Electrometer for repeated charge exchange measurements between a microparticle and a surface: Effect of water adsorption

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Summary

We report a new electrometer which allows the study of contact charging between a single microparticle and a metal surface. The electrometer is based on an electrodynamic levitator-trap and has a leakage current of about $10^{-29}$ A. The electrometer is applied to the study of the contact charging of spherical polystyrene-divinyl benzene copolymer particles against a Ni surface under ambient and a "dry" N$_2$ atmosphere. Significantly reduced charge exchange after eliminating water molecules from the particle would be strong evidence for an ionic charge exchange mechanism. Through a combination of gravimetric and light scattering measurements we have determined both the amount of water accreted in a humid atmosphere and the maximum amount of water that could be on the surface of the particle. Our experiments indicate approximately constant charging, independent of the amount of water on the particle.

1. Introduction

Recently there has been a great deal of interest in charge transfer processes associated with microparticles [1–3]. In most experiments involving micron size particles charge transfer is measured on a statistical basis. In electrophotography these micron sized particles (called toner) are charged against much larger particles and the charge exchanged is determined by blowing, with an air jet, the toner out of a Faraday cage fitted with screens which trap the larger particles [1,2]. In other experiments a continuous stream of particles is reflected off a surface and into a Faraday cup, where the accumulated charge is measured [4,5], or a particle may be driven to a surface (using an external electric field), and allowed to bounce several times [6]. None of these approaches allow one to investigate a given particle over an extended period (i.e. hours) or in the absence of an external applied electric field. Because of the
possible importance of deep trap states in insulators one would like to allow a particle to rest on a surface for a controllable period of time before determining the amount of charge transferred. In what follows we describe an electrometer with which one can experiment on a single micron size particle over an extended period. Aside from the ability to make repeated contacts, this new approach has a low enough leakage rate (about $10^{-20}$ A) that one has the time in between contact events in which to change the immediate environment. One particular application is the determination of the effect which ambient air has on charge transfer. By bringing a particle in and out of vacuum between charge transfer events one can ask specific questions such as the effects of relative humidity on the charge transfer process. It has been hypothesized by several authors that ionic transfer can be an important mechanism in contact charging, suggesting ambient humidity could play a central role in the charging process (see literature review in Ref. [1]). In this process, water molecules on the surface of the particle or the metal oxide dissociate and transfer $H^+$ or $OH^-$. The microparticle electrometer will be applied to testing this hypothesis for the specific case of polystyrene–divinyl benzene copolymer particles against a Ni surface.

2. Background

The basic idea behind the microparticle electrometer is the use of electrostatic levitation as a means for isolating a particle in between contact events and measuring the exchanged charge. The basic working equation is that of Millikan,

$$q = \frac{mg}{E}$$

where $mg$ is the weight of the particle and $E$ is the levitating field. In practice one merely has to measure the inverse of the electrostatic potential required for levitation. So long as the mass does not change, this number is proportional to the charge. The difficulty with charge exchange measurements in this apparatus is not the accuracy with which charge can be measured (the state of charge of a single particle is easily measured in such an apparatus with one-electron accuracy [7]), but the problems of (a) contacting a surface, (b) removing the particle from the surface, and (c) recapturing the particle for reanalysis of its charge. In addition, to eliminate from the experiment electric field driven contact charge exchange (other than that caused by precharge on the particle), the particle should make contact and be removed from the surface without using an external electric field. A reasonable means for removing a particle is through the use of a mechanical impulse. However, considering the level of acceleration needed to accomplish this (about $10^4g$), the resulting velocity makes recapture difficult in a conventional Millikan capacitor. To
overcome this limitation of traditional electrostatic levitation we have added an additional time-varying potential which creates an electrodynamic trap.

