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Flux-matching theory of particle charging

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A new flux-matching theory is formulated and applied to the study of particle charging by ions. Assuming that the ion-particle interaction includes the Coulomb + polarization forces the collisionless kinetic equation is solved and the ion concentration profile in the free-molecule zone (at the distances less than the ion mean free path) is found. This profile is then matched to that derived from the solution of the diffusion equation, which describes the ion transport outside the free-molecule zone. Three matching parameters are introduced: the ion flux, the matching distance, and the ion density at the matching distance; and three conditions are formulated for fixing these parameters: (i) the constancy of the total ion flux, (ii) the continuity of the ion concentration profile, and (iii) the continuity of the derivative of the ion concentration profile. The charging efficiencies are expressed in terms of their free-molecule values, the ion diffusivity in the carrier gas, and the ion thermal velocity. This approach is applied for calculating the efficiencies of particle charging in the transition regime (the particle size is comparable to the ion mean free path and the Coulomb length). The corrections due to ion-carrier gas interaction to the particle-ion recombination rate are shown to remain finite even for very small particles, whereas in the case of particle-ion repulsion the contribution of ion-molecular collisions to the rate of particle charging is suppressed in the free-molecule regime.

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I. INTRODUCTION

Charged aerosol particles have attracted the attention of scientists and technologists for already more than a century. Considerable efforts had been addressed to the study of the kinetics of charging processes [1–8].

The first simplest theories applied the continuous models (the particle radius a much exceeds the ion mean free path l) of the charging process based on the use of the diffusion equation. Such models were not able to describe very small particles with sizes less than the ion mean free path [9–12]. It was quite natural therefore to try to attack the problem starting with the free-molecule limit, i.e., to consider a collisionless motion of ion in the electric field created by the particle. Respective expressions for the charging efficiencies had been derived and can be found in Refs. [2,13–15]. But the free-molecule consideration does not save the situation even in the limit of very small particles, for the ion-particle interaction adds a new characteristic length, $l_c = qQe^2/kT$ (the Coulomb length) which is comparable or exceeds the ion mean free path at ambient conditions. Here q, Q are the numbers of elementary charges on the ion and the particle respectively, e is the electron charge, T is the temperature of the carrier gas, and k is the Boltzmann constant. It turns out that the criterion of the validity of the free-molecule approximation is $l \gg l_c$, rather than $l \gg a$, as in neutral systems.

Next, the ion bound states in the attractive potential well created by the particle charge lead to some additional difficulties. The point is that these states have negative energies and can be occupied by the incident ions only after their collisions with the carrier gas molecules (see Refs. [16,17]). The diffusion model assumes that all bound states are populated. In the free-molecule limit these states are always empty. Meanwhile, it is apparent that neither the first nor the second limit gives a true description of reality. The ions occurring in the potential well due to collisions with the carrier gas molecules have no time to lose enough part of their kinetic energy and to reach very deep states. Hence, only a part of these states can be occupied. This effect is very difficult to take into account, for at least a two-body problem in the external field should be solved for describing the dynamics of ion energy losses.

So called flux-matching theories are well adapted for studying the behavior of aerosol particles in the transition regime. Although these theories mostly had no firm theoretical basis, they successfully served for systematizing numerous experiments on the growth of aerosol particles and until now these theories remain a rather effective and very practical tool for studying the kinetics of aerosol particles in the transition regime (see Refs. [1,18–20]). On the other hand, these theories are always semiempirical, i.e., they contain a parameter that should be taken from somewhere else, not from the theory itself.

We introduce the reader to the ideology of the flux-matching theories by considering the condensation of a nonvolatile vapor onto the surface of an aerosol particle. The central idea of the flux-matching procedure is a hybridization of the diffusion and the free-molecule approaches. The concentration profile of a condensing vapor far away from the particle is described by the diffusion equation. This profile coincides with the real one down to the distances of the order of the vapor molecule mean free path. A limiting sphere is then introduced inside which the free-molecule kinetics governs the vapor transport. The concentration profile in the free-molecule zone is considered to be flat. The equality of the fluxes in the both zones and the continuity of the concentration profile at the surface of the limiting sphere define the flux and the reactant concentration at the particle surface. The third parameter, the radius of the limiting sphere, cannot be found from such a consideration.

We apply a more sophisticated scheme. We also introduce a limiting sphere outside of which the density profile of condensing vapor can be described by the diffusion equation. But inside the limiting sphere we solve the collisionless Boltzmann equation subject to a given boundary condition at the particle surface (complete sticking in our case) and set an additional condition: the concentration at the surface of the limiting sphere coincides with that found from the solution of the diffusion equation. Even in the absence of any potential created by the particle the vapor profile in the free-molecule zone depends on the radial coordinate, because the particle surface adsorbs all incoming molecules. We thus gain the possibility to call for the continuity of the first derivatives of the profile on both sides of the limiting sphere. This additional condition defines the radius of the limiting sphere.

In this paper we consider the processes of particle charging by ions suspended in the carrier gas assuming that the ion-particle interaction includes the Coulomb + polarization forces. The latter comes from the particle dipole moment induced by the approaching ion,

$$U(r) = \pm \frac{qQe^2}{r} - \frac{1}{2}\frac{\epsilon - 1}{\epsilon + 2}\frac{q^2e^2a^3}{r^4}. \tag{1}$$

The sign "+" in this equation corresponds to the Coulomb repulsion. The last term on the right-hand side (RHS) of Eq. (1) is just the dipole term of the expansion of the image potential over the Legendre polynomials [21]; ϵ is the dielectric permeability of the particle material. The image potential has a singularity at the particle surface. Although the singular potentials are not a principal problem for the theory proposed below, we postpone their consideration for a future article.

