Brownian Coagulation of Knudsen Particles on Evaporating/Condensing Aerosol Droplet; Modeling of Capture of Soot Particles by Marine Fog

Marek A. Sitarski*

School of Science and Humanities, Husson University, 1 College Circle, Bangor, Maine 04401, USA

ABSTRACT

The theoretical model presented in this work allows quantitative prediction of the rate of Brownian coagulation of pollutant particles on a condensing aerosol droplet. The coupling of the processes of condensation and Brownian coagulation is established through the hydrodynamic-diffusiophoretic force acting upon the Brownian particles in the vicinity of the droplet. The new analytical approach is based on the Grad's moment method of solution to the Fokker Planck equation. The aerosol system is assumed to be isothermal and close to the thermodynamic equilibrium (i.e., the condensation and coagulation fluxes are small). The numerical predictions of the diffusiophoretic enhancement of Brownian coagulation rates are provided for NaCl-water droplets capturing small (primary) soot particles. The results of calculations show substantial enhancement (10 to 200 times) of the capture of soot particles by the condensing marine droplets for typical conditions that occur on the north-eastern coast of the U.S.A.

Keywords: Marine aerosols; Fog processing; Diffusiophoretic enhancement; Transition regime coagulation.

INTRODUCTION

The presented theoretical model of Brownian coagulation in the presence of a hydrodynamic (diffusiophoretic) force allows estimating the rate of capturing (“filtering”) of particulates by fog droplets. In the case of marine fog formation, the process might dominate the air quality and resulting health conditions of some coastal areas located downwind from pollution sources. The developed theoretical model allows probing of the regions of physicochemical parameter space which are interesting for a particular environmental application. Kinetics of capture of submicron soot particles by marine fog droplets is the focus of our numerical calculations. The preliminary results show that the marine aerosol droplets can be efficient scavengers of primary soot particles during fog formation.

The proposed theory of coupling (via the diffusiophoretic force) of Brownian coagulation, and condensation/evaporation taking place in the vicinity of a micro-droplet consists of three interconnected parts:

I. Analysis of transport of vapor molecules to/from the absorbing droplet surface. In this part, the isothermal condensation theory by Sitarski and Nowakowski (1979) is utilized.

II. Analysis of transport of Brownian particles towards the absorbing droplet utilizing moments' method of solution to the Fokker-Planck equation (Huang and Seinfeld, 1990) modified by an addition of external diffusiophoretic force acting upon the Brownian particles.

III. Integration of the kinetic transport model with the thermodynamics of deliquescence allowing an investigation of the condensation-enhanced coagulation processes in the marine fog.

The obtained final results are in an analytical form ready for studies of this complex aerosol phenomenon in the whole domain of environmental parameters.

Theoretical descriptions of transport of vapor molecules as well as of Brownian particles to a small spherical absorber (the micro-droplet) have previously utilized Grad's moments method in a solution to the steady-state Boltzmann and Fokker-Planck kinetic equations (Sitarski and Seinfeld, 1977, Sitarski and Nowakowski, 1981, Mork et al., 1984, Budzinski and Sitarski, 1985, Huang and Seinfeld, 1990). Here, we combine the theory of isothermal condensation of trace vapor with the theory of Brownian coagulation (being enhanced by the condensation process) through the introduction of diffusiophoretic force into the Fokker-Planck equation.

The rate of deposition, \( \phi_c \), of aerosol particles on a condensing spherical drop was investigated theoretically by Derjaguin and Dukhin, 1959, (Fuchs, 1989) in the continuum regime of Knudsen numbers. They assumed additionally that the diffusion coefficients of all the components of the gas mixture (including the diffusion coefficient of the condensing vapor) were the same and equal to \( D_c \). The Stefan flow was used as the main mechanism of coupling of
the coagulation and the condensation fluxes. The obtained equation for the deposition rate of the aerosol particles on a spherical absorber relative to the classical (condensation-free) continuum limit, $\varphi_{0c}$, has been written as follows (Fuchs, 1989)

$$\frac{\varphi_c}{\varphi_{0c}} = \frac{x}{e^x - 1}$$

(1)

where $x = \frac{D_g (\rho_{10} - \rho_{1c})}{D_B \rho_g}$

(2)

$$\varphi_{0c} = 4\pi R D_B \rho_{1c}$$

(3)

$\rho_{1c}$ - denotes the concentration of the Brownian particles (at infinite distance from the absorbing droplet), $\rho_{10}$ - denotes mass concentration of the neutral gas, $\rho_{1c}$ - denotes the mass concentration of the condensing vapor (at infinite distance from the droplet), $\rho_{10}$ - is the equilibrium mass concentration of the vapor at the droplet surface, $D_g$ - denotes diffusion coefficient of the Brownian particles in the vicinity of the condensing droplet, $R = r_p + r_B$ - is the collision distance between the droplet of radius $r_p$ and a Brownian particle of radius $r_B$.

