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A simple model for charged particle aggregation and polarization

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HIGHLIGHTS

- Electric dipole moment of the largest aggregate increases with mass in neutral system.
- Net Charge of the largest aggregate increases with mass in overall neutral system.
- Net charge of the aggregate increases like the square root of mass.
- The increase in dipole moment depends on the fractal dimension of the aggregate.
- Internal electric fields emerge by random-walk processes without external fields.

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ABSTRACT

In this paper we introduce a charged particle diffusion based aggregation model, which exemplifies an aggregation process affected by the particles' "charge". Equal concentrations of two types (positive and negative) of randomly distributed charged particles are allowed to perform random walks and to aggregate with a given sticking probability. This process leads to the formation of a maximal cluster – called "cloud" – the mass of which, as well as net "charge" and electric dipole moment, increase with time, over a wide range of parameters. Through this simple field-free model, we find that the net "charge" of the maximal cluster, of the overall neutral system, increases with the square root of its (the cloud's) mass, while the electric dipole moment increases quasi-linearly and in fact super-linearly. Furthermore, the dependence of the electric dipole on the mass is determined by the fractal dimension of the formed maximal cluster (cloud). Thus, we show that an internal electric field, with a field-strength that increases with cloud size, can be spontaneously generated by a simple random-walk/sticking process, completely devoid of any kind of external fields. Potential implications on "real life" clouds are discussed, i.e., the electric dipole moment based possibility of having atmospheric intra-cloud lightning discharges, and the net electric charge based possibility of having extra-cloud lightning discharges (cloud-to-cloud and cloud-to-ground), all in the absence of gravitational or other external fields or forces. Potential applications to other kinds of clouds and to biology are also discussed.

1. Introduction

Several previous studies [1–4] examined the distributions of the sizes of clusters formed by aggregation of single particles, within the frame of both 2-D and 3-D lattices, and the corresponding dynamic scaling functions were derived. No

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charges were included in these studies; all clusters consist of neutral particles. In 2005, Kim et al. conducted experiments featuring aggregation of oppositely charged particles within polystyrene spheres, leading to cluster formation of varying structures, depending strongly on the background electrolyte [5]. Cluster aggregation has also been modeled in other studies, mainly related to gelation, with resulting fractal dimensions [4–16].

All the aforementioned studies either only consider uncharged particle aggregation or, even if the particles involved are charged, focus solely on the structural characteristics of the clusters ensuing from the aggregation processes but disregard other features, such as the resulting net charge and electric dipole moment. Theoretical or simulation models to study such properties of the generated clusters, which might provide valuable information concerning potential applications, are currently absent from the literature.

We propose a simple model consisting of two types of equally charged particles, but one kind positive and the other negative, performing random walks. They aggregate into clusters, with a bias for nearest neighbors to be of opposite "charge". We examine specific properties of the resulting "cloud", i.e. the maximal cluster formed, specifically its net "charge" and electric dipole moment. The question of interest is: Can such a process generate an internal electric field in the cloud, or, alternatively, form a cloud-wide large electrical dipole, even in the absence of any form of original or external field?

Our results show that the "charge" accumulated on the maximal cluster increases with time and cluster mass, and that, as a consequence, an electric dipole moment is generated, also increasing with time and cluster mass. Thus, we conclude that an internal electric field can indeed be spontaneously generated by a simple random-walk process of aggregating charged particles, in the absence of external fields. We also find that the resulting structures depend strongly on the initial particle concentration, as exemplified by the calculated fractal dimension. For low particle concentrations the fractal dimension is close to 1, resulting in a linear cluster type (see example in Fig. 1), while for higher initial concentrations the resulting clusters are more compact, with fractal dimensions up to 1.75.