The remainder of this paper is divided as follows. We first formulate the flux-matching theory of particle charging exactly. This is just a formal step allowing one to express the ion flux toward a particle of radius a in terms of a generalized charging efficiency $\alpha(a,R)$ depending on the radius R of a limiting sphere. At the distances exceeding R the ion profile is described by the diffusion equation. The requirement of the continuity of the profile at $r=R$ gives an expression for the ion flux $J(a)$. At this step we specify neither the radius of the limiting sphere nor the form of the generalized efficiency. The details of this exact formulation are given in the next section. Section III presents the approximations necessary for moving ahead. They are (i) the generalized efficiency $\alpha(a,R)$ is approximated by its free-molecule value found from the solution of the collisionless kinetic equation at $a<r<R$. (ii) At $R<r<\infty$ we describe the ion profile by the solution to the steady-state diffusion equation corresponding to a given ion flux J. (iii) The conditions of matching the profiles and their first derivatives allow us to find R. The details of the solution of the collisionless kinetic equations are given in Sec. IV. In Sec. V we calculate the ion concentration profiles and use them in Sec. VI for matching the first derivatives at the surface of the limiting sphere. Section VII contains the discussion of the main results of this paper. The efficiencies of particle charging are shown to depend on the particle size, the ion diffusivity in the carrier gas, the ion thermal velocity, and the Coulomb length.

II. FLUX-MATCHING EXACTLY

The steady-state ion flux $J(a)$ onto the particle of radius a can always be written as

$$J(a) = \alpha(a)n_\infty, \tag{2}$$

i.e., the flux is proportional to the ion density n_∞ far away from the particle. The proportionality coefficient $\alpha(a)$ is known as the charging efficiency. The problem is to find $\alpha(a)$.

Nobody, however, prevents us from generalizing Eq. (2) as follows:

$$J(a,R,n_R) = \alpha(a,R)n_R, \tag{3}$$

where n_R is the ion concentration at a distance R from the particle center. It is important to emphasize that n_R is (still) *an arbitrary* value introduced as a boundary condition at the distance R (also arbitrary) to a kinetic equation which is necessary to solve for defining $\alpha(a,R)$.

The flux defined by Eq. (2) is thus

$$J(a) = J(a,\infty,n_\infty) \quad \text{and} \quad \alpha(a) = \alpha(a,\infty). \tag{4}$$

The value of $\alpha(a,R)$ does not depend on n_R because of the linearity of the problem.

Let us assume for a moment that we know the exact ion concentration profile $n_{\text{exact}}(r)$ corresponding to the flux $J(a)$ from infinity [see Eq. (2)]. Then, using Eq. (3) we can express $J(a)$ in terms of n_{exact} as follows:

$$J(a) = J(a,R,n_{\text{exact}}(R)) = \alpha(a,R)n_{\text{exact}}(R). \tag{5}$$

Now let us choose R sufficiently large for the diffusion approximation to reproduce the exact ion concentration profile,

$$n_{\text{exact}}(R) = n^{(J(a))}(R), \tag{6}$$

with $n^{(J)}(r)$ being the steady-state ion concentration profile corresponding to a given total ion flux J. The steady state density of the ion flux $j(r)$ is the sum of two terms,

$$j(r) = -D\frac{dn^{(J)}(r)}{dr} - B\frac{dU(r)}{dr}n^{(J)}(r), \tag{7}$$

where D is the ion diffusivity, $U(r)$ is a potential (here the ion-particle interaction), and B is the ion mobility. According to the Einstein relation $kTB=D$. On the other hand, the ion flux density is expressed in terms of the total ion flux as follows: $j(r)=-J/4\pi r^2$, with $J>0$. Equation (7) can now be rewritten as

$$e^{-\beta U(r)}\frac{d}{dr}[n^{(J)}(r)e^{\beta U(r)}] = \frac{J}{4\pi D r^2},$$

where $\beta=1/kT$. The solution to this equation is

$$n^{(J)}(r) = e^{-\beta U(r)}\left(n_\infty - \frac{J}{4\pi D}\int_r^\infty e^{\beta U(r')}\frac{dr'}{r'^2}\right). \tag{8}$$

On substituting Eqs (6) and (8) into Eq. (5) gives the equation $J(a)=\alpha(a,R)n^{(J)}(R)$ or

$$J(a) = \alpha(a,R)e^{-\beta U(R)}\left(n_\infty - \frac{J(a)}{4\pi D}\int_R^\infty e^{\beta U(r')}\frac{dr'}{r'^2}\right). \tag{9}$$

We can solve this equation with respect to $J(a)$ and find $\alpha(a)$,

$$\alpha(a) = \frac{\alpha(a,R)e^{-\beta U(R)}}{1 + \dfrac{\alpha(a,R)e^{-\beta U(R)}}{4\pi D}\displaystyle\int_R^\infty e^{\beta U(r')}\frac{dr'}{r'^2}}. \tag{10}$$

Equation (10) is exact if $R \gg l$. We, however, know neither $\alpha(a,R)$ nor R.

III. FLUX-MATCHING APPROXIMATELY

There is not a chance to find $\alpha(a,R)$ exactly. We thus call upon two approximations.

We approximate $\alpha(a,R)$ by its free-molecule expression,

$$\alpha(a,R) \approx \alpha_{\mathrm{fm}}(a,R). \tag{11}$$

We define R from the condition

$$d_r n_{\mathrm{fm}}(r)_{r=R} = d_r n^{(J(a))}(r)_{r=R}, \tag{12}$$

where $n_{\mathrm{fm}}(r)$ is the ion concentration profile found in the free-molecule regime for $a<r<R$. The distance R separates the zones of the free-molecule and the continuous regimes.

IV. FREE-MOLECULE ZONE

In this section we reformulate the collisionless Boltzmann equation in the form maximally convenient for considering the ion transport in spherically symmetric systems, find its steady-state solution, and then derive the expression for the ion density profile.

A. Basic equations

The steady-state distribution of ions over coordinates and velocities inside the free-molecule zone is described by the collisionless Boltzmann equation,

$$v_i\frac{\partial f}{\partial x_i} - \frac{1}{m}\frac{\partial U}{\partial x_i}\frac{\partial f}{\partial v_i} = 0. \tag{13}$$

Here $f(\mathbf{r},\mathbf{v})$ is the ion distribution over coordinates and velocities, m is the ion mass, U is the potential of an external field. Because we are going to consider the free-molecule regime, the collision term is omitted. The convention on the summation over repeating indexes is adopted. The boundary conditions to Eq. (13) will be discussed in the end of this section.