The main assumption about the considered in this paper aerosol system is separation of masses of the three types of spherical particles: the droplet, the Brownian particles (depositing on the droplet), the condensing vapor molecules, and the bath gas molecules:

$$m_p >> m_B >> m_1 \equiv m_k$$

(4)

where: $m_p$, $m_B$, $m_1$, and $m_k$ - denote mass of the droplet, mass of the Brownian particles, mass of the vapor molecules, masses of the molecules of the non-condensing gas components ($k = 2, 3, ..., N$), respectively. The above mass assumptions support the chosen gas dynamic regimes for the aerosol particles:

1. The Brownian particles interact with the gaseous medium in the free molecular regime of Knudsen numbers, $K_{nB} = l_g/r_B >> 1$. Where $l_g$ denotes the mean free path of the bath gas molecules.
2. The interaction of the absorbing droplet with the vapor and the neutral gas molecules (the condensation kinetics) is not restricted to any particular regime of Knudsen numbers $Kn = l_i/r_p$ (where $l_i$ denotes mean free path of the condensing vapor molecules in the gas mixture)
3. The Brownian coagulation process is also not restricted to any particular range of effective Knudsen numbers, $\kappa$, defined (Sitarski and Seinfeld, 1977) as

$$\kappa = \frac{1}{h \zeta R}, \text{ where } h^2 = \frac{m_B}{kT}$$

(5)

$\zeta$ is the friction coefficient calculated for a Brownian particle in the free molecular regime of Knudsen numbers, $K_{nB} = l_g/r_B$.

According to the above assumptions, the aerosol droplet behaves like a stationary spherical absorber for the colliding Brownian particles as well as for the incident vapor molecules. The used three sets of Knudsen numbers: $\kappa$, $Kn$, and $K_{nB}$ define the kinetics of interaction of the absorbing droplet with the Brownian particles, with the vapor molecules, and the interaction of the Brownian particles with the bath gas, respectively. The effects of inter-particle interactions (Van der Waals, electrostatic, and elastic deformation) on the Brownian coagulation rate of polydispers aerosols were recently studied by Lin and Wang (2012) in the gas-slip regime, with linear dependence of the slip correction factor on the Knudsen number. The authors focused on the role interparticle interactions play in collision efficiency of the aerosol particles. The present work is focused on predicting the frequency of particle collisions based on the moments’ solutions to the Boltzmann and Fokker-Planck kinetic equations; therefore, it extends applicability of the results into the transition range of Knudsen numbers. The collision efficiency of aerosol particles is formally denoted here as the mass accommodation (“sticking”) coefficient defined by Eq. (34).

**FORCES ACTING UPON THE BROWNIAN PARTICLES**

In the vicinity of the condensing/evaporating aerosol droplet, in the absence of electric or magnetic interactions and a negligible particle acting upon the Brownian particle are only of the hydrodynamic nature. Let we place the origin of the coordinate system in the center of the stationary absorbing droplet which is surrounded by Brownian particles suspended in a gas mixture containing a condensing vapor. The mass flux of vapor molecules to/from the absorbing droplet exerts the diffusiophoretic force $F$ upon the particles. Due to the assumed low concentration of the vapor in the non-condensing gas bath and the relatively large heat capacity of the droplet we neglect the temperature differences between the droplet surface and the surrounding gas. The considered aerosol system is isothermal.

Approximating the Brownian particles by small spheres, we apply the results of Waldman (1981), when writing the total force acting upon the Brownian particle as a sum of the drag force, $K_f$, and the diffusiophoretic force, $F$. The forces are expressed in the free molecular regime of Knudsen numbers, $K_{nB}$, by the following equations:

$$K_f = -\zeta c$$

(6)

where $\zeta = \frac{32}{3} \frac{r_B^2}{m_B} \sum_{k=1}^{N} \left(1 + \frac{\pi}{8} \sigma_k \right) P_k c_k$

(7)

$$F = \frac{32}{3} \frac{r_B^2 kT}{m_B c_1} \left(1 + \frac{\pi}{8} \sigma_1 \right) n_1 v_1$$

(8)

The surface accommodation coefficient $\sigma_k$, for the k-th gas component, is defined as a fraction of molecules striking
the surface of the Brownian particle and undergoing the diffusive reflection with the Maxwellian velocity distribution. The rest, \( (1 - \alpha) \) - fraction, of the molecules is assumed to be reflected specularly. \( c_k \) - denotes the average speed of molecules of the k-th gas component:

\[
c_k = \sqrt{\frac{8kT}{\pi m_k}} , \text{ and } p_k = n_k kT
\]  

(9)

The index \( k = 1 \) pertains to the condensing vapor molecules; values of \( k > 1 \) pertain to the neutral, non-condensing gas bath component. \( p_k \) and \( n_k \) - denote the partial pressure and the number density of the k-th gas component, respectively. Vector \( c \) - denotes velocity of a Brownian particle, \( \zeta \) - denotes the friction coefficient, \( v_1 \) - denotes the mean velocity vector of condensing vapor molecules, and \( k \) - denotes the Boltzmann constant. At an arbitrary distance \( r \) from the absorbing droplet (measured from its center), the total transfer of vapor molecules must be the same. Therefore, the molecular flux vector of the vapor at a distance \( r \) is equal to

\[
j_i(r) = n_i v_1 = j_i \left( \frac{r}{r} \right)
\]  