2. Method of simulation

Positively charged, A, and negatively charged, B particles are placed randomly on a two-dimensional lattice of size L x L, with density $d_A = d_B$, respectively. At this point the particles are considered to be clusters of mass 1, with equal absolute "charges". Clusters are selected at random and they perform a random walk on the lattice to the nearest neighbor sites, under the constraint that a lattice site cannot be occupied by more than one particle at a time (excluded volume). When a move is to be made one of the four directions (up, down, left, and right) is chosen at random. If the chosen new position is not occupied the cluster moves into it, otherwise, it remains at its original position. All clusters have a mobility that is inversely proportional to their mass. This, in effect, means that a "lighter" cluster would move more frequently than a "heavier" one e.g. a cluster of mass 1 moves approximately in every MC step, whereas a cluster of mass 20 moves approximately once every 20 steps, etc. Notably, the diffusion of each cluster is independent of other clusters unless they are "hit". When all clusters have attempted to move once using this mechanism, regardless of whether the attempt is successful or not, this constitutes one Monte-Carlo time step (MCS). After all allowed moves have been made, any two clusters that happen to be now nearest neighbors are merged into one cluster, with probability p that depends on the type of the neighboring particles of the touching clusters. The merging probability between two particles of different type is $p_{A-B} = 1$, while the merging probability of two particles of the same type $p_{A-A} = p_{B-B}$ is an arbitrary external parameter in the range $0<p<1$. The mass and "charge" of the derived cluster is the algebraic sum of the respective masses and "charges" of the formerly separate clusters. Periodic boundary conditions are applied on the lattice. We let the system evolve for several steps while monitoring the amount of absolute net "charge" and the dipole moment of the clusters formed. The process continues until all clusters have been merged to one final cluster. In Fig. 1 we show a pictorial for the process after 1 million steps. We give two different initial concentrations, in (1a) d = 0.05, and (1b) d = 0.15. We observe that in (1a), where the initial concentration is low, we see that a single cluster has been formed that is composed of positive and negative particles, which is almost 1-dimensional. In (1b), where the initial concentration is high, a more complex structure has been formed.

3. Results

"Charge" accumulation

We followed the evolution of the system for five different particle densities, $d_A = d_B = 0.0025$, 0.005, 0.025, 0.05 and 0.15. We allow the system to proceed to 300,000 MCS, and we isolate the largest (maximal) cluster that is formed. The latter is often called "maxicluster" or "largest aggregate" and will also be called "cloud". We plot the "charge" in this maximal cluster for these five densities, producing Fig. 2. Additionally, we do the same for the cluster that is carrying the maximal "charge" (Supplementary Fig. 5). All lines in Fig. 2 can be fitted as power-law curves, with approximately the same exponent for all densities examined. The calculated exponent (Fig. 2) is $a \cong 0.51$, as expected from the following argument. As the A and B particles attach to a cluster with the same probability, the absolute net "charge" for a cluster consisting of a large number of particles, n, is expected to be proportional to $n^{1/2}$. The same holds true for the line of Supplementary Fig. 5.

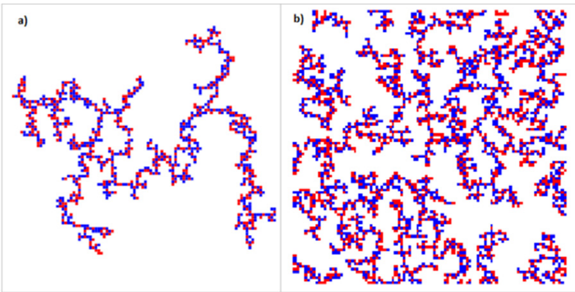

Fig. 1. A pictorial of the process studied, after 1 million steps at which time a single cluster has been formed. Red and blue particles designate the two different "charges". Density (a) $d_A = d_B = 0.05$, (b) $d_A = d_B = 0.15$, Lattice size: 100 × 100.

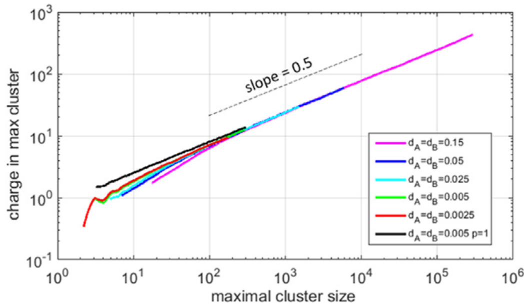

Fig. 2. "Charge" in the largest cluster vs. its mass, in the case of a 1000 × 1000 lattice with periodic boundary conditions. Five particle concentrations are studied in these systems after 300,000 Monte-Carlo steps. Averages are over 10,000 realizations.

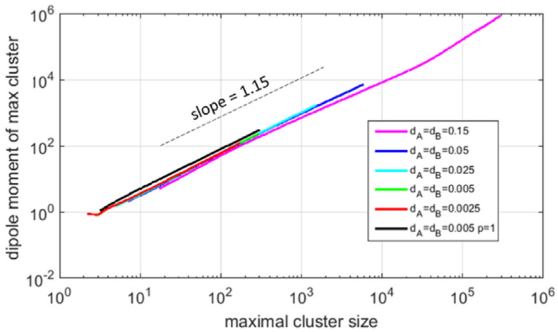

Fig. 3. Dipole moment of largest cluster vs. its mass, in the case of a 1000 × 1000 lattice with periodic boundary conditions. Five particle concentrations are studied in these systems after 300,000 Monte-Carlo steps. Average is over 10,000 realizations. The dotted line is a straight line with a slope = 1.15.