In what follows we consider only spherical particles. The potential U is then a function of $r=|\mathbf{r}|$, and the ion distribution depends only on three variables, the ion radial coordinate r, absolute ion velocity $v=|\mathbf{v}|$, and $\mu=\cos\theta$, with θ being the angle between the directions of $\mathbf{r}$ and $\mathbf{v}$.

In spherically symmetric systems another set of variables is more convenient. Namely, instead of r,v,μ we introduce r,E,L, with

$$E = mv^2/2 + U(r), \quad L = m|[\mathbf{v}\times\mathbf{r}]| = mvr\sqrt{1-\mu^2}. \tag{14}$$

In these variables the Boltzmann equation takes an especially simple form:

$$v_r\frac{\partial f_s}{\partial r} = 0, \tag{15}$$

where

$$v_r = \sqrt{\frac{2}{m}\left(E - U(r) - \frac{L^2}{2mr^2}\right)} = \frac{1}{mr}\sqrt{L^2(r) - L^2} \tag{16}$$

is the radial ion velocity, $s=\pm 1$ is an auxiliary variable defining the direction of ion motion along the radial coordinate ($s=-1$ corresponds to the direction toward the particle), and

$$L^2(r) = 2mr^2[E - U(r)]. \tag{17}$$

The functions f_1 and f_{-1} are coupled by a boundary condition on the particle surface. [see Eq. (23)]. Next, the ions passing by the particle change the directions of their velocities at the turning point ($v_r=0$). This fact, however, adds no complications, because in the steady-state conditions the numbers of ions flying toward and outward the origin of coordinates are always equal for the trajectories not crossing the particle surface.

The ion flux toward the particle is expressed in terms of f as follows:

$$J = -\int d^3v \int (\mathbf{v}\cdot d\mathbf{S})f(\mathbf{r},\mathbf{v}). \tag{18}$$

The integrals on the right-hand side (RHS) of this equation are taken over all $\boldsymbol{v}$ and the surface of a sphere of radius r. The sign "−" in the definition of the flux makes J positive. In spherical coordinates Eq. (18) is rewritten as

$$J = -8\pi^2 r^2\int_0^\infty v^3\,dv\int_{-1}^1 f(r,v,\mu)\mu\,d\mu. \tag{19}$$

The rule for replacing the variables $(r,v,\mu)\to(r,E,L)$ readily follows from definition (14) of the variables E and L,

$$2\pi v^2 dv\,d\mu \to \frac{\pi}{m^2 r}\sum_s \frac{dE\,dL^2}{\sqrt{L^2(r)-L^2}}. \tag{20}$$

The restrictions on the intervals of integration over E and L^2 are defined by the conditions, $L^2 \leqslant L^2(r), L^2, L^2(r) \geqslant 0$. In what follows we do not specify the limits of integrations except for the cases, where they play a decisive role.

The expressions for the ion density profile $n(r)$ and the ion flux J in r,E,L variables look as follows:

$$n(r) = \frac{\pi}{m^2 r}\sum_s \int dE\int \frac{dL^2}{\sqrt{L^2(r)-L^2}}f_s(r,E,L) \tag{21}$$

and

$$J = -\frac{4\pi^2}{m^3}\sum_s s\int dE\int dL^2\, f_s(r,E,L). \tag{22}$$

The ion flux is independent of r.

We conclude this section by formulating the boundary condition to Eq. (15). We assume that no ions escape from the particle surface,

$$f_1(a,E,L) = 0, \tag{23}$$

and the particle number concentration at $r=R$ is fixed,

$$\frac{\pi}{m^2R}\sum_s\int dE\int\frac{dL^2}{\sqrt{L^2(R)-L^2}}f_s(R,E,L) = n(R). \tag{24}$$

In addition we assume that the distribution function at $r=R$ contains the factor $e^{-\beta[E-U(R)]}$ (Maxwell's distribution over the ion velocity).

Because the total flux J is independent of r, Eq. (22) can be rewritten in terms of f_{-1} alone,

$$J(a) = \frac{4\pi^2}{m^3}\int dE\int dL^2\, f_{-1}(a,E,L). \tag{25}$$

B. Free-molecule ion distribution

Before constructing the general solution to the kinetic equation describing the motion of ions in the free-molecule regime we find the interval of angular momenta corresponding to the ion trajectories intersecting the particle surface.

Here we consider only the nonsingular potentials for which the function $L^2(r)$ monotonously grows at $r>a$. It is clear that at positive E the ion trajectories with

$$L^2 < L_a^2 = 2ma^2[E-U(a)] \tag{26}$$

intersect the particle surface. At negative E the situation changes, if $2mR^2[-|E|+|U(R)|]<2ma^2[-|E|+|U(a)|]$ then the trajectories with $L^2<2mR^2[-|E|+|U(R)|]$ will cross the particle surface (see Fig. 1). Otherwise the restriction $L^2<2ma^2[-|E|+|U(a)]$ works. Hence,

$$L_a^2 = \min(L^2(a),L^2(R)) \tag{27}$$

for the attractive nonsingular potentials. The notation L_a stands for the angular momentum separating the trajectories crossing the particle surface from those passing by. It is easy to find that $L_a^2=L^2(R)$ in the interval of negative energies,

$$|U(R)| < |E| < E_0 = \frac{R^2|U(R)|-a^2|U(a)|}{R^2-a^2}. \tag{28}$$

Now we can solve the kinetic equation Eq. (14). The solution to this equation is

$$f_s(r,E,L) = C_Re^{-\beta(E-U(R))}\theta(E-U(R))\theta(L^2)\theta(L^2(r)-L^2)$$
$$\times[\theta(L^2-L_a^2)+\delta_{s,-1}\theta(L_a^2-L^2)], \tag{29}$$

where $\theta(x)$ is the Heaviside step function and $\delta_{i,k}$ is Kroneker's delta. The multiplier C_R will be found later from the condition Eq. (24). The last multiplier is introduced to satisfy the boundary conditions Eq. (23).

