J Mater Sci (2007) 42:8242–8247
DOI 10.1007/s10853-007-1733-4

Controlled formation of dielectric chain aggregates on material surfaces

Guofeng Li · Zhiqiang Wang · Ninghui Wang

Received: 24 January 2007 / Accepted: 27 March 2007 / Published online: 28 June 2007
© Springer Science+Business Media, LLC 2007

Abstract This paper investigated the formation of chain aggregates from fine particles suspended in gas stream onto material surfaces under the action of electric field. The results showed that the shape of aggregate formed on material surface was greatly influenced by the field intensity and the surface condition of materials. In a weak electric field without corona discharge, particles tended to form clustered aggregates on a metal plate with smooth surface, but on a metal mesh and a porous alumina substrate, to form chain aggregate. On the other hand, in a corona discharge field, these surfaces were coated uniformly. Consequently, for forming chain aggregates on material surface, an electric field without corona discharge and a rough surface are necessary conditions. On rough surface, chain aggregates of dielectric particles or conductive particles grew from the protrusions of the surface and could form a rough and porous layer. When the external electric field was removed, the chain aggregates remained long time due to the Van der Waals forces. After sintered at proper temperature, the chain aggregates became fiber-like. The results indicate that the formation of chain aggregate can be controlled by electrostatic force, and sintering can be used as a method for increasing their mechanical strength.

Introduction

In the handling-processes of fine particles, the main problems are the adhesion of particles onto material surface, the agglomeration of particles, etc. As a method for controlling fine particles, electric field is widely used. Under the action of electric field, fine particles are agglomerated to large aggregates because of particle charging and dipole moment induced by the field, and collected on electrodes. Such aggregates can be classified into chain or cluster-like aggregates according to their shape. Frequently, the aggregates formed in electric field have very unpredictable shape, some more chain-like, some more clustered. In some cases, it is desirable to obtain a layer composed of chain aggregates on material surface, for example, fabricating catalytically active layer having large contact surface area. Thus, it is important to understand the relationship between electric field, the behavior of those aggregates, and the surface condition of materials. Furthermore, control the adhesion state of particles.

Processes of chain aggregates formation in electric field

Analytical and numerical treatments of chain forming have been published for many important cases [1–5]. According to these works, particles experience a dielectrophoresis force only when the electric field is non-uniform; dielectric particles in an electric field become polarized and cause the distortion of the applied field in the vicinity of each particle; Chain formation is due to the strong attractive particle interactions, in other word, due to the dipole-dipole interactions. The strong attractive particle interactions responsible for chaining exist in almost any physical situation where polarizable or magnetizable particles are subjected to electric or magnetic fields. The applications of chain aggregates have received widely attention in electrofusion of biological cells, chaining in electrorheological fluids, electrofluidized and electropacked beds, etc. [6–8].

G. Li (✉) · Z. Wang · N. Wang
Department of Electrical Engineering, Institute of Electrostatics, Dalian University of Technology, 116024 Dalian, China
e-mail: guofenli@dlut.edu.cn

For the particles suspended in gas phase, the basic interpretation of the formation of chain aggregates is attributed to Zebel, who treated the formation of chain aggregates with a fine-particle aerosol of spherical magnetic and electrical dipoles theoretically, and assumed an external force field imparts to the dipoles a parallel orientation [9]. Flossmann and Schütz reported a method depending on coagulation and precipitation of the chain-like iron oxide particles in an electrostatic field as a result of induced dipole forces [10]. In practice it is difficult to predict the dominant aggregate shape on electrodes. However, according to the above research works, the necessary conditions for forming chain aggregate are non-uniform field and polarized particles. Consequently, there is possibility to control particles to form chain aggregates as dominant aggregates on material surfaces by changing the roughness of the surfaces and using weak electric field without particle charging process. A rough surface will distort the imposed field in its vicinity and create non-uniform field, and a weak electric field makes particles polarized. In this paper, fine-particles are dispersed uniformly into the space between electrodes. The behavior of the particles adhering to material surfaces is investigated. The purpose is to coat the surfaces by particle chain aggregates.

Experimental setup

Two kinds of fine powders were used as coating materials, Al_2O_3 and Sr doped $LaMnO_3$ (LSM), both have average particle size 0.5 μm in diameter. Dispersion of the fine powders into ambient gas is an important operation in this experiment. The fine particles are often in the state of particle aggregates due to the adhesive forces interacting between particles. Homogeneously dispersed particles, not aggregates, are expected to suspend in gas.