Electric dipole moment

In Fig. 3 we calculate the dipole moment of the largest cluster as a function of its mass, for the same five different densities. We observe that all curves for all densities collapse into one line with a slope α in the range ∼1.07–1.24 and a mean value of approximately 1.15.

Fractal dimension

We calculated the fractal dimension d_f of the maximal cluster using the box counting method [17], for several particle concentrations. We plot our results in Fig. 4 (blue squares) and observe two different regimes. One for low particle concentrations, where the rate of increment is slow, and one for higher concentrations, where the rate is higher, with a crossover at about density d≈0.03

In all the above simulations we used $p_{A-A} = p_{B-B} = 0.1$.

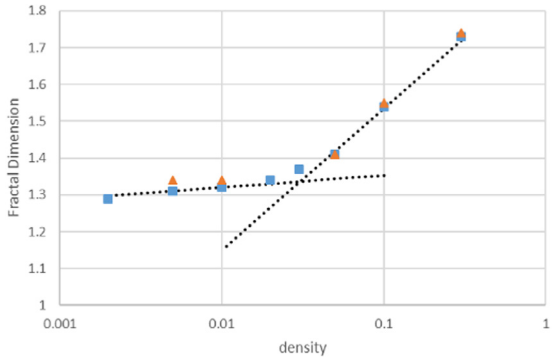

Fig. 4. Fractal dimension of the largest cluster as a function of the total particle concentration (blue squares). A number of 100 realizations were averaged. Red squares are the d_f values as calculated by Eq. (13), see discussion later.

4. Discussion

Total "Charge":

As the A and B particles attach to a cluster with the same probability, the absolute "charge" for a cluster consisting of a large number of particles, N, is expected to be proportional to $N^{1/2}$.

Let q_i be the "charge" of particle i, with $q_i = +1$ or -1 with equal probability. Then for the total "charge" Q of a cluster of N particles, we have:

$$Q = \sum_{i=1}^{N} q_i$$

$$Q^2 = \sum_{i=1}^{N} q_i \sum_{j=1}^{N} q_j = \sum_{i=1}^{N} (q_i)^2 + \sum_{i \neq j} q_i q_j = N + \sum_{i \neq j} q_i q_j$$

$$\langle Q^2 \rangle = N + \left\langle \sum_{i \neq j} q_i q_j \right\rangle = N$$

since $q_i = +1$ or -1 with equal probability. Therefore,

$$\sqrt{\langle Q^2 \rangle} = \sqrt{N}$$

$$|Q| \sim \sqrt{N}$$

"Charge" to mass ratio:

Since the total "charge" increases with the cluster mass as $Q \sim N^{1/2}$ the "charge" to mass ratio decreases with the cluster mass as $Q/N \sim N^{1/2}/N = N^{-1/2}$.

Electric dipole moment

The dipole moment $\vec{p}$ of N charged particles and non-zero overall (total) "charge" is defined as:

$$\vec{p} = \sum (\vec{r}_i - \vec{r}_{ref}) q_i \tag{1}$$

where the sum runs over all charged particles of the cluster; the vector $\vec{r}_i$ is the position of the ith particle, measured from an arbitrary origin; q_i is its "charge" and $\vec{r}_{ref}$ a reference point.

The results of the simulations indicate that the relation between the dipole moment P and the mass N of the cluster is (see Fig. 3):

$$P \sim N^a \tag{2}$$

where the exponent α is in the range 1.07–1.24.

This result is rationalized as follows: N (positive and negative) is the number of particles ($N_+ \approx N_- \approx N/2$), i.e. the mass of the cluster. **R** is the cluster's linear dimension, and $\mathbf{X_i}$ is the position (abscissa) of droplet i, on the X axis ($i = 1$ … N). Focusing on the horizontal axis, we make the following assumption: The abscissas of the particles are uniformly distributed in [0, R] and independent. Therefore, the position X_i can be seen as a random variable, assuming independent random values, uniformly distributed in the range [0, R] (see Fig. 5)