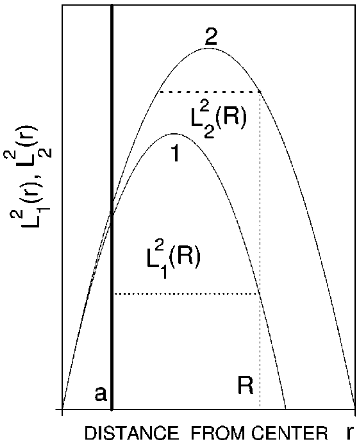

FIG. 1. The dependence of $L^2(r)$ on the distance r from the particle center. Two curves corresponding to the negative energies $E_1<E_2<0$ are schematically shown. At the energy E_1 (curve 1) all bound ions occupy the states with $L^2<L_1^2(R)$, i.e., all these ions can reach the particle surface. Curve 2 displays the situation when not all bound ions reach the particle surface. The ions in the states with $L^2>L_2^2(a)$ pass by the particle and return to the diffusion zone.

It is easy to see that the distribution in this form contains no outgoing ions at $r=a$, for the factor $\theta(L^2-L_a^2)$ in the first term does not permit the trajectories crossing the point $r=a$. Hence, $f_1(a)=0$, in accordance with the boundary condition Eq. (23). The factor $\theta(E-U(R))$ reflects the fact that no ions with the energy lower $U(R)$ can appear in the free-molecule zone (such ions could appear only due to collisions with the carrier gas molecules). The last term in the square brackets on the RHS of Eq. (29) can be rewritten as

$$\theta(L^2-L_a^2)+\delta_{s,-1}\theta(L_a^2-L^2) = \delta_{s,-1}+\theta(L^2-L_a^2)\delta_{s,1}. \tag{30}$$

The $s=-1$ component of the distribution is seen to be independent of L_a which means that all ions with $L^2<L^2(r)$ can move toward the particle center (but not all can reach the particle surface). The outgoing component f_1 does not contain the contribution from the trajectories crossing the particle surface.

V. ION DENSITY PROFILE

In this section we find the expressions for the ion concentration profile. Our starting point is Eq. (21). Substituting there Eqs. (29) and (30) and integrating over L^2 give the coordinate dependence of the profile,

$$n(r) = \frac{2\pi C_Re^{\beta U(R)}}{m^2r}\int e^{-\beta E}\{L(r)[1+\theta(-L_a^2)]$$
$$+[\sqrt{L^2(r)-L_a^2}]\theta(L_a^2)\}dE. \tag{31}$$

The term $\theta(-L_a^2)$ gives a nonzero contribution only in repulsive potentials at the energies within the interval $U(a)>E>U(r)$. The constant C_R entering this equation can be readily found from the boundary condition (24),

$$C_R = n(R)e^{-\beta U(R)}\left(\frac{m\beta}{2\pi}\right)^{3/2}\frac{2}{G_0(R)+G_A(R)}, \tag{32}$$

where the functions $G_0(r)$ and $G_A(r)$ are

$$G_0(r) = \frac{2}{\sqrt{\pi}}\int_X^\infty dx\, e^{-x}\sqrt{x-\beta U(r)}[1+\theta(U(a)-E)], \tag{33}$$

$$G_A(r) = \frac{2}{\sqrt{\pi}}\int_Y^\infty dx\, e^{-x}\sqrt{x-\beta U(r)-[x-\beta U(a)]\frac{a^2}{r^2}}. \tag{34}$$

The lower integration limits X and Y depend on the type of ion-particle interaction and will be specified separately for each concrete potential.

Now the profile satisfying the boundary condition Eq. (24) can be restored,

$$n(r) = n(R)\frac{G_0(r)+G_A(r)}{G_0(R)+G_A(R)}. \tag{35}$$

The expressions for the flux follows from Eq. (25):

$$J(a,R,n_R) = \frac{4\pi^2}{m^3}C_R e^{\beta U(R)}\int_X^\infty e^{-\beta E}L_a^2\, dE. \tag{36}$$

VI. MATCHING DISTANCES

The general expression Eq. (35) for the ion profile is used in this section for performing the program outlined in the Introduction. We match the profiles and their derivatives on both sides of the surface of the limiting sphere, find its radius (the matching distance) and then use Eq. (10) for deriving the expressions for charging efficiencies.

A. Free condensation

In the simplest case $U(r)=0$ (condensation of neutral molecules on neutral particles),

$$L^2(r) = 2mr^2E, \quad L_a^2 = L^2(a), \quad X = Y = 0,$$

$$G_0(r) = 1, \quad G_A(r) = \sqrt{1-\frac{r^2}{a^2}}. \tag{37}$$

We have

$$n(r) = n(R)\frac{1+\sqrt{1-a^2/r^2}}{1+\sqrt{1-a^2/R^2}}. \tag{38}$$

One sees that even in the absence of external fields the density of condensing molecules depends on r.

