming independent of R and equal to I_s/k if $hR/3k \ll 1$.

2.3. Effects of material properties

The surface concentration of excited charge carriers, n_s , depends critically on the relative magnitudes of h , k , and the charge carrier diffusion coefficient, D . The values of these parameters can range over orders of magnitude. For example, the bulk recombination rate h can range from 10^3 to 10^9 s^{-1} depending on the nature of the solid, the impurities and the crystalline quality; k from 1 to $10^4 \text{ m} \text{ s}^{-1}$ for passivated and unpassivated surfaces; and D from 10^{-5} to $10^{-2} \text{ m}^2 \text{ s}^{-1}$ depending on the nature of the crystal, scattering mechanism, and whether the charge carriers are electrons or holes. In many situations of interest, for example sand particles, values of h , k and D are not known.

To illustrate the types of response that can be expected, in Table 1 we give estimated values of h , k and D and the dimensionless parameters, αR , $hR/(3k)$, $h/(k\alpha)$ and $k/(D\alpha)$, for silicon and silica-based particles of 1 and 100 micron radii. For silicon a diffusion coefficient of $3 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$ corresponds to an electron mobility of $1200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. For silica-based solids a value of $10^{-4} \text{ m}^2 \text{ s}^{-1}$ corresponds to a mobility of $36 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [30]. Charge carrier lifetimes of 10^{-8} s have been reported for amorphous silica [31]. Values of α for silicon and silica are estimates for band-to-band absorption at energies well above the absorption edge [32]. The value of α for silica(OH) is an estimate for mid-gap absorption, which is much lower than band gap absorption [33]. Since many examples of interest will be for untreated silica-based particles, we use an estimated value of k near the high end of its range.

The last column on the right of Table 1 gives the sign of dn_s/dR , which determines whether charge transfer is from large to small particles ($dn_s/dR > 0$) or from small to large particles ($dn_s/dR < 0$). (A fuller description of this behavior is given in Section 4.) From Table 1 for one-micron-radius, passivated silicon particles $\alpha R < 1$ and $hR/3k < 1$ so from Equation (3) one expects n_s to increase with increasing R ; for 100 micron passivated silicon particles $\alpha R \gg 1$, $hR/(3k) \gg 1$ and $h/D\alpha \ll 1$ so from Equation (4) one expects n_s to decrease with increasing R . However, for unpassivated silicon one finds that n_s increases with R for the one micron particles and is essentially independent of R for the 100 micron particles.

For 1 micron radius silica particles with only strong band-to-band absorption, n_s is essentially independent of R . For the 100 micron particle n_s decreases with R . A common situation involves mid-gap absorption from impurities, which is illustrated with the entries for silica(OH). In this case $\alpha R \ll 1$ and $k/D\alpha \gg 1$ for both size particles so the approximate Equation (3) cannot be used; a numerical solution is required. However, since Equation (1) is linear in n , separate independent solutions can be obtained for mid-gap and band-to-band absorption. The complete solution can be obtained by superposition.

Download English Version:

<https://daneshyari.com/en/article/10406710>

Download Persian Version:

<https://daneshyari.com/article/10406710>

[Daneshyari.com](https://daneshyari.com)