The mean, variance and standard deviation of such a random variable, are:

$$\overline{X}_i = \frac{R}{2} \tag{3a}$$

$$\sigma^2_{X_i} = \frac{R^2}{12} \tag{3b}$$

$$\sigma_{X_i} = \frac{R}{\sqrt{12}} \tag{3c}$$

If we take a sample of the random variables X_i, the mean μ (i.e. the center of mass), the variance of the mean $\sigma^2{}_{cm}$, and the standard deviation σ_{cm} of the mean are:

$$\mu = \sum \frac{X_i}{N} = \frac{R}{2} \tag{4a}$$

$$\sigma^2_{cm} = \frac{\sigma^2_{X_i}}{N} \tag{4b}$$

$$\sigma_{cm} = \frac{\sigma_{X_i}}{\sqrt{N}} \tag{4c}$$

The mass of the cluster depends on its linear dimension R, following a power law:

$$N \sim R^{d_f}$$

where d_f is its fractal dimension. It follows that:

$$R \sim N^{1/d_f} \tag{5}$$

Combining (3c), (4c) and (5) we derive the following relation:

$$\sigma_{cm} \sim \frac{N^{1/d_f}}{\sqrt{12N}} \sim N^{\frac{1}{d_f}-\frac{1}{2}} \tag{6}$$

We will use Eq. (6), to find an expression for the relation between the dipole moment P of the cluster and its mass N (mass).

The total positive and negative "charges" are almost equal, and of the order of N:

$$Q \approx Q_+ \approx Q_- \approx N/2 \tag{7}$$

The dipole moment P is defined as the product of the "charge" Q, times the distance Δx of the centers of mass of the positive and negative "charges". The distance Δx is of the order of σ_{cm}:

$$\Delta x \sim \sigma_{cm} \tag{8}$$

By combining (6) and (8), we get:

$$\Delta x \sim N^{\frac{1}{d_f}-\frac{1}{2}} \tag{9}$$

Since the same reasoning holds for the y-axis, we can assume that $\Delta y \sim \sigma_{cm}$, and

$$\Delta r = \sqrt{\Delta x^2 + \Delta y^2} \sim \sigma_{cm}$$

is also of the order of σ_{cm}.

Finally, from (7) and (9) we get for the dipole moment P:

$$P \sim Q \cdot \Delta r \tag{10}$$

$$P \sim N^{\frac{1}{2}+\frac{1}{d_f}} \tag{11}$$

Therefore, the exponent α is:

$$\alpha = \frac{1}{d_f} + \frac{1}{2} \tag{12}$$

and

$$d_f = \frac{1}{a - \frac{1}{2}} \tag{13}$$

In Table 1 we show in the second column the slope as derived from the simulations. In the third column we list the fractal dimension of the maximal cluster, as it was found from the simulations using the box-counting method [17]. In

Table 1
Fractal dimension of the maximal cluster from simulation using the box-counting method and calculations using Eq. (13).

Total density	Slope (α) from simulation	Fractal dim from simulation using box-count	Fractal dim from calculation (Eq. (13))
0.3	1.073	1.73	1.74
0.1	1.145	1.54	1.55
0.05	1.210	1.41	1.408
0.01	1.245	1.32	1.342
0.005	1.242	1.31	1.348

the fourth column, we list the fractal dimension of the maximal cluster as it was calculated from Eq. (13), using the slope of the curves of Fig. 3 (second column). We find excellent consistency for the fractal dimension.

Dipole moment to mass ratio:

Since the electric dipole moment increases with the cluster mass as P $\sim N^{1/2+1/df}$, the dipole moment to mass ratio also increases with the mass as P/N $\sim N^{-1/2+1/df}$, i.e. the exponent is positive for $d_f < 2$.

Fractal dimension vs. concentration

In Fig. 4 we added (red triangles) the fractal dimension as calculated by Eq. (13), and we see that it is in very good agreement with the values derived from the box counting method (blue squares), with the same trends and crossover point as discussed earlier.

In our model we simply assume that each particle can be represented by a fixed absolute "charge", positive or negative, and that the sticking probability between any two depends on their positive, or negative attraction. The "cloud" formation process is modeled by the formation of clusters, followed by the aggregation of such clusters into progressively larger ones, all based on a simple random walk and sticking probability model. A well-known similar simple model, Diffusion Limited Aggregation (DLA) [18] has found much application in physics, chemistry and biology [19].