(10)

with the scalar function \( j_i \) derived previously by Sitarski and Nowakowski (1979):

\[
j_i = \frac{a_i}{r^2}
\]  

(11)

\[
a_i = \frac{(n_{10} - n_{1\infty})}{4} C(Kn) \frac{\beta(1 + z)^2}{4(3 + 5z)} Kn
\]

\[
a_i = \frac{(n_{10} - n_{1\infty})}{4} C(Kn) [\frac{\beta(1 + z)^2}{4(3 + 5z)} Kn + \frac{9(1 + z)^2}{8(3 + 5z)} Kn^2]
\]  

(12)

\[
\beta = \frac{a_1}{2 - a_1} , \text{ Kn} = \frac{l_1}{r_p} , \text{ z} = \frac{m_l}{m_g}
\]  

(13)

\( m_l \) is mass of a vapor molecule, \( m_g \) is the average mass of non-condensing gas molecules, \( n_{10} \) is the saturation vapor concentration at the droplet surface, \( n_{1\infty} \) is the number concentration of the vapor molecules at infinite distance from the droplet, \( a_i \) - denotes the “sticking” coefficient for the vapor molecules incident upon the droplet surface.

The mean free path \( l_1 \) of the vapor molecules necessary for determination of the Knudsen number \( Kn \) governing the regime of condensation, is calculated according to Chapman and Cowling (1970):

\[
l_1 = \frac{1}{\pi \sum_{k=1}^{N} n_k \alpha_{ik}^2 \sqrt{1 + m_l m_k} \pi n_k \alpha_{ik}^2 \sqrt{1 + z}} \approx \frac{1}{\pi n_k \alpha_{ik}^2 \sqrt{1 + z}}
\]  

(14)

In the Eq. (14), we replace the individual molecular masses of the neutral gas components by the weighted average mass of the gas bath molecules, \( m_g \), in calculation of the ratio \( z \). Also, the individual binary collision diameters \( \sigma_{ik} \) between the vapor molecule and the k-th gas component molecules are replaced by the average collision diameter \( \sigma_{ik} \). The direction of the external diffusiophoretic force acting upon the Brownian particle depends on the concentration of the vapor relative to the saturation vapor pressure over the surface of the droplet. If the vapor is supersaturated, the force is directed towards the center of the droplet and the condensation flux enhances the capture of the Brownian particles.

### THE FOKKER-PLANCK DESCRIPTION OF BROWNIAN COAGULATION IN THE PRESENCE OF DIFFUSIOPHORETIC FORCE

The theory of Brownian motion in the presence of an external force field starts with the Langevin’s equation

\[
dc/dt = -\zeta c + A(t) + F(r,t)
\]  

(15)

The forces of the surrounding medium acting on the Brownian particle are split into two parts:

1. The systematic forces - representing dynamic friction experienced by the particle \( \zeta c \), and the hydrodynamic (diffusiophoretic) force \( F(r,t) \);

2. The fluctuating force \( A(t) \) - characteristic of the Brownian motion. It is assumed that the fluctuating force is independent of the particle velocity and varies extremely rapidly compared to the variations of the velocity vector \( c \).

For the times long compared to the period of fluctuations of \( A(t) \) but short compared to intervals during which velocity of the Brownian particle changes by appreciable amounts the Langevin’s equation leads to the Fokker-Planck equation for the one-particle probability distribution function \( f_r(c,e,t) \) of finding the Brownian particle at a position \( r \) with velocity \( c \) at the time \( t \) (Chandrasekhar, 1943). Subsequently, the quasi-stationary process of Brownian coagulation can be described by the steady-state Fokker-Planck equation:

\[
\mathbf{c} \cdot \nabla_r f(r,c) + \mathbf{F} \cdot \nabla_c f(r,c) = \zeta \nabla_c \mathbf{c} \cdot \nabla_r f(r,c) + \frac{kT}{m_B} \nabla_c f(r,c)
\]  

(16)

where \( T \) - denotes temperature of the gas bath surrounding the Brownian particle, and \( \mathbf{v} \) - denotes the nabla-operator. Let we associate a hydrodynamic potential \( \Phi \) per unit mass of the Brownian particle with the diffusiophoretic force \( \mathbf{F} \)

\[
\mathbf{F} = -\nabla_r \Phi
\]  

(17)

The Fokker-Planck equation with an external force has been reformulated in terms of Grad’s thirteen-moments by Huang and Seinfeld (1990) for studies of Brownian coagulation of interacting aerosol particles. The authors solved the resulting equations for the moments by a numerical algorithm for various interparticle potentials. The moments’
equations derived by Huang and Seinfeld (1990) are utilized in this work. Instead of the numerical solution, the differential equations for the moments are simplified by the assumption of conditions close to the thermodynamic equilibrium (i.e., small fluxes) and are solved analytically.