Now let us find the matching distance and the condensation efficiency. The profile in the diffusion zone [see Eq. (8)] is

$$n^{(J)}(r) = n_\infty - \frac{J}{4\pi Dr}. \tag{39}$$

The free-molecule profile is given by Eq. (38). The condition Eq. (12) then gives

$$\frac{a^2 v_T}{4DR^2} = \frac{a^2}{2R^3\sqrt{1-\frac{a^2}{R^2}}}. \tag{40}$$

The solution to this equation is readily found,

$$R = \sqrt{\left(\frac{2D}{v_T}\right)^2 + a^2}. \tag{41}$$

The combination $2D/v_T$ is of the order of the ion mean free path l. The condensation efficiency can be found from Eqs. (10) and (41). The result is

$$\alpha(a) = \frac{2\pi a^2 v_T}{1+\sqrt{1+\left(\frac{av_T}{2D}\right)^2}}. \tag{42}$$

B. Repulsion

At $U(r)>0$

$$L^2(r) = 2mr^2[E-U(r)], \quad L_a^2 = L^2(a),$$

$$X = \beta U(r), \quad Y = \beta U(a). \tag{43}$$

Hence, $n(r)$ is given by Eq. (35) with

$$G_0(r) = 2e^{-\beta U(r)} - \frac{2}{\sqrt{\pi}}\int_{\beta U(a)}^\infty dx\, e^{-x}\sqrt{x-\beta U(r)} \tag{44}$$

and

$$G_A(r) = \frac{2}{\sqrt{\pi}}\int_{\beta U(a)}^\infty dx\, e^{-x}\sqrt{x-\beta U(r)-[x-\beta U(a)]\frac{a^2}{r^2}}. \tag{45}$$

Now let us find the equation for the matching distance. Replacing $n(R)$ by $n^{(J)}(R)$ in Eq. (35) casts the condition Eq. (12) into the form

$$\left.\frac{d\ln n^{(J)}}{dr}\right|_R = \frac{d}{dr}\left.\left[\frac{G_0(r)+G_A(r)}{G_0(R)+G_A(R)}\right]\right|_R. \tag{46}$$

On differentiating the profile in the diffusion zone [see Eq. (8)] yields

$$\left.\frac{d\ln n^{(J)}}{dr}\right|_R = -\beta U(R)' + \frac{\alpha(a,R)}{4\pi DR^2}. \tag{47}$$

In deriving Eq. (47) we used the inversion of Eq. (10),

$$\alpha(a,R) = \frac{\alpha(a)e^{\beta U(R)}}{1-\frac{\alpha(a)}{4\pi D}\int_R^\infty\frac{e^{\beta U(r')}dr'}{r'^2}}. \tag{48}$$

Equation (36) allows us to find

$$\alpha_{\mathrm{fm}}(a,R) = \frac{2\pi a^2 v_T e^{-\beta U(a)}}{G_0(R)+G_A(R)}. \tag{49}$$

The following two formulas help much in finding the derivatives on the RHS of Eq. (46),

$$G_0'(r) = -\beta U'(r) G_0(r) - \frac{2}{\sqrt{\pi}} e^{-\beta U(a)} \beta U'(r) \sqrt{\delta} \tag{50}$$

and

$$G_A'(r) = e^{-\beta U(r)} \frac{a^2}{r^3} Z(r) + \frac{2}{\sqrt{\pi}} \frac{e^{-\beta U(a)} \beta U'(r) \sqrt{\delta}}{1 - a^2/r^2} - \frac{\beta U'(r)}{1 - a^2/r^2} G_A(r). \tag{51}$$

Here $\delta = \beta(U(a) - U(r))$ and

$$Z(r) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x e^{-x}\, dx}{\sqrt{x + \delta}}. \tag{52}$$

These formulas together with Eqs. (46)–(49) give the equation for R,

$$\frac{R v_T}{2D} = \frac{2}{\sqrt{\pi}} \beta R |U'(R)| \int_0^\infty \frac{x e^{-x}\, dx}{\sqrt{x(1 - a^2/R^2) + \delta} + \sqrt{\delta}} + \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x e^{-x}\, dx}{\sqrt{x(1 - a^2/R^2) + \delta}}. \tag{53}$$

C. Attraction

In the case of nonsingular attractive potentials we have

$$X = -\beta |U(r)|, \quad Y = \beta E_0, \quad L^2(r) = 2 m r^2 (E + |U(r)|),$$

$$L_a^2 = L^2(a)\, \theta(E + E_0) + L^2(R)\, \theta(-E - E_0). \tag{54}$$

The energy E_0 here is defined by Eq. (28).

Equation (31) now gives

$$n(r) = n(R) \frac{G_0(r) + G_A(r)}{e^{\beta |U(R)|} + G_A(R)}, \tag{55}$$

with

$$G_0(r) = \frac{2}{\sqrt{\pi}} \int_{-\beta |U(R)|}^\infty dx\, e^{-x} \sqrt{x + \beta |U(r)|}, \tag{56}$$

$$G_A(r) = \frac{2}{\sqrt{\pi}} \int_{-\beta E_0}^\infty dx\, e^{-x} \sqrt{x + \beta |U(r)| - [x + \beta |U(a)|] \frac{a^2}{r^2}}, \tag{57}$$

and

$$G_0(R) = e^{\beta |U(R)|}, \quad G_A(R) = e^{\beta E_0} \sqrt{1 - \frac{a^2}{R^2}}. \tag{58}$$

Equations (27) and (31) explain why the ion states with the energies lower than E_0 do not contribute to G_A. Indeed, the last term on the RHS of Eq. (31) contains the contribution from all the trajectories passing by the particle. At $E < E_0$ and thus $L < L(R)$ all ion trajectories cross the particle surface (see Fig. 1).

Equations (36) and (58) now give

$$\alpha_{\mathrm{fm}}(a, R) = \frac{2 \alpha_o}{1 + e^{-\beta \Delta} \sqrt{1 - a^2/R^2}}. \tag{59}$$

Here

$$\alpha_o(a, R) = \frac{4\pi^2}{m^3} \int_{\beta U(R)}^\infty e^{-\beta E} L_a^2\, dE = \pi a^2 v_T\, e^{-\beta \Delta} \left[1 + \beta |U(a)| + \beta E_0 + \frac{R^2}{a^2} (e^{\beta \Delta} - 1 - \beta \Delta) \right] \tag{60}$$

and $\Delta = |U(R) - E_0|$.