Figure 1 shows the schematic diagram of the experimental setup, which includes two parts: disperser and coating chamber. Fine powders were dried sufficiently by an electric oven before put into the disperser, and were dispersed by nitrogen stream and a conical tube. Since the speed of fine-particles in the conical tube was high and the gas stream was turbulent, a filter with pore size 10 μm (filter1 shown in Fig. 1) was set on the outlet of the tube to slow down the speed and get uniform gas distribution. The effective dispersion of Al_2O_3 powder was observed, as shown in Fig. 2. Powders were dispersed into the coating chamber in which DC high voltage imposed. The electrode structures were pin to plate, creating corona discharge field, and plate-to-plate, creating an electric field without corona discharge. For comparison, powders were coated, respectively, into the following materials: (1) copper (Cu) substrate; (2) stainless steel sieve (2300 mesh in pore size); (3) a porous alumina substrate (10 × 10 × 5 mm in size). These materials were located on the plate electrode, while the material surfaces were set in parallel with the gas stream and perpendicular to the electric filed. In this experiment, Scanning Electron Microscope (SEM) was used to observe the adhesion state of particles. The chain aggregates formed on the substrates were sintered in an electric furnace.

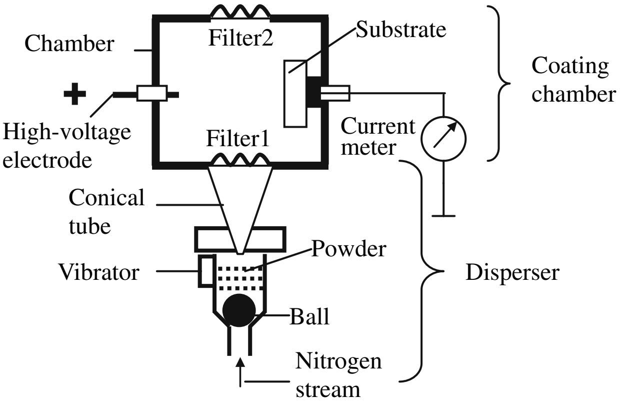

Fig. 1 Experimental setup

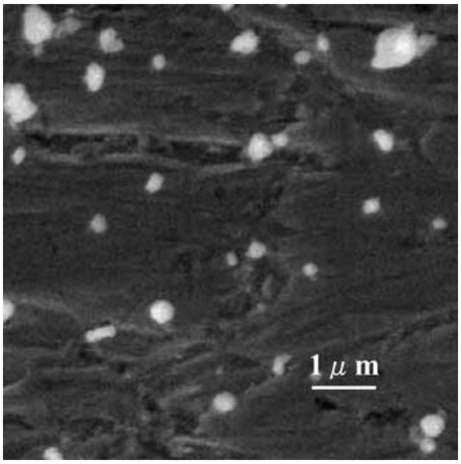

Fig. 2 Dispersed Al_2O_3 powder

Results and discussions

The influence of electric field intensity and material surface on the formation of chain aggregates

The adhesion state of Al_2O_3 particles on the copper substrate and the stainless steel sieve is shown in Fig. 3. By using pin-to-plate electrodes and the following experimental conditions: DC high voltage 12 kV, 2 cm of the