THE THIRTEEN-MOMENT EQUATIONS

The thirteen-moments method developed by Grad (1949) for an approximate solution to the Boltzmann equation was applied before by Sitarski and Seinfeld (1977), Mork et al. (1984), and Huang and Seinfeld (1990) to the solution of the Fokker-Planck equation using the following moments (1984), and Huang and Seinfeld (1990) to the solution of the model system. All of the fluxes as well as the diffusiophoretic force acting upon the Brownian particles are functions of the radial distance $r$ from the center of the absorbing droplet.

\[ j = j(r) \left[ \frac{r}{r} \right] \]  
\[ q = q(r) \left[ \frac{r}{r} \right] \]  
\[ F = F(r) \left[ \frac{r}{r} \right] \]  

The moments satisfy the following system of differential equations (Huang and Seinfeld, 1990), which is the starting point of our analysis:

\[ \frac{dj'}{dr'} + \frac{2j'}{r'} = 0 \]  
\[ \frac{dn'}{dr'} + n' \frac{d \Phi'}{dr'} - j' \frac{d^2 \Phi'}{dr'^2} - \frac{3}{5} \left( \frac{d^2 q'}{dr'^2} + \frac{2}{r'} \frac{dq'}{dr'} - \frac{2q'}{r'^2} \right) = -j' \]  
\[ \frac{d^2 q'}{dr'^2} + \frac{2}{r'} \frac{dq'}{dr'} - \frac{2q'}{r'^2} + \frac{1}{11} \frac{d \Phi'}{dr'} \left( 15j' \frac{d \Phi'}{dr'} + 11 \frac{dq'}{dr'} \right) + \frac{14q'}{r'} \]  
\[ + \frac{5}{11} \left( \frac{d \Phi'}{dr'} \frac{dj'}{dr'} + 3j' \frac{d^2 \Phi'}{dr'^2} \right) - \frac{15}{11} \left( 2q' - 5j' \right) \]  

All the primed parameters are dimensionless and defined as follows:

\[ n' = nR^2 \kappa^2, j' = jR^2 \kappa^2 \zeta, q' = q \zeta^2, r' = r/(R \kappa) \]

The above set of Eqs. (21–23), does not have an analytical solution and has been solved numerically for certain parameters and interaction potentials by Huang and Seinfeld (1990). However, based on the assumption that the aerosol system is not far from the thermodynamic equilibrium, the Eqs. (21–23) can be simplified by neglecting terms "quadratic" with respect to the thermodynamic fluxes: condensation, coagulation, energy. The linearization of Eq. (22) allows us to neglect the quadratic third term proportional to the product of the small flux $j'$ of the Brownian particles and the potential, $\Phi'$, of the hydrodynamic force $F'$ proportional to the small flux of the condensing vapor molecules, according to the Eq. (8). The assumption of constant temperature allows us to associate the transfer of kinetic energy $q$ solely with the mass flux $j$ of the coagulating particles.

\[ q' = \text{const} \times j' \]  

The same method of linearization has been applied in the kinetic theory of condensation by Sitarski and Nowakowski (1979). Accordingly, the above Eqs. (21–22) reduce to

\[ \frac{dj'}{dr'} + \frac{2j'}{r'} = 0 \]  
\[ \frac{dn'}{dr'} + n' \frac{d \Phi'}{dr'} = -j' \]  

Solutions to the Eqs. (25–27) containing three integration constants $A_j$, $A_q$, and $C$ are as follows:

\[ q'(r') = \frac{A_j}{r^{c_2}} \]  
\[ n'(r') = \frac{A_j}{b} + C \exp \left( -\frac{b}{r'} \right) \]  
\[ j'(r') = \frac{A_j}{r^{c_2}} \]

For potential-free Brownian coagulation, the solutions take the following form:

\[ q'(r') = \frac{A_{j0}}{r^{c_2}}, \quad n'(r') = \frac{A_{j0}}{b} + C_0, \quad j'(r') = \frac{A_{j0}}{r^{c_2}} \]

The above solutions have been obtained by utilization of the symbolic mathematics package Maple, Maplesoft, Inc. The dimensionless parameter $b$ determines strength of the diffusiophoretic force per unit mass of Brownian particles and of the associated potential.
Utilizing Eqs. (8–11, and 24) we obtain the following expression for the parameter $b$

$$b = \frac{32\beta^2 a_1 (1 + \frac{\pi}{8}\sigma_1)}{3c_0 R\kappa}$$

$$= \frac{8r_0^2 (1 + \frac{\pi}{8}\sigma_1)(n_{10} - n_{1\infty})r_p^2 Kn}{3R\kappa} C(Kn)$$

The integration constants $A_j, A_q,$ and $C$ in the Eqs. (28–30) are determined from the boundary conditions at the surface of the droplet, and at the infinite distance from it. At the surface of the absorbing droplet, we use the following two accommodation coefficients:

1. Mass accommodation ("sticking")

$$\alpha_s = (j^- - j^+)/j^-$$

(34)

2. The energy, or thermal accommodation

$$\alpha_e = (q^- - q^+)/q^-$$

(35)