The derivation of the equation for R follows along the same line as for repulsive potentials. The expression for $G_A'(R)$ is simpler, for E_0 is independent of R,

$$G_A'(R) = \frac{e^{\beta E_0}}{\sqrt{1 - \frac{a^2}{R^2}}} \times \left[\beta |U(R)|' + \frac{a^2}{R^3} \{1 + 2[\beta |U(a)| - \beta E_0]\} \right]. \tag{61}$$

The equation for determining R then takes the form

$$\frac{\alpha_o(a, R)}{2\pi D R} = \frac{e^{-\beta \Delta}}{\sqrt{1 - \frac{a^2}{R^2}}} \times \frac{a^2}{R^2} [\beta |U(R)|' R + 1 + 2\beta(|U(a)| - E_0)]. \tag{62}$$

VII. RESULTS AND DISCUSSION

Once the matching distance is known as a function of the particle size, it is easy to find the charging efficiencies for any potential. We therefore begin with the analysis of the dependencies of $R = R(a)$ and then present the results on the dependence of the charging efficiencies on particle sizes for the potentials given by Eq. (1).

A. Matching distances

We return first to Eq. (41) describing the dependence of the matching distance on the particle size for $U(r) = 0$. It has the structure

$$R(a) = \sqrt{R_0^2(a) + a^2}, \tag{63}$$

with

$$R_0(a) = \frac{2D}{v_T}. \tag{64}$$

The value of $R_0(a)$ is independent of a, so at very small particle size the matching distance is of the order of the molecular mean free path, as has been expected. At large particle size $a \gg l$ the difference $R(a) - a \propto l$.

When the ion-particle interaction is turned on, the analysis becomes more complex. Equations (53) and (62) should be solved. This can be done only numerically, but first we analyze the behavior of the function $R(a)$ at small $a \ll l, l_c$. In our analysis we assume that $U(a) \to \infty$ as $a \to 0$.

Let us begin with the attractive potentials [Eq. (62)]. As is seen from Eq. (60) at small particle size $\alpha_0 \approx \pi a^2 v_T \beta |U(a)|$ [the leading term in $U(a)$ is retained]. The term of the same order of magnitude on the RHS of Eq. (62) is $2\beta|U(a)|(a^2/R^2)$. Equation (62) then gives

$$R(a) \approx \frac{4D}{v_T}. \tag{65}$$

Again, in the limit of small a the matching distance is of the order of the ion mean free pats and independent of the particle size. Moreover, it is independent of the ion-particle potential.

In the limit of large particles $a \gg l$ the LHS of Eq. (62) becomes large. This can happen due to the growth of the expression under the square root on the RHS of this equation when R approaches to a. Our numerical analysis showed that the solution to Eq. (62) can be well approximated by the formula of the type of Eq. (63), with

$$R_0(a) = \frac{2D}{v_T}\frac{1+2\beta|U(a)|}{1+\beta|U(a)|}. \tag{66}$$

Let us now analyze the repulsive potentials. In the limit of small a the leading term on the RHS of Eq. (53) for R is small as $1/\sqrt{\delta} \propto 1/\sqrt{\beta U(a)}$. Equation (53) gives at small a and the potential Eq. (1) $(q=Q=1)$,

$$R \approx \pi^{-1/4}(2D/v_T)^{1/2} l_c^{1/4} a^{1/4}\left[\frac{2(\epsilon+2)}{\epsilon+5}\right]^{1/4}. \tag{67}$$

The dependence of the matching distance $R(a)$ on the particle size is shown in Fig. 2 for the potentials given by Eq. (1) with $\epsilon=4$, and $q=Q=1$.

In contrast to zero or attractive potentials, where the matching distance has the order of the ion mean free path and does not depend on the particle size, the ion-particle repulsion leads to the matching distances decreasing with diminishing the particle size. From the first sight this fact is very unpleasant, for the diffusion approximation cannot work at the distances much smaller than the ion mean free path. On the other hand, the dependence of $R(a)$ is very weak, and even for $a=1$ nm R is comparable with the ion mean free path.

B. Charging efficiencies

In the case of free condensation (the ion-particle interaction is turned off) the result is especially simple

$$\alpha(a) = \frac{2\pi a^2 v_T}{1+\sqrt{1+\left(\frac{a v_T}{2D}\right)^2}}. \tag{42a}$$

We compared this result with the most successful semiempirical Fuchs-Sutugin's formula [18] which describes satisfactorily a rich collection of the experimental data on the vapor condensation onto the surfaces of aerosol particles in a wide interval of their sizes. The result is presented in Fig. 3. The deviation of two curves does not exceed 10%.

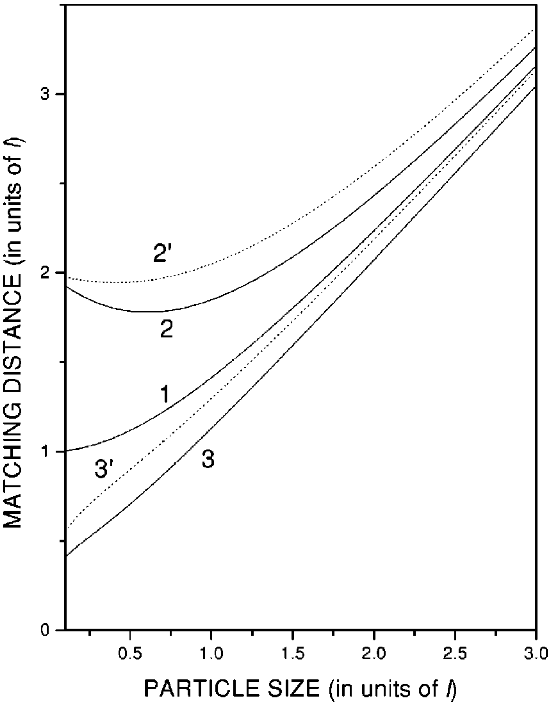

FIG. 2. The dependence of matching distance $R(a)$ on the particle radius a. The scale of both axes is $l=2D/v_T$, the ion mean free path. Curve 1 shows the function $R(a)$ for the potential-free condensation. Curves 2 and 2′ are the matching distances for the attractive potential [Eq. (1)] at different Coulomb's lengths: $l_c=l$ (solid line) and $l_c=3$ (dot line). Curves 3 and 3′ display the same for the repulsive potential.