3. Microparticle Electrometer

A schematic of the Microparticle Electrometer is shown in Fig. 1. The basic levitator-trap in Fig. 1 consists of three electrodes; top and bottom hyperboloids of revolution and a hyperbolic torus [8]. The separation between the vertices of the hyperboloids of revolution is 9 mm. The power supplies provide 0–2000 V ac (rms) and 0–±1000 V dc. For the current discussion we will ignore the pin in the bottom. A polystyrene–divinyl benzene copolymer particle (dried from hydrosol Mfg. by Dow Diagnostics) precharged by rubbing it against a teflon surface with a teflon wand, is allowed to fall through the center hole in the top hyperbolic electrode. The alternating field $E_{ac}(r)\cos(\omega t)$ is what distinguishes the Microparticle Electrometer from the Millikan capacitor. The particle executes rapid oscillations in the presence of this field. Since these oscillations occur in a field having a gradient, a time-averaged force is produced [9]. For the limit of small and rapid oscillations it can be shown that a particle treated electrically as a point charge $q$, experiences a time-averaged force given by [10]

$$\langle \mathbf{F}_{ac} \rangle_t = -[q^2b(\omega)\nabla\mathbf{E}_{ac}^2]$$

where $b(\omega)$ is a positive frequency-dependent function. This simple expression adequately describes the trapping force and is consistent with experiments on microparticles in a levitator-trap having similar dimensions to that shown in Fig. 1 [11]. Thus the particle moves toward a minimum in the square of the field, $E_{ac}^2$. For the apparatus in Fig. 1 the alternating potential is azi-

![Fig. 1. Microparticle electrometer for charge exchange measurements.](image)
muthally symmetric about the vertical axis and has a horizontal mirror plane intersecting the center. This guarantees that $E_{ac}$ is zero at the center and $E_{ac}^2$ grows in all directions away from the center. Thus $\langle F_{ac} \rangle_t$ traps the particle. In the absence of gravity the particle would simply remain at the center. However, in the presence of gravity the particle is pulled below center and oscillates with its center of oscillation at a displacement such that $\langle F_{ac} \rangle_t$ balances gravity. It should be noted that the force $\langle F_{ac} \rangle_t$ is proportional to $q^2$ which allows particles to be trapped independent of the sign of charge. In addition the trapping force is large enough for the particle to be contained while the chamber encasing the electrometer is pumped down from atmospheric pressure to about $10^{-3}$ Torr in less than $\frac{1}{2}$ hr. Aside from $\langle F_{ac} \rangle_t$ an additional levitating force $F_{dc}$ is produced by utilizing the dc power supply, $V_{dc}$. This force enables the particle to be pulled to the center of the levitator-trap where oscillations stop and eqn. (1) applies. The levitated particle "leaks" charge at an average rate of one electronic charge every three hours, a leakage current of about $10^{-23}$ A [10]. This "leakage" rate is principally due to discharge of the particle by ions in the gas. Obviously this new tool for studying contact charge exchange requires the particle to be precharged in some manner. Also, similar to all other contact charge exchange experiments the actual, microscopic contact area is not well defined, although estimates for it can be obtained from elasticity theory (the Hertz model) [6].

In Fig. 1 the particle is shown sitting on a pin which is at the potential of the bottom electrode. For our experiments this pin was polished Pt or Ni. During the initial levitation phase the particle's charge to mass ratio $(q/m)_0$ was measured by adjusting $V_{dc}$ to balance with the pin extracted from the chamber and applying eqn. (1); it has been established for an identical levitator that the electric field at the center is $0.71 \frac{V_{dc}}{2z_0}$ (where $2z_0$ is the distance between vertices, 9 mm) [12]. Following this procedure the aerodynamic diameter of the particle was determined by measuring the level of alternating voltage required to produce the 1st parametric instability of the particle [13]. Since the density of polystyrene is well known, the determination of diameter enabled us to calculate the particle mass. The pin was then inserted and although the levitating voltage was changed to $V_{dc,1}$, the charge to mass ratio remained the same (i.e., $(q/m)_1 = (q/m)_0$), so that all subsequent charge to mass ratios, $(q/m)_n$, measured in the presence of the pin could be obtained from $(q/m)_n = \left( \frac{V_{dc,1}}{V_{dc,1}} \right) (q/m)_1$. The particle was placed near the center of the pin by allowing it to fall under gravity after being levitated at the center of the levitator-trap; at the time of contact no external field was present (i.e., both the ac and dc potentials were zero). Contact was maintained until the particle was driven off the pin by using an impulsive mechanical force. This single impulse was formed by using a solenoid driver to shot an impeller toward the bottom of the pin. Since the impeller was trimmed in order to be slightly smaller in mass than the pin, it recoiled on impact. In this way the primary impulse was given to the
pin and not to the levitator-trap. In practice the current supplied to the solenoid was increased incrementally until the particle was driven from the pin. All further detachments for a given particle were made with this same current setting. The particle was driven from the pin in the absence of an external field. As the particle ascended a few millimeters it entered the region of a focused laser beam where light scattering by the particle was used to activate the alternating trapping potential. The particle was then rebalanced by adjusting $V_{dc}$ and its new charge to mass ratio was calculated. The entire cycle was repeated as many as thirty times.