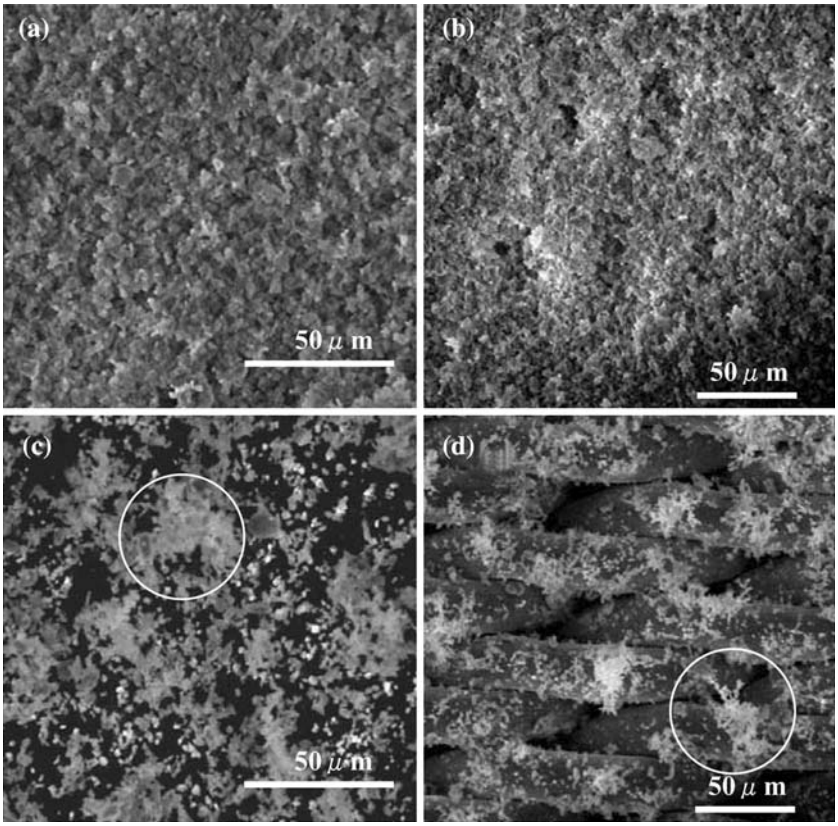

Fig. 3 Adhesion state of Al_2O_3 powder on metal plate (**a**) and (**c**), and mesh (**b**) and (**d**). (**a**) and (**b**) uniform layer formed in corona discharge field, (**c**) and (**d**) clustered aggregate and chain aggregate formed in weak electric field without corona discharge

distance between the pin and the surfaces, nitrogen gas flow rate 5 L/min, and particle concentration 200 mg/ m^3, corona discharge field were created and these surfaces were coated uniformly in several seconds (Fig. 3a, b). In corona discharge field, the particles were charged and attracted to the surfaces by Coulombic force and image force. The particle charging process blocks the formation of particle aggregates because the particles repulse each other due to the excess charges on particle surfaces.

By using plate-plate electrodes, which create electric field without corona discharge and the same other conditions with the above experiment, on the copper substrate, Al_2O_3 particles were agglomerated to clustered-like aggregates (Fig. 3c), but in the sieve surface most particles adhered to the protuberant parts and formed chain aggregates (Fig. 3d). In a non-uniform electric field without corona discharge, polarization effects may induce motion of particles. Since a particle is polarized by the field, the separation into positive and negative charges produces a dipole that is subjected to a net force in a divergent field. When an insulating dielectric sphere of radius R and permittivity ε_2 suspended in a medium of permittivity ε_1 is subjected to a non-uniform electric field of magnitude E, the electrostatic force can be expressed as

$$F = 2\pi\, \varepsilon_1 R^3 \left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} \right) \nabla E^2 \tag{1}$$

If $\varepsilon_2 > \varepsilon_1$, the force tends to pull polarized particle toward the higher field (whatever the sign of the field). In this experiment, the permittivity of Al_2O_3 is larger than that of nitrogen gas, while the protrusions in the mesh surface distorted the electric field in the vicinity of mesh and produced non-uniform field. Thus, polarized Al_2O_3 particles were attracted to these protrusions and were agglomerated to chain aggregates along the electric field direction. The clustered aggregates formed on the copper substrate could also produce non-uniform field and attract polarized particles. It was observed that the size of clustered aggregate grew with coating time, and there were many short chain aggregates formed on its surface, as shown in Fig. 4 (coating time 10 min).

The above results show that an electric field without corona discharge and a rough surface are necessary conditions for forming chain aggregates on material surface. These results also can be applied in forming chain aggregates on dielectric substrate. The formation of chain aggregates on dielectric material surfaces is probably of greater technological significance than on metallic material surfaces, because it can be processed and applied in high temperature environment.

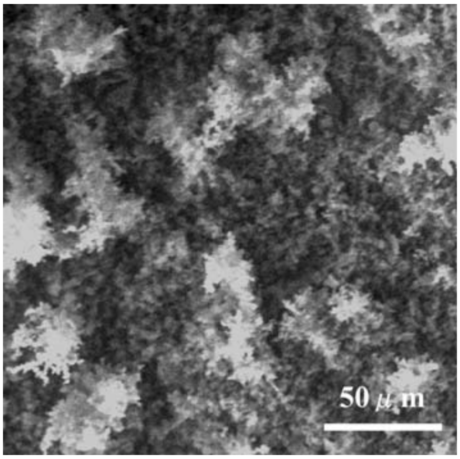

Fig. 4 Clustered aggregate of Al_2O_3 particles result of 10 min adhesion

Figure 5 shows the adhesion state of Al_2O_3 particles on the Al_2O_3 substrate. For comparison, the Al_2O_3 substrate surface before adhesion is also shown (Fig. 5a). The substrate was located between two metal plate electrodes. The particle concentration was 200 mg/m^3 and the coating time was 10 min. As shown in Fig. 5, a layer composed of chain aggregates was formed on the substrate.