For charged particles the general result Eq. (10) should be used. The approximations Eqs. (11) and (12) allow us to express $\alpha(a)$ in terms of the charging efficiency $\alpha_{\mathrm{fm}}(a,R)$ found in the free-molecule limit and the matching distance R,

$$\alpha(a) = \frac{\alpha_{\mathrm{fm}}(a,R)e^{-\beta U(R)}}{1+\frac{\alpha_{\mathrm{fm}}(a,R)e^{-\beta U(R)}}{4\pi D}\int_R^{\infty} e^{\beta U(r')}\frac{dr'}{r'^2}}, \tag{68}$$

where the values of $\alpha_{\mathrm{fm}}(a,R)$ are given by Eq. (50) for repulsive potentials and by Eq. (59) for attractive potentials. The numerical calculations were performed for the potential given by Eq. (1) with $q=Q=1$ and $l_c=l$ or $l_c=3l$.

The results are presented in Figs. 4 and 5 in terms of the correction factors $\xi(a)$, the ratios of the charging efficiencies found from Eq. (68) to their values in the free-molecule regime,

$$\xi(a) = \frac{\alpha(a)}{\alpha_{\mathrm{fm}}(a)}, \tag{69}$$

where $\alpha_{\mathrm{fm}}(a) = \alpha_{\mathrm{fm}}(a, R=\infty)$.

Let us analyze the expression for charging efficiency [Eq. (68)] in the free-molecule limit $a \ll l$. First, we notice that at $a \ll l$ the denominator in Eq. (68) can be always replaced by unity. Then for the recombination rate Eqs. (59) and (65) give

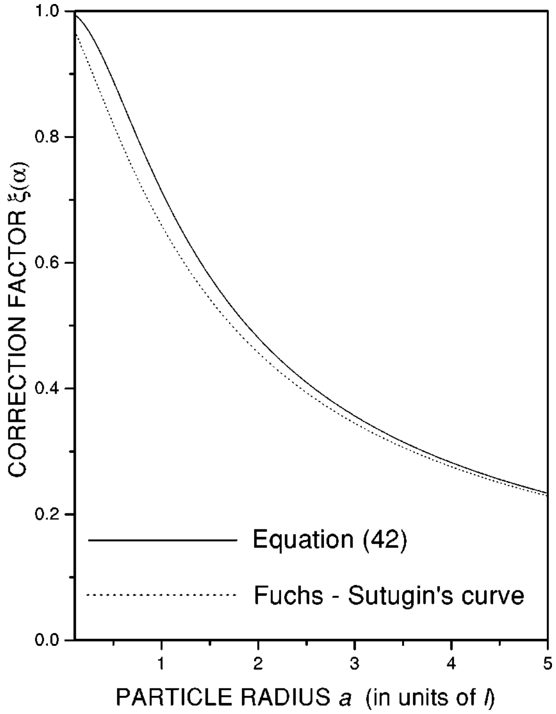

FIG. 3. The correction factor $\xi(a)=\alpha(a)/\alpha_{\mathrm{fm}(a)}$ for the efficiency of potential-free vapor condensation as a function of particle radius (in units of $l=2D/v_T$). Solid curve displays the dependence given by Eq. (42). It is seen that this curve reproduces well the semiempirical dependence found in Ref. [18] (dot curve).

$$\alpha(a) \approx \pi a^2 v_T[1+\beta|U(a)|+\beta|U(4D/v_T)|]e^{\beta|U(4D/v_T)|}. \tag{70}$$

In order to obtain the widely cited free-molecule limit $\alpha(a) = \pi a^2 v_T[1+\beta U(a)]$ the term $\beta U(4D/v_T)$ should be small compared to 1. The inequality $\beta U(4D/v_T) \ll 1$ does not hold for the Coulomb potential at ambient conditions. Indeed, $l_c = \beta e^2 \approx 6\times 10^{-6}$ cm $\approx l$. For the attractive potential given by Eq. (1) one finds

$$\alpha(a) \approx \pi a^2 v_T\left[1+qQ\frac{l_c}{a}\left(1+\frac{q}{2Q}\frac{\epsilon-1}{\epsilon+2}\right)+qQ\frac{l_c v_T}{4D}\right]e^{qQl_c v_T/4D}. \tag{71}$$

Figure 4 clearly demonstrates the role of the Coulomb distance in the case of the Coulomb attraction. It is seen that even at small particle sizes $a \ll l$ the free-molecule expression for the ion-particle recombination does not work. On the other hand, no modifications related to the Coulomb interaction appear in the case of repulsive potential. The free-molecule formula works for small particles ($a \ll l_c$) and only when the particle size becomes comparable to the Coulomb distance the corrections become perceptible.

In the case of repulsion nothing interesting comes up. Equation (68) reproduces the well-known free-molecule limit,

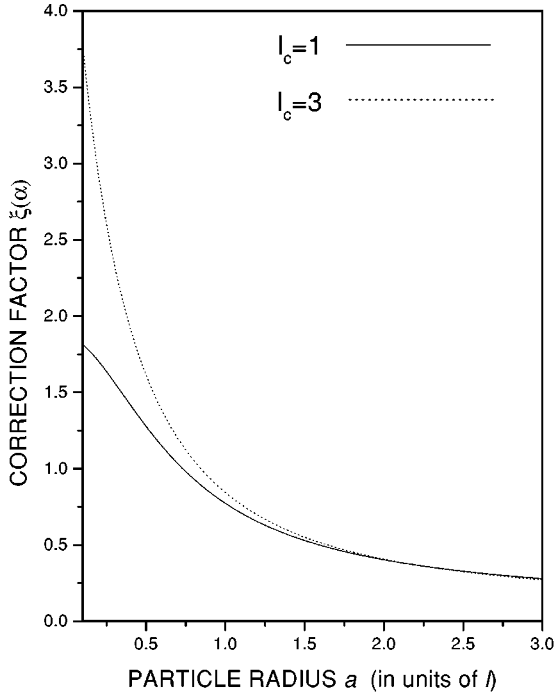

FIG. 4. The correction factor $\xi(a)=\alpha(a)/\alpha_{\mathrm{fm}(a)}$ for ion-particle recombination [attractive potential, Eq. (1)] as a function of particle radius (in units of $l=2D/v_T$). Solid and dot curves display $R(a)$ for $l_c=1$ and $l_c=3$, respectively. It is seen that even at small particle sizes these curves deviate from unity, i.e., the free-molecule approximation is noticeably corrected by ion-carrier gas interaction $l_c \propto l$.

