

COAGULATION OF CHARGED NANOPARTICLES: REFINED CLASSICAL APPROACH AND ITS LIMITS

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Abstract. Electro-Brownian coagulation of charged nanoparticles has been theoretically investigated, in the range of the moderate Knudsen numbers, $0.1 < Kn < 10$, which correspond to the transition flow regime. New results include: (a) refining a classical theory of the coagulation in the transition regime, (b) criteria of the coagulation of charged fine particles (the “aerosol analogy” of the DLVO theory), (c) the exact charge-size distribution function of charged aerosol ensemble in bipolar ion atmosphere (Boltzmann's equilibrium), (d) criteria of applicability and limits of the refined classical approach. A comparison of theoretical and experimental data demonstrates adequacy of the theory in the range of its validity.

Key Words: boundary sphere method; charge distribution function; coagulation; Knudsen's transition regime; nanoparticles

1. Introduction

Charging of aerosol particles affects the coagulation and evolution of aerosol, in part its size distribution. The efficiency of particulates to penetrate and deposit into the human respiratory tracts and their carcinogenic and mutagenic health effects dramatically depends on their electric charges and sizes, especially, in nano-scale. Since most aerosols carry electrical charge, there are many diverse reasons for studying the coagulation dynamics of charged particles. It presents an interest for both science and technology, e.g., cloud and atmospheric physics, electrostatic propulsion for space vehicles and space thrusters, preventing dust/soot explosion, electrostatic atomization and mass spectrometry, nano-instrumental techniques, nano- and environmental technology, “nano-medicine”, etc. (1-6). But still the fundamentals of electrical phenomena in the coagulation of nano-particulates are not clearly understood. Let us review and refine the classical concept of the electro-Brownian coagulation of charged nanoparticles corresponding to the flow transition regime. The main questions we want to answer are: “What are essential peculiarities and criteria of charged nanoparticles coagulation?” and “What is a range of validity of the classical concept of coagulation?”

2. Peculiarities of the coagulation motion of fine particles

Characteristic lengths, times, and scale in coagulation of particles. For analyzing coagulation of particulate matter, first, one has to account for the mean free path of aerosol particulates, or the average distance over which the particle loses all correlation with the initial direction of its motion (the correlation length), and the correlation time¹, τ . The correlation length, l_p is defined as $l_p = \overline{v_p} \tau$, where $\overline{v_p} = \sqrt{8kT / \pi m_p}$ is the thermal velocity of the particle, $\tau = m_p / B$, B is the particle mobility, m_p is the particle mass, k is the Boltzmann factor, and T is the temperature (7). The effective Knudsen number, Kn_p , in aerosol motion is: $Kn_p = l_p \sqrt{2} / 2a$; it differs from the molecular “free path” in air. For particulates of unit density the values of the spherical particle radii, a , l_p and Kn_p suspended in air were analyzed in (8). Knudsen numbers for aerosol particles in range $r \approx 1 \div 100$ nm belong to the range: $Kn_p \approx 0.1 \div 46.4$. The transition Knudsen regime between the diffusion and the gas-kinetic (or “free molecular”) motion, $Kn_p \in [0.1, 10]$, is an essential part of nanoparticle motion. Let us focus on this range.

The slip flow regime. For extending the continuum diffusion theory results to particle sizes comparable with the correlation length, for moderate Kn_p when Stokes' formula is invalid, Cunningham proposed to modify the Stokes drag force by an empirical factor, $C(Kn_p) = 1 + AKn_p$,

¹ In literature one can find using both couples of terms: the correlation length and the correlation time, and the free path and the relaxation time; their senses are very close, reflecting the same matter from different viewpoints.

where $A \approx 0.70$ for rough spheres (7). Weber introduced another empirical formula which is valid for still smaller particles: $C(Kn_p) = 1 + Kn_p \left[A_1 + A_2 \exp(-A_3 / Kn_p) \right]$. Then Stokes' drag force and, correspondingly, a diffusion coefficient are corrected: $F_a = 6\pi a \eta V / C(Kn_p)$, $D_a = kTC(Kn_p) / 6\pi a \eta V$; here V is the particle velocity, η is the medium viscosity. But even if the correction factor accurately describes the drag change with Knudsen number, unfortunately, it does not lead to a correct form of the coagulation coefficient (9).