5. Potential applications?

Can our model be applied to atmospheric or other clouds? The interest in the relation between electric charge formation and lightning goes back to antiquity but at least to Benjamin Franklin [20]. Atmospheric clouds presumably form by the condensation and aggregation of water droplets ("particles"), in various freezing states. Each "particle" (could be an ice crystal or a "hailstone") may contain a minute amount of "charge", negative or positive. Though a complete picture may not yet have been established, the "standard model" assumes gravity induced height segregation between the positive and negative "charge" carrying units [21]. Also, the lightning discharge to ground is attributed to the latter's surface charge [22]. Similarly to our current problem, we know that the dynamics of the onset of rainfall in warm clouds has also been poorly understood. Large Deviation Analysis is used to describe the growth of a raindrop by the collision of microscopic droplets, a problem which is equivalent to the current problem [23].

Notably, additional parameters, such as gravity, are excluded from our model. It also does not include convection or charge screening at larger than nearest neighbor distances. The latter may be particularly important for aqueous solutions. However, we note that the electrostatic interaction range can be easily tuned by varying the ionic strength of the solvent. The value of the field at the second nearest neighbor can drop to 0.1% of the value at the nearest neighbor, if $\kappa\sigma > 6$, where κ^{-1} is the Debye screening length and σ is the particle diameter [24,25]. Considering dilute solvents, such as thin air or a vacuum, could this simple model contribute towards a more complete model regarding terrestrial clouds and lightning? Could this model contribute towards the understanding of interstellar or planetary or volcanic clouds? Future work will have to tell.

Also, a conundrum similar to that of storm cloud formation (but with no lightning and thunder) appears to be the unexpected formation of very large electric fields in the cytosol of a biological cell [26,27]. Presumably their formation has to do with the aggregation of proteins, with their inherent charged groups. While this protein aggregation may be of a more complex nature, involving not only translation and sticking, but a more precise accounting of screening, as well as that of protein orientation (and possible conformational changes and/or hydrogen bonds), the simple model presented here for the process of cloud formation may serve as a very rough first approximation for the cellular process, or may at least serve as a guide for forming a reasonable model that represents the biological situation.

6. Conclusions

A simple hetero-aggregation model, starting with an equal number of insulator particles (e.g., frozen water particles) with positive and negative "charges", of equal absolute magnitudes, randomly distributed in 2-dimensional space, is able to show the formation of a maxicluster or largest aggregate (called "cloud"), increasing in time, followed by the formation of a net "charge", as well as an electric dipole, both increasing in time, while the overall electrical neutrality of the system is still maintained. Regarding the growth in net ''charge'', as well of the dipole moment, with aggregate mass, the Monte-Carlo simulations agree with simple theoretical relations, where the fractal dimension of the aggregate maxicluster mass is the only parameter. Notably, there are only (non-screened) internal Coulomb forces implied, but there is no need to introduce gravity or external polarization fields, in contrast to existing models that explain atmospheric cloud formed lightning phenomena. In principle, such a dipole may lead to an electric discharge, i.e., the formation of ''intra-cloud lightning'', in the proper medium, without any need for external fields (such as gravity). Similarly, the net ''charge'' accumulations may help explain inter-cloud and cloud-to-ground lightning discharge phenomena. It is intuitively obvious that, qualitatively, similar results would be gotten in 3-dimensions, with a quasilinear dependence of the dipole on the mass, and still a square root dependence of the net ''charge''. Several questions arise now as a result of these findings. Could such a model be helpful in understanding natural or lab generated phenomena? Could it be relevant to atmospheric or even extraterrestrial or interstellar clouds? Could it be relevant to the build-up of electric fields in biological cells or subcellular compartments? We hope that this study will encourage future work on these interesting questions.

Declaration of competing interest

None.

Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.physa.2019.121433.