The "half-range" fluxes $q^\pm$ and $j^\pm$ can be obtained by the integration of half-range distribution functions $f^\pm$ expanded into truncated Grad’s series of moments. $f^-$ and $f^+$ represent one-particle velocity distribution functions for the incoming and outgoing Brownian particles at the surface of the droplet, respectively. In this way the half-range fluxes can be evaluated analytically in terms of full range moments. The full range energy, and mass fluxes are the net fluxes expressed by the half-range moments, as follows

$$q = q^+ - q^-$$

(36)

$$j = j^+ - j^-$$

(37)

The energy and mass accommodation coefficients are generally not known. Therefore, in this model, both of the coefficients are assumed to be the same ($\alpha_s = \alpha_e = \alpha$). It means that if a Brownian particle sticks to the droplet surface during a collision it equilibrates its thermal energy with the droplet as well. The above boundary conditions together with the derived by Huang and Seinfeld (1990) relations between the half-range fluxes and full-range moments for Brownian particles in an external force field, lead to the following set of equations for the dimensionless moments at the surface of the absorbing droplet (indicated with the subscript, $s$)

$$n_s' = -\frac{\sqrt{2\pi}}{2}(1 - \frac{1}{\alpha})j_s' - \frac{1}{2}(j_s' F_s' - \frac{3 dq'}{5 dr'} - \frac{2 q_s'}{5 r_s'})$$

(38)

At the infinite distance from the droplet surface the number density of the Brownian particles expressed by Eq. (29) becomes

$$n_{1\infty} = \frac{A_j}{b} + C$$

(40)

Substituting Eqs. (28–30) into Eqs. (38–39) we obtain the following equations:

$$\frac{b\kappa^4 A_j}{2} + \sqrt{2\pi}\left(\frac{1}{\alpha} - \frac{1}{2}\right)\kappa^2 A_j + A_j/b + Ce^{-bk} = -\frac{2\kappa^3 A_q}{5}$$

(41)

$$b\kappa^4 A_j + A_j/b + Ce^{-bk} = -\frac{3\kappa^3 A_q}{5} - \frac{\sqrt{2\pi}}{2}(1 - \frac{1}{\alpha})\kappa^2 A_q$$

(42)

Solution to the above system of linear Eqs. (40–42) gives expressions for the unknown constants: $A_j, A_q,$ and $C$:

$$C = -n_{1\infty} \frac{b\kappa^5}{10} - \frac{\sqrt{2\pi}}{4}\left(\frac{1}{\alpha} - \frac{1}{2}\right)b\kappa^4 - \frac{3\sqrt{2\pi}}{5}\left(\frac{1}{\alpha} - \frac{1}{2}\right)\kappa^3$$

(43)

$$\left(-\pi\left(\frac{1}{\alpha} - \frac{1}{2}\right)^2\kappa^2 - \kappa - \frac{\sqrt{2\pi}}{2b}\left(\frac{1}{\alpha} - \frac{1}{2}\right)\right)\right)/Den$$

$$A_j = e^{-bk}n_{1\infty} \left[\frac{\sqrt{2\pi}}{2}(1 - \frac{1}{\alpha} - \frac{1}{2})\kappa^\frac{5}{2}\right]/Den$$

(44)

$$A_q = -n_{1\infty} e^{-bk} \left[-10\left(\frac{1}{\alpha} - \frac{1}{2}\right)^2\pi + \frac{5}{2}\sqrt{2\pi}\left(\frac{1}{\alpha} - \frac{1}{2}\right)\kappa^2 b$$

$$-6\sqrt{2\pi}\left(\frac{1}{\alpha} - \frac{1}{2}\right)\kappa + 3b\kappa^3\right]/\left(6\kappa + 5\sqrt{2\pi}\left(\frac{1}{\alpha} - \frac{1}{2}\right)\right)Den$$

(45)

where the denominator, $Den$, is expressed as follows:

$$Den = \frac{b\kappa^5}{10} - \frac{\sqrt{2\pi}}{4}\left(\frac{1}{\alpha} - \frac{1}{2}\right)b\kappa^4 - \frac{3\sqrt{2\pi}}{5}\left(\frac{1}{\alpha} - \frac{1}{2}\right)\kappa^3$$

$$\left(-\pi\left(\frac{1}{\alpha} - \frac{1}{2}\right)^2\kappa^2 + \frac{\sqrt{2\pi}}{2}\left(\frac{1}{\alpha} - \frac{1}{2}\right)\right)/\left(\kappa + e^{-bk}ight)$$

(46)

**ANALYSIS OF THE NEW EQUATIONS FOR DETERMINATION OF THE BROWNIAN COAGULATION RATES**

In the condensation-free limit, $b \to 0$, the flow of Brownian particles in the vicinity of the aerosol droplet is expressed by the following equations:
\[ j'_0(r') = \frac{A_{j0}}{r'^{n}} \]  

where

\[ A_{j0} = -n'_r \left[ \frac{\sqrt{2}\pi}{2} \left( \frac{\alpha - \frac{1}{2}}{2} \right) ^2 + \frac{\kappa}{5} \right] \left[ \frac{3\sqrt{2}\pi}{5} \left( \frac{\alpha - \frac{1}{2}}{2} \right) ^3 \right] \]