The “boundary sphere” approach to the coagulation in the transition regime. As the particle size approaches molecular dimensions, the correction factor, $C(Kn_p)$, becomes very large which is incompatible with kinetic theory. For resolving this anomaly, Fuchs (7) has analyzed the transition regime between continuum and free molecular flow, and developed a famous method of the “boundary sphere” (or the “jump distance”). According to Fuchs, the “probe” particle is included into a concentric sphere of the radius $R_0 + \delta$, where $\delta \sim l$, and $R_0 = a + b$, is the radius of the “influence sphere” presenting a sum of radii of the two colliding particles. Inside of the inner zone, at $R_0 \leq r < R_0 + \delta$, a particle movement is regarded as free, and a flux is calculated by an elementary kinetic theory. In the external zone, at $r > R_0 + \delta$, one regards a diffusion. At a boundary, $r = R_0 + \delta$, both fluxes have to be equal. The value of δ is defined as the mean length reached by the reflected particle until the first collision in medium. For coagulation of particles in the Knudsen transition regime, Fuchs derived a formula for the correction factor, $C_F^{a,b} = f(a, b, l, \delta)$ (7). The Fuchs approximation gives correct expressions of the flux onto the probe sphere both in the diffusion and kinetic regimes (at $Kn_p \ll 1$, and $Kn_p \gg 1$, respectively). Therefore Fuchs' correction expresses the transition from diffusive to gas-kinetic coagulation regime just as Cunningham's correction presents the transition from the hydrodynamic to the gas-kinetic regime of particle motion. However Fuchs underestimated and dropped an important effect of viscous forces in the relative particle motion.

Effect of viscous forces. In fact, the relative motion between two colliding particles, in the vicinity of the “sphere of influence” is correlated over the distance of the correlation length order. It is caused by velocity gradients generated with a moving particle in the viscous air. Thus two particles approaching each other have friction coefficients quite different from that of single particle. Last years this problem is thoroughly investigated (10-16). For accounting viscous forces, the effective diffusion (tensor) coefficient is introduced: $D_{ef}(r) = D_0 \beta(r)$, where $\beta(r)$ is the “hydrodynamic factor” as a function of the particle separation, r . The effective diffusion coefficient of closing particles depends on the particle separation and loses its additivity: $\overline{D_{12}} \neq (D_1 + D_2) / 2$. A convenient formula to describe the effect of viscous forces on diffusion of two equal spherical particles is derived in (12): $1 / \beta(u) = (6u^2 + 4u) / (6u^2 + 13u + 2)$, where $u = (r - 2a) / a$. The effect of viscous forces is to reduce collision efficiency and thereby retard the coagulation rate in the continuum and the transition regime. Especially it is essential in the coagulation of nanoparticles, as we will see later. Thus the Fuchs theory of coagulation has to be corrected by including the hydrodynamic factor (viscous forces).

3. Refining the classical theory of coagulation of charged nanoparticles

Initial model, major forces and effects. For simplicity sake, one can take a case of the electro-Brownian coagulation of identical fine particles of spherical shape. As major forces in coagulation dynamics one regards a contribution of molecular van der Waals', Coulomb's, and “image forces”. The hydrodynamic factor is taken into account too. A laminar flow of identical particles at low Peclet's and Reynolds' numbers is considered. The conceptual background of this theoretical approach is based on Fuchs' “flux-matching” classical theory of the transition regime in the laminar aerosol coagulation, a “general” coagulation theory (9, 17), and accounting for the hydrodynamic factor in diffusion.