References

[1] P. Meakin, Formation of fractal clusters and networks by irreversible diffusion-limited aggregation, Phys. Rev. Lett. 51 (1119) (1983).
[2] M. Kolb, R. Botet, R. Jullien, Scaling of kinetically growing clusters, Phys. Rev. Lett. 51 (1123) (1983).
[3] P. Meakin, T. Vicsek, F. Family, Dynamic cluster-size distribution in cluster-cluster aggregation: effects of cluster diffusivity, Phys. Rev. B 31 (564) (1985).
[4] S. Jungblut, J.-O. Joswig, A. Eychmüller, Diffusion-limited cluster aggregation: Impact of rotational diffusion. arXiv:181007109 [cond-mat] [Internet]. 2018 Oct 16 [cited 2018 Nov 1]; Available from: http://arxiv.org/abs/1810.07109.
[5] A.Y. Kim, K.D. Hauch, J.C. Berg, J.E. Martin, R.A. Anderson, Linear chains and chain-like fractals from electrostatic heteroaggregation, J. Colloid Interface Sci. 260 (149) (2003).
[6] A. Al-Sunaidi, M. Lach-Hab, A.E. González, E. Blaisten-Barojas, Cluster-cluster aggregation in binary mixtures, Phys. Rev. E 61 (1) (2000) 550.
[7] A.M. Puertas, A. Fernandez-Barbero, F.J. de las Nieves, Colloidal aggregation induced by attractive interactions, J. Chem. Phys. 115 (5662) (2001).
[8] J.C. Gimel, T. Nicolai, D. Durand, 3D Monte-Carlo Simulations of diffusion limited cluster aggregation up to the sol-gel transition: structure and kinetics, J. Sol-Gel Sci. Technol. 15 (2) (1999) 129–136.
[9] S. Díez Orrite, S. Stoll, P. Schurtenberger, Off-lattice Monte Carlo simulations of irreversible and reversible aggregation processes, Soft Matter 1 (5) (2005) 364–371.
[10] M. Rottereau, J.C. Gimel, T. Nicolai, D. Durand, Monte Carlo Simulation of particle aggregation and gelation: I. Growth, structure and size distribution of the clusters, Eur. Phys. J. E 15 (2) (2004) 133–140.
[11] F. Li, D. Sun, T. Wu, Y. Li, Aggregation and deposition of in situ formed colloidal particles in the presence of polyelectrolytes, Soft Matter 13 (8) (2017) 1539–1547.
[12] S. Abbas, I. Yadav, S. Kumar, V.K. Aswal, J. Kohlbrecher, Structure and interaction in pathway of charged nanoparticles aggregation in saline water as probed by scattering techniques, Chem. Phys. Lett. 675 (2017) 124–130.
[13] T. Curk, J. Dobnikar, D. Frenkel, Rational design of molecularly imprinted polymers, Soft Matter 12 (1) (2016) 35–44.
[14] S. Lazzari, B. Jaquet, L. Colonna, G. Storti, M. Lattuada, M. Morbidelli, Interplay between aggregation and coalescence of polymeric particles: Experimental and modeling insights, Langmuir 31 (34) (2015) 9296–9305.
[15] P.J. Lu, E. Zaccarelli, F. Ciulla, A.B. Schofield, F. Sciortino, D.A. Weitz, Gelation of particles with short-range attraction, Nature 453 (7194) (2008) 499–503.
[16] A.-C. Genix, J. Oberdisse, Nanoparticle self-assembly: from interactions in suspension to polymer nanocomposites, Soft Matter 14 (25) (2018) 5161–5179.
[17] D.A. Russell, J.D. Hanson, E. Ott, Dimension of strange attractors, Phys. Rev. Lett. 45 (14) (1980) 1175–1178.
[18] T.A. Witten Jr, L.M. Sander, Diffusion-limited aggregation, a kinetic critical phenomenon, Phys. Rev. Lett. 47 (19) (1981) 1400.
[19] J.M. Garcia-Ruiz, E. Louis, P. Meakin, L.M. Sander, Growth Patterns in Physical Sciences and Biology, Springer, New York, 1993.
[20] E.P. Krider, Benjamin franklin and lightning rods, Phys. Today 59 (1) (2006) 42–48.
[21] M.A. Uman, All About Lightning, Dover Publications, New York, 1987.
[22] V. Cooray, An Introduction to Lightning, Springer, Dordrecht, 2015.
[23] M. Wilkinson, Large deviation analysis of rapid onset of rain showers, Phys. Rev. Lett. 116 (1) (2016).
[24] K. Singh, A. Raghav, P.K. Jha, S. Satapathi, Effect of size and charge asymmetry on aggregation kinetics of oppositely charged nanoparticles, Sci. Rep. 9 (1) (2019).
[25] A.-P. Hynninen, M.E. Leunissen, A. van Blaaderen, M. Dijkstra, Cuau structure in the restricted primitive model and oppositely charged colloids, Phys. Rev. Lett. 96 (1) (2006).
[26] V.P. Andreev, Cytoplasmic electric fields and electroosmosis: Possible solution for the paradoxes of the intracellular transport of biomolecules. lytton ww, editor, PLoS One 8 (4) (2013) e61884.
[27] K.M. Tyner, R. Kopelman, M.A. Philbert, Nanosized voltmeter enables cellular-wide electric field mapping, Biophys. J. 93 (4) (2007) 1163–1174.