In electric field, charge will be induced on the substrate surface. As suggested in Fig. 6, the surface roughness will cause the charge concentration on the protuberant parts. Therefore, like the adhesion on the metal mesh surface, chain aggregates grew from the protrusions in the substrate along the external electric field. So the chain aggregates could be realized on both metal and dielectric material surfaces where protrusions exist.

When the external electric field was removed, the formed chain aggregates remained long time and had the strength that allow us to move the substrate and observe the adhesion state by Scanning Electronic Microscope (SEM).

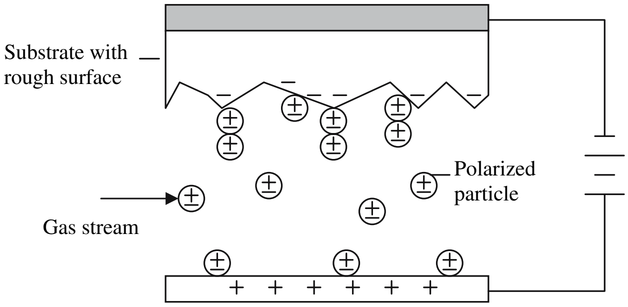

Fig. 6 Physical model of chain formation on rough surface

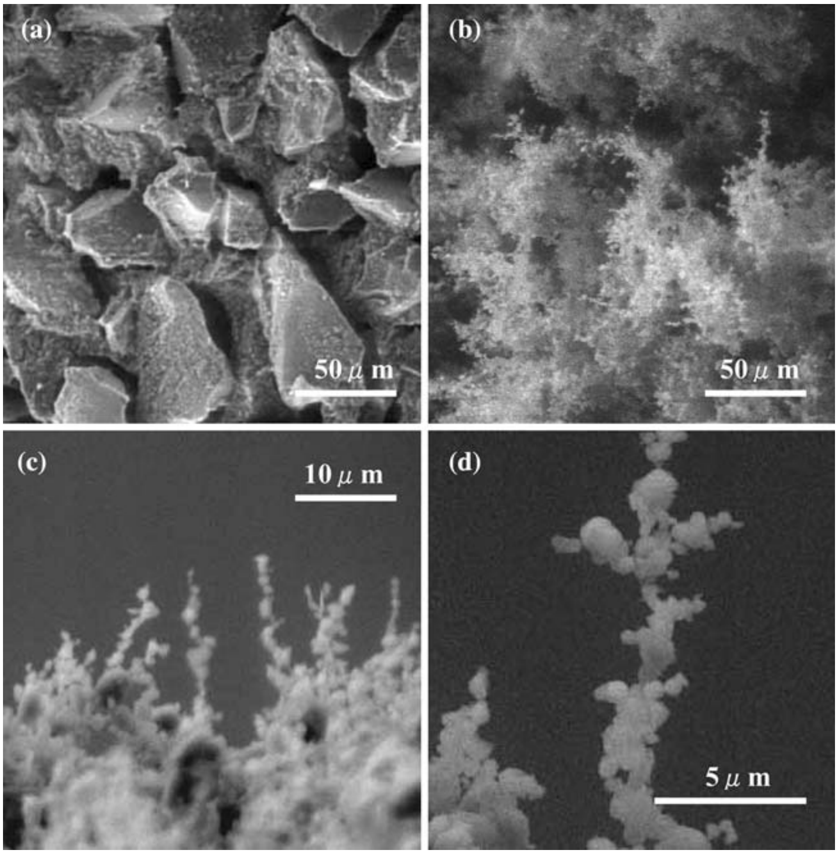

Fig. 5 Adhesion state of Al_2O_3 particles on Al_2O_3 substrate (**a**) Surface of Al_2O_3 substrate (**b**) After coated (**c**) Section view (**d**) micro-structure of one chain aggregate