This is a new formula for the potential-free Brownian coagulation flux. The continuum limit of the potential-free Brownian coagulation rate is well established theoretically, and is given by the Maxwell expression (Seinfeld and Pandis, 1996)

\[ \varphi_0 = 4\pi RD_B n_o \]  

where \( D_B \) denotes diffusion coefficient of the Brownian particles expressed by the Einstein equation

\[ D_B = \frac{1}{\zeta h^2} \]  

The new Eqs. (47–48) express the rate of capture of Brownian particles, \( \varphi_0 \), in the whole range of effective Knudsen numbers, \( \kappa \)

\[ \varphi_0 = -4\pi R^2 j(R) = -4\pi \zeta A_{j0} \]

\[ = 4\pi RD_B n_o \left[ \frac{\sqrt{2}\pi}{2} \left( \frac{\alpha - \frac{1}{2}}{2} \right) ^2 + \frac{\kappa}{5} \right] \left[ \frac{3\sqrt{2}\pi}{5} \left( \frac{\alpha - \frac{1}{2}}{2} \right) ^3 \right] \]

In the continuum limit, \( \kappa\to0 \), the expression for the enhanced coagulation rate becomes

\[ \lim_{\kappa\to0} \varphi_0 = \varphi_{0c} = 4\pi R D_B n_o \frac{b\kappa}{e^{b\kappa} - 1} \]  

In order to compare exactly the above Eq. (54) with their expression, we have calculated the term \( b\kappa \), assuming masses of the gas molecules being the same, \( m_k = m_1 \), and \( Kn\to0 \). Then, taking the first approximation to the diffusion coefficient of vapor molecules (according to Chapman and Cowling, 1990) our limit differs only by a factor of (20/19) from the expression of Derjaguin and Dukhin (1959). However, taking the second approximation to the diffusion coefficient our result differs only by the numerical factor of 1.017.

In the free-molecular limit, \( \kappa\to\infty \), the potential-free Brownian coagulation rate becomes

\[ \lim_{\kappa\to\infty} \varphi_0 = 4\pi R^2 n_o \frac{1}{3h\sqrt{2}\pi \left( \alpha - \frac{1}{2} \right) ^2} = \frac{\pi R^2 c_B}{3} \frac{1}{\left( \alpha - \frac{1}{2} \right) ^2} \]

\[ = \frac{1}{3} \left( \frac{\alpha - \frac{1}{2}}{\alpha - \frac{1}{2}} \right) \varphi_{fm} \]

\[ \varphi_{fm} = \pi R^2 c_B \] - denotes the free molecular limit of capture of colliding particles by an absorber of radius \( R \), and \( c_B = \frac{8kT}{\pi m_B} \) - denotes the average thermal speed of Brownian particles.

The obtained free-molecular limit has a right functional dependence except for the numerical coefficient dependent on the particle-droplet accommodation, \( \alpha \). Assuming perfect accommodation (\( \alpha = 1 \)), Eq. (55) becomes

\[ \lim_{\kappa\to0} \varphi_0 = \frac{2}{3} \varphi_{fm} \]  

The same free-molecular limit of Brownian coagulation rate was obtained by Sitarski and Seinfeld (1977), Mork et al. (1984), and Huang and Seinfeld (1990). In this limit, changes of the particle velocity distribution function in the vicinity of the absorbing droplet are especially large and the applied moments’ approximation might be not capable of providing the adequately large perturbation to the equilibrium velocity distribution. In the free molecular limit, \( \kappa\to\infty \), the coagulation rate in the presence of hydrodynamic potential, Eq. (53), becomes

\[ \varphi = \frac{4\pi R D_B n_o \kappa}{5} = \frac{\varphi'}{3} \frac{\varphi_{fm}}{2\sqrt{2}\pi} \]
The free molecular limit is hard to achieve without violating any of the assumptions of the considered model. For example, the lowest gas density must be still higher than the saturated vapor pressure, and the size of the droplet (in order to stay stationary) must be much larger than the size of the captured Brownian particles.

DIFFUSIOPHOTIC ENHANCEMENT OF THE BROWNIAN PARTICLES CAPTURE RATE

Estimation of the coagulation rate in the presence of vapor condensation, relative to the condensation-free case, is the main objective of this study. The ratio of the rate \( \phi \), expressed by Eq. (53), and the potential-free rate \( \phi_0 \), expressed by Eq. (51), represents the coagulation enhancement

\[
\frac{\phi}{\phi_0} = \frac{3\sqrt{2}\pi}{5} \left( \frac{1}{\alpha} \right)^2 + \left( \frac{\pi}{\alpha} - \frac{1}{2} \right) \kappa + \left( \frac{\pi}{\alpha} + \frac{1}{2} \right) \kappa \left[ \frac{3\sqrt{2}\pi}{5} \left( \frac{1}{\alpha} - \frac{1}{2} \right)^2 + \frac{3\sqrt{2}\pi}{5} \left( \frac{1}{\alpha} - \frac{1}{2} \right) \kappa^2 \right] e^{-b\kappa} \left( \frac{b\kappa^4}{10} + \frac{3\sqrt{2}\pi}{4} \left( \frac{1}{\alpha} - \frac{1}{2} \right) b\kappa^3 + \frac{3\sqrt{2}\pi}{5} \left( \frac{1}{\alpha} - \frac{1}{2} \right) \kappa^2 \right)
\]