The equilibrium charge distribution function of aerosols in the bipolar ion atmosphere. For the charging process to be regarded as quasi-stationary, the relaxation time of the ion atmosphere around aerosols should be much less than the mean time between the charge-transfer events. Under

these conditions the electric field set up by the non-uniform distribution of the ions around the particulates, i.e., the screening effect, can be ignored. Such conditions are indeed conducted in the laboratory and in the atmosphere. For any initial charge distribution of particulates, a steady-state (or stationary) distribution is eventually established in aerosols (8). A steady-state charge distribution of particles in a bipolar ion atmosphere, when concentrations, mobilities and other properties of the ions of both signs coincide, conventionally, is described by the Boltzmann distribution (7, 18). But the Fuchs-Sutugin charge distribution (limited with particle sizes $a \geq 10^3$ nm) shows tendencies of deviation from the Boltzmann law (8). However in (19-20) the Boltzmann distribution was confirmed in recent experiments with nano-aerosols in the bipolar ion atmosphere. Suggesting the Boltzmann equilibrium, one can derive a known formula for the average particle charge as a function of its size: $\bar{Z} = f(d) \approx \sqrt{dkT/\pi e^2}$, if $d \geq 50$ nm (18). Here \bar{Z} is the mean number of elementary charge units, e is the electron charge, d is the particle diameter. Let us refine this formula, extending its validity up to zero size. It is easy realized by replacing the method of averaging Z used in (18) with its direct summing (integrating). After simple transformations, a final useful formula is derived:

$$\bar{Z} = \{x \mathfrak{G}_3(0, \text{Exp}(-x))\}^{-1}, \quad x = \frac{e^2}{dkT}, \quad d \geq 0 \quad [1]$$

$$\text{where } \mathfrak{G}_3(u, q) = \prod_1^{\infty} (1 + 2e^{-x(2n-1)} + e^{-2x(2n-1)})(1 - e^{-2nx})$$

Here $\mathfrak{G}_3(u, q)$ is the elliptic theta function (21). A numerical comparison of difference between this exact and previous formulas shows a large deviation at $a < 10$ nm. Probably it could partially explain the Fuchs-Sutugin results noted above.

The inter-particle potential. In a general form, the total interaction potential of central forces between two particles, $U_{\Sigma}(r)$, including molecular, $U_M(r)$, electrostatic, $U_C(r)$, and the “image”, $U_{im}(r)$, parts, is: $U_{\Sigma}(r) = U_M(r) + U_C(r) + U_{im}(r)$. The molecular potential of identical particles as a function of the separation distance, within the framework of the pairwise additive concept is found in (22). For particulates in the range $a \leq 10$ nm, the Hamaker constant (22) depends on the particle size due to quantum effects. For nanoparticles the “retardation” effect is vanish (23). For simplicity we can employ a “point” approximation of charged equal particles: $a = b \rightarrow 0$. If two like charged particles do approach closer, they induce a charge of opposite polarity so that a force of attraction is formed, additionally to initial repel, “the force of image”. At smaller distances the image force can change its sign, from repulsion to attraction. In general, this effect is suggested to be marginal for coagulation of large identical like charged particles; but it has to be considered in coagulation of charged particles with uncharged ones. The real value of the image force depends on the particles stage, conductivity, dielectric permittivity, structure, etc. Analyzing contribution of image forces, one has to distinguish two character cases: (A) interaction of charged and neutral particles, and (B) interaction of like charged particles. A third case of interaction of oppositely charged particles is trivial and dropped. (A). *Interaction of the charged particle with the neutral one.* For this case, neglecting the details for brevity, we obtain the condition of dominating the dispersion attractive force, when the image effect can be ignored:

$$Ze^2 / aA \ll 1 \quad [2]$$

For estimations, let us take, e.g., soot nanoparticles with a typical value of Hamaker’s constant $A \sim 10^{13}$ erg; then from this criterion, for a particle with $Z=1$, one can find that the criterion can be satisfied only for particles with $d > 250$ nm, and larger for $Z > 1$. We find that for nanoparticles image forces must be always taken into account, while for larger particulates they can be dropped when the criterion [2] is satisfied. (B). *Coagulation of two like charged particles.* A general conclusion is the same: analyzing coagulation of charged particles one can drop the image effect if the criterion [2] is satisfied. The image forces of nanoparticles cannot be neglected since they are the same order as molecular forces. Attractive image forces increase coagulation of nanoparticles.