The adhesive force between particles or particle and surface arise primarily from Van der Waals force, electrostatic attractions, and surface tension. Van der Waals forces are due to instantaneous polarizaion of atoms and molecules due to quantum mechanical effects [11]. Electrostatic forces arise from charge generation or charge transfer during contact. Surface tension effects arise from interactions of layers of adsorbed moisture on the two surfaces. In electric field, electrostatic force become predominant force, as has been shown in this experiment, electrostatic force made Al_2O_3 particles aligns along the field direction and form chain aggregates. But in the situation without external field, it has been reported that the primary forces of adhesion of particles less than 50 μm diameter on a dry surface are Van der Waals forces [12, 13]. Moreover, the Van der Walls forces become important interaction forces between particles less than one micron [14]. Assumed that Al_2O_3 particle has spherical surface, the Van der waals force interacting between the particles can be calculated by the following equation:

$$F_{vdw} = hr/12Z^2 \tag{2}$$

where h is Lifshitz-van der Waals constant (for Al_2O_3 the constant is 4.0 eV), r is the particle radius (in this experiment $r = 0.25$ μm), and Z is the atomic separation between the surfaces (in ideal condition $Z = 4$ Å). Then, the Van der Waals force between Al_2O_3 particles is 5.2×10^{-8} (N). For a spherical particle the gravitation force is:

$$F_{\mathrm{grav}} = (4/3)\pi r^3 \rho g \tag{3}$$

where $\rho = 3930$ kgm^{-3} is the density of Al_2O_3. So, the gravitation force of one Al_2O_3 particle is 2.6×10^{-14} (N). The Van der Waals force exceeds the gravitation force by a factor of 10^6. The surface tension was not considered because dry powder was used in the experiment. Although the calculation used ideal conditions, it proves that the self-sustentation of chain aggregates is due to Van der Waals forces.

The former results can also be obtained from testing conductive particles. As shown in Fig. 7, chain aggregates of LSM particles, having average particle size 1 μm and conductivity larger than 100 S cm^{-1}, was formed on the Al_2O_3 substrate.

In electric field, the force imposed on a sphere of conductivity σ_2 suspended in a medium of conductivity σ_1 is expressed as:

$$F = 2\pi\varepsilon_1 R^3 \left(\frac{\sigma_2 - \sigma_1}{\sigma_2 + 2\sigma_1}\right) \nabla E^2 \tag{4}$$

It is identical to Eq. 1, except that now it is expressed in terms of conductivities. According the equation, LSM particle is attracted to the region with strong electric field because the conductivity of LSM is larger than nitrogen gas. After the electric field was removed, the formed chain aggregate of LSM particles remained despite of the conductivity.

Sintering of the formed chain aggregate

After the electric field removed, chain aggregate remained long time due to the Van der Waals forces. This is important for studying their behaviors in high temperature.

Figure 8 shows the micrograph of chain aggregates of Al_2O_3 particles (a, b) and LSM particles (c, d) on the Al_2O_3 substrate after sintered. For Al_2O_3 particles, the heating rate was 10 °C/min, the sintering temperature was 1300 °C in 2 h. For LSM particles, the sintering temperature was 1200 °C, and the heating rate and sintering time were same with that of Al_2O_3. After sintered, the structure of chain aggregates remained as shown in Fig. 8. The chain aggregates became fiber-like. The sintering process is divided into three successive elementary stages. The initial stage corresponds to neck formation and growth, the intermediate stage to the growth of cylindrical vacancies,

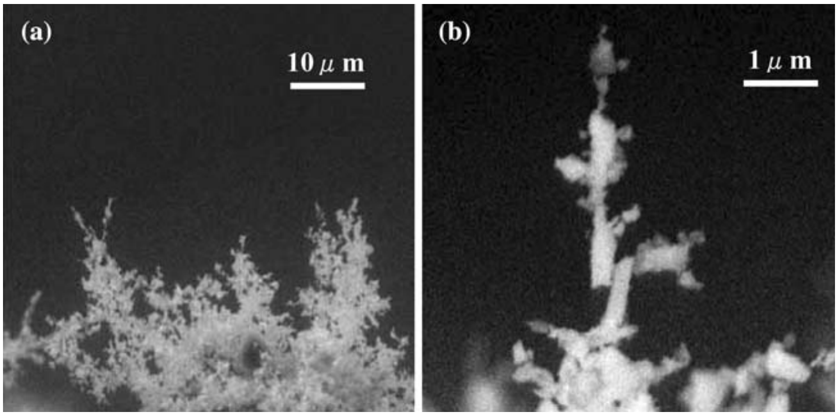

Fig. 7 Chain aggregates of LSM particles on Al_2O_3 substrate (**a**) Section view (**b**) microstructure of chain aggregate