(58)

Assuming, that the Brownian particles always stick to the liquid surface upon collision (the mass and energy accommodation coefficient, \( \alpha = 1 \)) the above Eq. (58) becomes

\[
\frac{\phi}{\phi_0} = \frac{3\sqrt{2}\pi}{10} \kappa^2 + \left( \frac{\pi}{4} + \frac{1}{5} \kappa \right) \sqrt{2}\pi \kappa + \left( \frac{\pi}{4} - \frac{1}{5} \kappa \right) e^{-b\kappa} \left( \frac{b\kappa^4}{10} + \frac{3\sqrt{2}\pi}{10} \kappa^2 + \frac{3\sqrt{2}\pi}{4} \kappa - \frac{3\sqrt{2}\pi}{5} \kappa e^{-b\kappa} - \frac{\kappa}{b\kappa^2} \right)
\]

(59)

ENHANCEMENT OF CAPTURE OF PRIMARY SOOT PARTICLES BY CONDENSING MARINE AEROSOL DROPLETS

The above theoretical analysis is applied here to the process of capture of soot particles by marine fog droplets at atmospheric conditions common to the coastal Northeastern United States. In summer, the humid and polluted air from urban areas of the East Coast is carried by the dominant southwestern winds over the cold waters of the North Atlantic towards the New England coast. When the continental air enters marine environment of the Gulf of Maine the temperature lowers significantly and the relative humidity (RH) reaches quickly the deliquescence relative humidity (DRH) and a fog is formed. The temperature dependence of DRH has been derived by Tang and Munkelwitz (1993)

\[
DRH(T) = DRH(298) \times \exp \left\{ \frac{\Delta H_f}{R_g} \left[ A \left( \frac{1}{T} - \frac{1}{298} \right) - B \ln \frac{T}{298} - C(T - 298) \right] \right\}
\]

(60)

The constants in the above Eq. (60) for the NaCl–water system have the following numerical values: \( A = 0.1805 \), \( B = -5.310 \times 10^{-4} \), \( C = 9.965 \times 10^{-4} \). \( \Delta H_f = 1.88 \text{kJ/mol} \) is the heat of solution of NaCl in water, \( DRH(298) = 75.3\% \) for NaCl crystals, and \( R_g = 8.31 \text{J/mol/K} \) is the universal gas constant. The specific parameters of the atmospheric aerosol system chosen for computations are as follows:

- Radius of the marine droplet, \( r_p = 100–10000 \text{nm} \)
- Radius of the Brownian soot particles, \( r_B = 10–50 \text{nm} \)
- Density of the soot particles, \( d_p = 2.0 \text{g/cm}^3 \) (Hand and Kreidenweis, 2002).
- Air temperatures, \( T = 280–300 \text{K} \) (typical as observed by NOAA Gulf of Maine monitoring program).
- RH = 80–105\% (all are larger than the deliquescence relative humidity for the sea salt).
- Barometric pressure, \( P = 1 \text{atm} \)
- Composition of the dry air is assumed to be according to the following volume fractions: 0.781 N\textsubscript{2}, 0.210 O\textsubscript{2}, and 0.009 Ar (Bohren and Albrecht, 1998).
- The mean free path of the vapor molecules necessary for determination of the Knudsen number \( \kappa_n \) governing the regime of condensation, is calculated by use of Eq. (14) where we replace the individual molecular masses of the gas components by the weighted average mass of air molecules in order to calculate the ratio \( z \)

\[
z \approx \frac{m_1}{0.781m_{N_2} + 0.210m_{O_2} + 0.009m_{Ar}}
\]

(61)

- The collision diameters, \( \sigma_{ik} \), for the water vapor molecules with the \( k \)-th air component molecules are replaced by an average collision diameter \( \sigma_{ik} \) calculated from the value of diffusion coefficient of water vapor in air: \( D_{ik} = 0.239 \text{cm}^2/\text{sec} \) at \( T = 281 \text{K} \), and \( P = 1 \text{atm} \) (Weast, 1986). The applied equation for determination of the average collision diameter of the rigid elastic spheres utilizes the first approximation to the diffusion coefficient (Chapman and Cowling, 1990)

\[
\sigma_{ik}^2 = \frac{3}{16} \sqrt{\frac{2kT(1+z)}{\pi m_1}} \frac{1}{n_{ik}D_{ik}}
\]

(62)

- The Clausius-Clapeyron equation is used to predict the water vapor saturation pressure within the selected temperature range (Bohren and Albrecht, 1998)

\[
\rho_{ig} = 617 \exp \left( 6808 \left( \frac{1}{273} - \frac{1}{T} \right) - 5.09 \ln \frac{T}{273} \right)
\]

(63)

The above parameters determine values of the three Knudsen numbers (\( \kappa_n, \kappa_B, \) and \( \kappa \)) which define the hydrodynamic regime of the studied aerosol system. Results
of the sample calculations are presented on Figs. (1–4) in a form of 3-D plots of the enhancement of the rate of Brownian capture of primary soot particles by condensing marine droplets at vapor pressures exceeding the deliquescence point for NaCl.