4. Results and Discussion

Figure 2(a) shows typical results for contact charging between a polystyrene–divinyl benzene copolymer particle 11 μm in radius and a polished Ni pin in ambient laboratory air. The particle has an initial negative charge to mass ratio of $-2.7 \mu\text{C/g}$. After 10 contacts this charge is seen to increase to $-3.15 \mu\text{C/g}$; charge is exchanged on average by $-0.045 \mu\text{C/g}$ per “contact” (i.e. considering the size of the particle this represents an exchange of about 1500 electronic charges per contact). After these points were taken the chamber was evacuated to about $10^{-3}$ Torr with the particle levitated. The vacuum was held for 4 hours after which the chamber was backfilled with purified N$_2$ to 760 mm Hg. Charge exchange experiments were then performed as shown in the second segment of data in Fig. 2(b). Here the charge is seen to further increase from $-3.15 \mu\text{gC/g}$ to $-3.80 \mu\text{gC/g}$ for another 10 contacts; charge is exchanged on average by $-0.065 \mu\text{C/g}$ per “contact”. It appears that going from a lab atmosphere to a relatively dry N$_2$ atmosphere does not decrease the charge exchange;

![Fig. 2. Charge exchange measurements between a polystyrene–divinyl benzene copolymer particle and a Ni pin.](image-url)
In fact the charge transfer process may be slightly increased. To further test these tentative conclusions the chamber was once again evacuated while the particle was levitated. This time the evacuation to $10^{-3}$ Torr was carried out for 24 hours. At the end of this procedure the chamber was once again back-filled with $N_2$ to 760 mm Hg. The next ten "contacts" (i.e. "contact" 21 to 30 inc., Fig. 2c) revealed an ever increasing charge from $-3.90 \mu C/g$ to $-4.70 \mu C/g$; charge is exchanged on average by $-0.080 \mu C/g$ per "contact". The experiment was subsequently terminated with the loss of the particle. Similar results were obtained with several particles of different size and precharge. In all cases the particle's charge increased and changes in humidity produced no decrease and always a slight increase in the average charge exchanged per contact.

It is interesting to note that the variations in charge exchange from one contact to the next as demonstrated in Fig. 2 appear to be far from that expected from Poisson statistics. Since the particle is likely to change its angular orientation from one contact to the next, "patch" effects associated with an inhomogeneous surface may explain this behavior.

Effects associated with water will depend on its ability to be accreted by the particle. Thus an attempt was made to measure water accretion on a levitated particle by operating the levitator as a pico-balance [13]. In this mode one monitors accretion by continuously measuring the levitation voltage as the particle accretes vapor. Specifically the chamber was first evacuated to $10^{-3}$ Torr with a particle (polystyrene–divinyl benzene copolymer, 5 \mu m in radius) levitated and vapor was bled in, up to a relative humidity of 80% (as monitored by a capacitive monometer). Figure 3 shows the results. We see that the particle takes on 0.25% water at 80% RH (relative humidity), and this accretion is in proportion to the humidity. It is not possible through this gravimetric

![Graph](attachment:image.png)

Fig. 3. Measured mass of a polystyrene–divinyl benzene copolymer microparticle (about 5 \mu m radius) vs. relative humidity.
means to know whether the water stays on the surface or distributes throughout the bulk. However, it is possible by utilizing elastic light scattering to obtain an answer to this question.