The coagulation coefficient and the enhancement factor. For the case of identical charged nanoparticles in the transition regime a coagulation coefficient is:

$$K(a, a) \approx 16\pi D_a C_F^{a,a} W_{\Sigma}(a, a) = \frac{8kT}{3\eta} C_F^{a,a} W_{\Sigma}(a, a) \quad [3]$$

Here the “enhancement” factor as a measure of the inter-particle interaction, $W_{\Sigma}(a, a)$, equals

$$W_{\Sigma}(a, a) = \left\{ 2a \int_{2a}^{\infty} \frac{\beta(r)}{r^2} \exp \left[\frac{U(r)}{kT} \right] dr \right\}^{-1} \quad [4]$$

The DLVO-type criterion for the electro-Brownian coagulation of aerosol particles. Let us expand the extremum criteria of the “slow” coagulation of hydrosols formulated in the Derjaguin-Landau-Verway-Overbeek (DLVO) theory, $[dU(r=r_m)/dr]=0$, $U(r=r_m)=0$, for the electro-Brownian coagulation of identical charged aerosol particles. Dropping details, after some transformations, we obtain a simple analytical criterion for coagulation of two like charged dielectric particles driven with molecular, Coulomb’s, and image forces:

$$0.544eZ^{1.015} / aA \leq 1 \quad [5]$$

This criterion estimates whether two like charged colliding particles may coagulate.

Criterion of the coagulation of like charged particles in the steady-state bipolar ion atmosphere. Substituting in the formula above the mean equilibrium charge, $\bar{Z} = \alpha \sqrt{dkT/e^2}$, after simplifications we obtain:

$$\alpha^2 kTe^2 / 2aA^2 \leq 1 \quad [6]$$

Here $\alpha = const \sim 1$. In addition to the three driving forces in the particles motion this criterion includes their Brownian energy (the factor kT). Satisfying the condition [6] leads to coagulation (sticking) two colliding like charged particles in the steady-state bipolar ion atmosphere. It can be treated as a condition of the minimal value of Hamaker’s constant at a given particle size when coagulation is yet possible, i.e., the attractive dispersion and image forces prevail over repulsive Coulomb’s and “distractive” Brownian ones. The case of equality means equilibrium between attractive molecular forces and repulsive electrostatic forces, or, in other words, a “turning point” when a coagulation barrier equals zero.

Criterion of applicability of the “sphere of influence” concept. In the classical theory one does employ a notion of the “sphere of influence” or the “absorbing” sphere”: $R_{12} \approx a_1 + a_2$ (7). Employing a notion of the “sphere of influence” or the “absorbing sphere” in the classical theory, one keeps a suggestion that during (convective) diffusion of the particle to the sphere, the particle may go to infinity from any vicinity of the sphere, despite the influence of its field. But if the field is strong enough, the moving particle may not have energy for leaving vicinity of the absorbing sphere. In fact, diffusion goes to shorter distance: $R_{ef} > R_{12}$. One has to introduce some “sphere of capture”, $R_{ef} \equiv R_c$, to reflect this fact. For example, let us regard two interesting cases: (a) two neutral identical particles with attractive molecular force, and (b) two strongly unlike charged particles with dominating attractive Coulomb force (over molecular one). Elementary calculations show that in the first case (a) always $R_{ef} > R_{12}$ if Hamaker’s constant, $A \geq A^* \approx 4.04 \cdot 10^{-14}$ erg. If so, the Fuchs “sphere of influence” concept fails. Since typically A much larger, it means that a notion of the “sphere of influence” in theory of Brownian coagulation (for this case) is not adequate. From other side, if $A \leq kT$, coagulation is impossible due to dominating thermal excitations. From our data it follows that even relatively low unlike charging particles leads to dominating the “radius of capture” over the “radius of influence”. Influence of attractive molecular forces increases this effect. Therefore, for any unlike charged particles, in general, $R_{ef} > R_{12}$, and the concept of the “sphere of influence” is not adequate. In the case of the interaction of like charged particles, due to compensating the molecular attraction with electrostatic repulsion, the value of critical A^* can be larger. Namely this case was chosen for finding the criterion of coagulation.