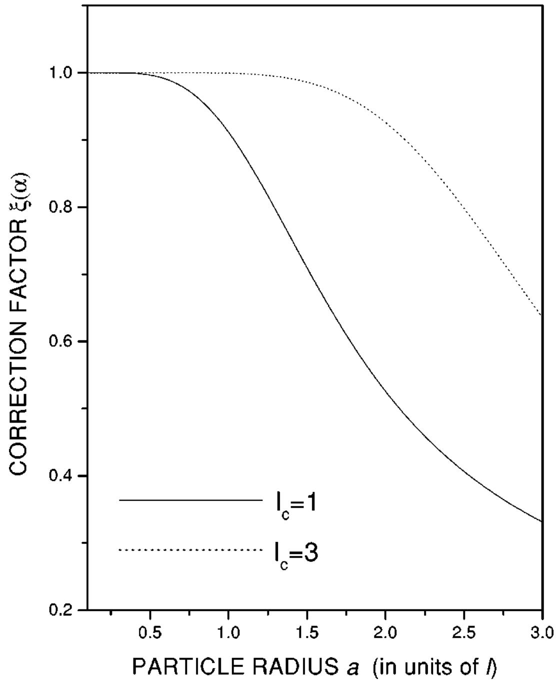

FIG. 5. Same as in Fig. 4, but for repulsive potential, Eq. (1). In contrast to attraction, in this case the free-molecule limit works even when the particle size is comparable to the ion mean free path.

$$\alpha(a) \approx \pi a^2 v_T e^{-\beta U(a)}. \tag{72}$$

Indeed, at small a we find that the integrals in Eqs. (44) and (45) are small compared to 1. Then, as follows from Eq. (49),

$$\alpha_{\mathrm{fm}}(a) \approx \pi a^2 v_T e^{-\beta U(a)} e^{\beta U(R)}. \tag{73}$$

On substituting this expression into Eq. (68) one comes to Eq. (72).

At large a, Eq. (68) always reproduces the diffusion limit,

$$\alpha_{\mathrm{diff}}(a) = \frac{4\pi D}{\displaystyle\int_a^\infty r^{-2} e^{\beta U(r)}\, dr}. \tag{74}$$

VIII. CONCLUSION

We have proposed a new flux-matching theory of particle charging. Starting with the exact formulation of the flux-matching procedure we have determined all functions entering the resulting expression (10). In contrast to existing flux-matching theories our version does not contain any free parameter (usually the radius of the limiting sphere). Next, we do not operate with such not well defined values like the ion mean free path. Our final result Eq. (68) expresses the charging efficiency in terms of the ion diffusivity D, ion thermal velocity v_T, and the Coulomb distance l_c. All these values are unambiguously defined.

We have shown that in the case of the particle-ion recombination the corrections due to the interaction of ion with the carrier gas are essential irrespective of the particle size. The free-molecule limit works only for very diluted carrier gases when the ion mean free path much exceeds the Coulomb length.

In the case of repulsive Coulomb forces the situation is opposite, the contribution of ion-molecular collisions to the rate of particle charging is suppressed by the strong Coulomb repulsion. Only at sufficiently large particle sizes the kinetic corrections become noticeable.

[1] N. A. Fuchs, Geofis. Pura Appl. **56**, 185 (1963).

[2] G. L. Natanson, Sov. Phys. Tech. Phys. **5**, 538 (1960).

[3] K. T. Whitby and B. U. H. Liu, in *Aerosol Science*, edited by C. N. Davies (Academic, London, 1966).

[4] P. C. Reist, *Introduction to Aerosol Science* (Macmillan, New York, 1984).

[5] K. T. Whitby, in *Fine Particles*, edited by B. Y. H. Liu (Elsevier, New York, 1976).

[6] B. Y. H. Liu, *Fine Particles, Aerosol Generation, Measurement, Sampling, and Analysis* (Academic, New York, 1976).

[7] D. Y. H. Pui, S. Fruin, and P. H. McMurry, Aerosol Sci. Technol. **8**, 173 (1988).

[8] K. Okuyama, Y. Kousaka, and K. Hayashi, J. Colloid Interface Sci. **113**, 42 (1986).

[9] W. R. Harper, Proc. Cambridge Philos. Soc. **28**, 219 (1932).

[10] J. M. Hidy and J. R. Brock, *The Dynamics of Aerocolloidal Systems* (Pergamon, Oxford, 1970).

[11] B. M. Smirnov, *Physics of Ionized Gases* (Wiley, New York, 2000).

[12] B. M. Smirnov, Phys. Usp. **170**, 495 (2000).

[13] D. Keefe, P. J. Nolan, and J. A. Scott, Proc. R. Ir. Acad., Sect. A **66**, 2 (1968).

[14] W. H. Marlow, J. Chem. Phys. **73**, 6284 (1980).

[15] D. D. Huang, J. H. Seinfeld, and W. H. Marlow, J. Colloid Interface Sci. **140**, 258 (1990).

[16] W. A. Hoppel and G. M. Frick, Aerosol Sci. Technol. **5**, 1 (1986).

[17] B. M. Smirnov, *Clusters and Small Particles in Gases and Plasma* (Springer, New York, 2000).

[18] N. A. Fuchs and A. G. Sutugin, *Highly Dispersed Aerosols* (Ann Arbor, London, 1971).

[19] J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry and Physics* (Wiley, New York, 1998).

[20] M. M. R. Williams and S. K. Loyalka, *Aerosol Science, Theory & Practice* (Pergamon, Oxford, 1991).

[21] J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York and London, 1941).