Elastic light scattering can be used to distinguish between a particle with a uniform refractive index and one with a radially discontinuous refractive index (i.e. a layered particle) as described below. The light scattering at 90° to an incident beam by a particle depends on the polarization and wavelength of the incident light for a given size and refractive index. At particular wavelengths the particle resonates and the scattering at 90° has pronounced peaks at the resonant wavelengths. These resonant modes are of two types, transverse electric (TE) and transverse magnetic (TM). When a particle accretes water, the water may form a layer or diffuse into the bulk and lead to an altered, but radially uniform refractive index. If the water resides principally on the surface, we expect through a self-consistent electromagnetic calculation that both the TE and TM modes will shift toward longer wavelengths and that the TM mode will have a shift in excess of the TE mode by about 30%. On the other hand if the water goes uniformly into the bulk we expect no differential shift between the TE and TM modes. By utilizing a dye laser we excited the natural electromagnetic resonant modes of a particle. This vector wave excitation allows us to excite both TE and TM type resonances. This new technique is termed Resonant Ellipsometry [14]. The measured shift in the resonant wavelength of two TM optical resonances of the particle, as a function of relative humidity, is shown in Fig. 4. Since we were more sensitive to the resonant shift than the mass, measurements of the shift could be started below 10% RH. For relative humidities above 5% the measurements show a linear shift of the resonant mode wavelength with additional water concentration. The differ-

![Fig. 4. Shift in natural electromagnetic resonances with relative humidity for a polystyrene-di-vinyl benzene copolymer particle approx. 5 μm in radius.](image-url)
ence between the TE and TM mode shift was measured at 90% RH and found to be considerably below the 30% level predicted for isolated water on the particle surface. The experimental uncertainty would permit, at most, 30% of the added water to remain at the surface. In addition, the expected overall shift of the TM mode as shown in Fig. 4 is only half of what would have been expected for surface isolated water on the basis of the added mass. Therefore our measurements are consistent with the water going primarily into the bulk; however we cannot eliminate the possibility that a monolayer or submonolayer of water molecules exists on the surface.

The goal of this experiment was to test the effect of surface water on the contact charging of one individual microparticle. If the contact charging had significantly decreased upon elimination of all water molecules from the surface of the polymer particle and the Ni surface, we believe that this would have been a strong case for the ionic mechanism of charge exchange involving the transfer of H\(^+\) and OH\(^-\). An experimental result in which the charge exchange remained unchanged does not completely rule out the ionic exchange mechanism because it can be argued that a monolayer or a submonolayer of water remains on the surfaces. Although we have been able to demonstrate large changes in the water content of these particles after putting them in a vacuum environment, our technique can not rule out the existence of a monolayer of water molecules on the polystyrene particles. Our data (Fig. 2) indicate some degree of inhomogeneity of the surfaces: for an ion exchange mechanism it could indicate that a water layer is not continuous; for an electronic charge exchange mechanism, it could indicate nonuniform surface states which participate in the charging.

While we did not observe a decrease in contact charging after significantly decreasing the water content of our particles, we believe this experiment could potentially be a model experiment for distinguishing between an electronic and an ionic charge exchange mechanism in insulators. An obvious improvement would be to further reduce the possibility that water remains on the surfaces. Higher vacuums and heating have traditionally been used to eliminate moisture from high vacuum equipment. Such techniques could be adopted here.

5. Conclusion

In conclusion we have demonstrated a new instrument for performing contact charge exchange measurements with individual microparticles in a controlled atmosphere. This microparticle electrometer has been applied to the contact charging of 10 \(\mu\)m polystyrene–divinyl benzene copolymer particles against a Ni surface. We have searched for decreased charging after eliminating most of the water from the particle, which would indicate an ionic charge exchange mechanism. Our observation of constant or slightly increased charging does not provide evidence for the mechanism of charge exchange. This
electrometer based on an electrodynamic levitator-trap is a new tool for studying contact charging of individual microparticles with an accuracy of one electron and a low enough leakage current that the experiment can be done over several days time.

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References