4. Comparing and discussing theoretical and experimental data

The hydrodynamic factor. As it follows from our data, a dramatic decrease of the coagulation efficiency as particle size decreases (especially in the range of particle diameters less than 10-20 nm) can be explained with a prevailing of Brownian motion over the molecular attraction in this range, evidently under a strong influence of the viscous forces. On this basis we would interpret experimental data on the soot nano-particles in (24-26) that demonstrate a rapid decrease of the soot

coagulation rate in the nano-size area. Additionally, in this case some influence can be also caused by the quantum size dependence of Hamaker's constant.

Concerning the charge distribution of particles in the bipolar ion atmosphere. The conventional approximate formula for the charge distribution overestimates the real (exact) equilibrium charge; the relative deviation between the exact function and the approximation sufficiently grows with decreasing of the particle size in a range 1-15 nm. As shown in experimental measurements of charged soot particles in bipolar ion atmosphere (20), the soot particle fraction in this range may have charges: $Z=\pm 1, \pm 2$. Therefore, in this region one has to employ our exact formula [1] but not an old approximation. These data give a challenge to experimenters who could realize a thorough verification of the real charge distributions.

Charge effects. Our analysis of the charge effect on the coagulation half-life time demonstrated fitting the experimental in (27-28) on coagulation of the charged organic carbon nanoparticles. It is well fitted at small charges. Further increasing the particle charge leads to a disagreement which can be explained by theoretically overestimating the Coulomb's interaction energy using the "point" approximation. Refining the model may bring us closer to reality.

Theoretical verification. In the range of fine aerosol fraction when the effect of charge has vanished, our theory shows agreement with corresponding results in (29). These authors developed a general comprehensive theory of Brownian coagulation of uncharged particles. Both approaches are able to explain the fast decay of aerosol coagulation in the nano-scale range. Also we have analyzed data on coagulation kernel using the "refined" Fuchs model and other theories. All theories missing the hydrodynamic factor must be revised.

5. Summary

We have reviewed essential aspects of the dynamics of charged aerosol nanoparticles and proposed the refined classical model (RCM) of coagulation of charged nano-sized aerosols. This theory of the laminar electro-Brownian coagulation of charged particles is based on the Fuchs' "boundary sphere" concept which is completed with the hydrodynamic factor; it includes major van der Waals', Coulomb's and "image" forces; for simplicity, coagulation of particles of the equal radii has been only regarded. The RCM and its theoretical tool can be used for describing coagulation of charged and uncharged nano-aerosols in the transition Knudsen range. The limits of the RCM have been discussed. The major new results are: (a) the exact steady-state charge distribution function describing aerosol ensemble in the bipolar ion atmosphere, (b) the DLVO-type criteria of the coagulation of charged particles, (c) the refined electro-Brownian coagulation coefficient and the enhancement factor in the Knudsen transition regime, and (d) criteria of the RCM validity and its limits. A comparison of the theory with other theoretical and experimental data showed a good semi-quantitative agreement in some important cases.

Acknowledgement

I would like to cordially thank Profs. JoAnn Lighty and Adel Sarofim (University of Utah, Salt Lake City, USA) for stimulating my interest to this problem, useful discussions and a partial support, as well as Drs. D'Alessio, D'Anna, and Sagro (Napoli, Italy) for their data.

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