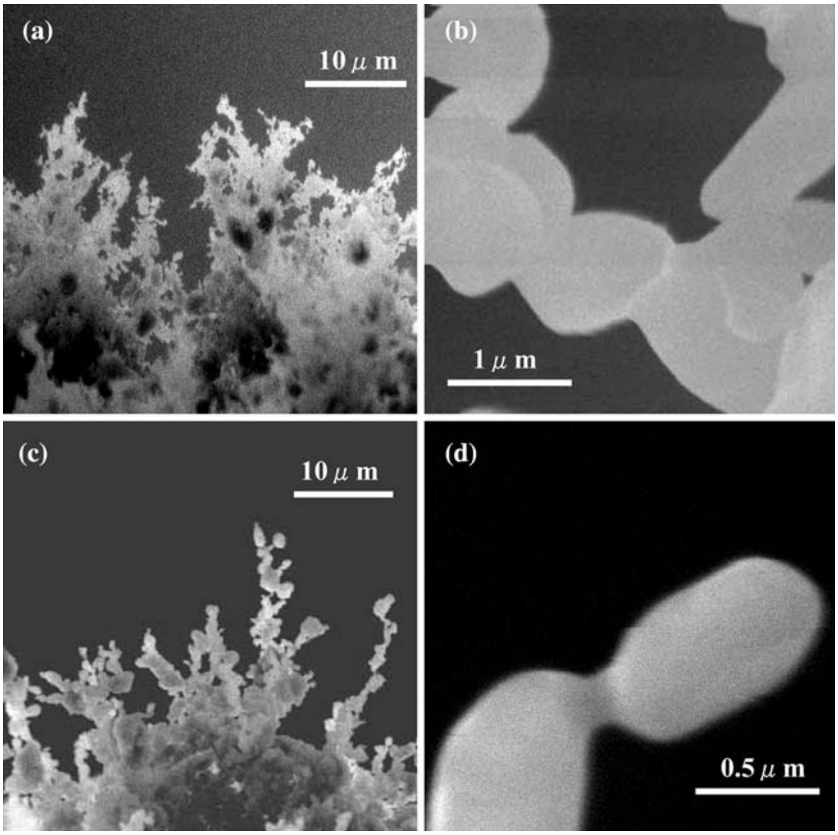

Fig. 8 Chain aggregates after sintered on Al_2O_3 substrate, (**a**) and (**b**) Al_2O_3, (**c**) and (**d**) LSM

and the final stage to diffusion and disappearance of the vacancies. Figure 8(b, d) shows that the sintered Al_2O_3 particles and LSM particles are in the first stage of sintering because necks are formed at the contact point of particles. More importantly, the structure of chain aggregate was not destroyed by high temperature. On the contrary, the mechanical strength was increased. After processed by an ultrasonic cleaner for 5 minutes, chain aggregates were stable against ultrasonication in water. These results show that sintering can be used as a method for fixing the formed chain aggregates onto material surface and raising the mechanical strength.

Conclusion

Chain aggregates can be formed from fine dielectric and conductive particles less than 1 micron suspended in gas stream under the action of electric field. After sintered, the chain aggregates became fiber-like, especially. The results presented in this paper can be considered as a new method for fabricating fine-fiber and porous layer onto material surfaces.

References

1. Davis MH (1969) Am J Phys 37:26
2. Godin YuA, Zil'bergleit AS (1986) Sov Phys Tech Phys 31:632
3. Chen Y, Sprecher AF, Gonrad H (1991) J Appl Phys 70:6796
4. Jones TB, Miller RD, Robinson KS, Fowlkes WY (1989) J Electrostatics 22:231
5. Nakajima Y, Matsuyama T (2000) Calculation of pearl chain forming force by re-expansion method. In: Proceedings of 2000 Annual Meeting of The Institute of Electrostatics Japan, Yamagata, pp 241–244
6. Zimmermann U, Vienken J (1982) J Membrane Biol 67:165
7. Halsey TC (1992) Science 258:761
8. McLean KJ (1977) J Air Pollut Contr Assoc 27:1100
9. Zebel G (1963) Staub Bd. 23, Nr. 5, S. 263
10. Flossmann R, Schütz A (1963) Staub Bd.23, Nr. 10, S. 443
11. Israelachvili JN (1978) Contemp Phys 15(2):159
12. Hecht L (1990) J IES 33(2):33
13. Allen Bowling R (1985) J Electrochem Soc: Solid-State Sci Technol 132(9):2208
14. Jones TB (1995) Electromechanics of particles. Cambridge University Press, Preface