- The 3-D plot on Fig. 1 shows that the enhancement increases more strongly with the size of the soot particles than with the size of the condensing droplet. The magnitude of the effect is quite substantial: from a few times (for 10 nm soot particles) to about 200 times (for 50 nm soot particles). The relative humidity in these calculations is 100% at the assumed temperature of air equal to 290 K.

- The graphical results on Fig. 2 show that the enhancement of capture of soot particles increases with the ambient temperature and with the size of the Brownian particles. In the temperature range of 275–300 K, the enhancement increases by only a few times (for 50 nm soot particles).

- For larger absorbing droplets (2–10 μm), the dependence on temperature is strong and the enhancement due to condensation can reach 50 to 200 times (at the relative humidity 100% and for the soot particles radius of 40 nm), Fig. 3.

- At higher ambient temperatures (300 K), the dependence of the enhancement on RH (in the 75–105% range) is quite substantial and achieves the value of 140 times for droplet size of 1.0 μm, and soot particles size of 30 nm, as depicted in Fig. 4.

Results of all the calculations, in Figs. (1–4), might provide a theoretical justification of the importance of fog processing of anthropogenic aerosols. Interaction of particulates with marine droplets responsible for the fog “filtering” effect is predicted to be significantly enhanced by the concurrent process of water vapor condensation.

SUMMARY

The problem of diffusiophoretic enhancement of coagulation of aerosol particles in supersaturated vapor has been formulated mathematically in terms of Brownian motion in a hydrodynamic (diffusiophoretic) force-field surrounding a condensing/evaporating droplet. The applied steady-state Fokker-Planck equation allows to include (in the description of the synergy of condensation and coagulation) the non-continuum effects (transition regime of Knudsen numbers). The applied linearization of the Grad's moments equations, based on the assumption of close to thermodynamic equilibrium conditions, has made possible analytical solution to the system of moments’ equations and derivation of formulas for Brownian coagulation rates. Eqs. (53, 58 and 59) provide the first estimate of the enhancement of coagulation process due to vapor condensation in the transition regime of Knudsen numbers as a function of temperature, pressure, relative humidity, droplet size, captured Brownian particles size and density, as well as the surface accommodation coefficients. The application of the derived theoretical formulas in calculations of the rates of capture of primary soot particles by condensing marine droplets for typical atmospheric conditions of the New England coast suggest a significant enhancement (by as much as 10 to 300 times) as compared with the normal (condensation-free) Brownian coagulation mechanism. Therefore, the “filtering” of primary particulates by a condensing marine fog might be much more effective than expected.

Fig. 1. Diffusiophoretic enhancement of Brownian capture of soot particles by a condensing salt-water droplet at the relative humidity 100% and the temperature 290 K. Radii of the Brownian soot particles, r_B, vary from 10 to 50 nm and the radius of the absorbing salt-water particle, r_p, ranges from 1 μm through 10 μm.
Fig. 2. Diffusiophoretic enhancement of Brownian capture of soot particles by a 1.0 μm condensing salt-water droplet as a function of temperature of the air and the radius of soot particles at the relative humidity 100%. Radii of the Brownian soot particles, $r_{B}$, vary from 10 to 50 nm and the temperatures range from 275 K through 300 K.

Fig. 3. Diffusiophoretic enhancement of Brownian capture of 40 nm soot particles by a condensing salt-water droplets as a function of temperature of the air and the radius of the droplets at the relative humidity 100% (exceeding the DRH). Radii of the salt-water droplets vary from 1 μm to 10 μm and the temperatures range from 275 K through 300 K.

The introduced coupling of the two processes could be utilized in studies of dynamics of aerosols through the dependence of coagulation kernel on the condensation flux in the general dynamic equation. Often studies of aerosol dynamics are focused on Brownian coagulation only (absence of condensation). In these studies, the solutions to the dynamic equation for Brownian particles have applied coagulation coefficients in two limit cases: the free molecule regime and the continuous regime, Yu et al. (2008), or a combination of the two regimes using some flux matching method, such as harmonic mean, Park et al. (1999), or the Dahneke approach, Otto et al. (1999). In the absence of condensation, the potential-free rate expression, Eq. (51), provides a new coagulation frequency formula which can be used in studies of Brownian coagulation dynamics in the transition regime of Knudsen numbers.
Fig. 4. Diffusiophoretic enhancement of Brownian capture of 30 nm soot particles by a condensing 1.0 μm salt-water droplet as a function of relative humidity of the air and the temperature. The relative humidity varies from 75% to 105% and the temperatures range from 275 K through 300 K.

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