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Binary homogeneous nucleation and growth of water–sulfuric acid nanoparticles using a TEMOM model

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ABSTRACT

Binary homogeneous nucleation and growth process of water–sulfuric acid nanoparticles in atmospheric environment is studied using a new developed moment model (i.e. TEMOM model). The underlying mechanisms due to Brownian motion are employed in the general dynamic equation which is further closed by Taylor-expansion technique. The newly proposed model provides high precision and efficiency in studying the present binary nucleation system as compared to exiting models. The competition between nucleation, coagulation and condensation in the whole nucleation and subsequent growth processes is systemically investigated in both cases with background particles and without particles. The results show the nucleation kinetics and aerosol dynamics are strongly dependent of production rate of sulfuric acid, and also dependent of the competition ability to scavenge sulfuric acid between pre-existing particles and nucleated particles.

1. Introduction

Formation of new atmospheric aerosol particles by nucleation and subsequent growth are key mechanisms determining atmospheric aerosol dynamics. Although there are already some different and even conflicting proposed nucleation mechanisms including kinetic (or barrierless), binary, ternary, and ion-induced (or ion-mediated) [1–3], the binary H_2SO_4–H_2O mechanism may be a sufficient theory serving as the formation of nucleated particles in the free troposphere and some engineering exhausts [4]. In theory, the spatial temporal evolution of aerosol dynamics in evolving flows can be properly traced if the mechanisms of formation and growth are appropriately expressed in particle general dynamics equation (PGDE) as well as computational fluid dynamics [5]. At this case, it is possible to simultaneously capture the details of flow, the evolution of aerosol dynamics, and complex chemical kinetics. Up to now, there are a lot of studies for incorporating nucleation kinetics and aerosol dynamics into mathematical models based on sectional method which fully solve the time-dependent system [6,7].

The sectional method is capable to produce the most accurate results as compared to other methods such as moment method and Monte Carlo method, and was shown to be robust to solve atmospheric aerosol problems [6,7], but it consumes the largest computational time which may limit its wide application in specific environments, especially the huge computational cost is required. The present study, however, is to provide a framework for incorporating detailed nucleation kinetics and aerosol dynamics into moment methodology in which the competition between nucleation, condensation and coagulation will be assessed. The moment method is prior to the sectional method in its less requirement for computational cost and much easier for implementation. Although the competition between nucleation, condensation and coagulation has been investigated in great detail in the nucleation process [8–11], their competing in the whole nucleation and subsequent growth process is still unsolved sufficiently.

The PGDE has an ability to describe the combined physical/chemical processes for very fine particles, such as the internal processes of nucleation, condensation and coagulation as well as the external transport processes of diffusion, convection and thermophoresis. However, as the moment methodology is introduced, the closure for PGDE is difficult to be achieved due to its highly non-linear and partial integro-differential characteristics. In the past, four prominent methods were proposed to close PGDE, i.e. making a prior assumption for the shape of the aerosol size distribution [12], approximating the integral moment by an n-point Gaussian quadrature [13], assuming the pth-order polynomial form for the moments [14], and achieving closure with interpolative method [15]. Here, an alternative numerical approach, i.e. Taylor-series expansion method of moments (TEMOMs), is proposed. The underlying idea of this solution is that the closure of the integral equations is approached

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Nomenclature

A	constant (= 1.591)
B_1, B_2	collision coefficient for the free molecule regime and continuum regime
$\bar{c}$	mean thermal velocity (m s^{-1})
C	Cunningham correction factor
d_p	volume-averaged particle diameter
D	particle diffusion coefficient (m^2 s^{-1})
D_f	mass fractal dimension
f	$1/D_f$
G	volume growth rate (m^3 s^{-1})
J	nucleation rate (m^{3-} s^{-1})
k_b	Boltzmann constant (J K)
Kn	particle Knudsen number
m_k	kth moment of particle size distribution
N	particle number concentration (m^{-3})
n_s	reference concentration (m^{-3})
P	pressure
t	time (s)
T	temperature (K)
u	the point of Taylor-series expansion (m_1/m_0)
v, v_1	particle volume (m^3)
v_a	volume of sulfuric acid molecule (m^3)
v_w	volume of water molecule (m^3)
v_g	geometric mean particle volume (m^3)
v^*	nuclei volume (m^3)
Y_1	the concentration of sulfuric acid (m^{-3})

Greek letters

ν	kinematic viscosity (m^2 s^{-1})
ρ	gas density (kg m^{-3})
ρ_p	particle density (kg m^{-3})
β	particle collision kernel
μ	gas viscosity (kg m^{-1} s^{-1})
λ	mean free path of the gas (m)
σ_g	geometric mean deviation of particle size distribution
θ	dimensionless coagulation time, B_2Nt
χ	the mole fraction of sulfuric acid in an aerosol

using the Taylor-series expansion technique. Unlike the log-normal method, this TEMOM has no prior requirement for particle size distribution, and it produces the accurate results with less computational requirement [16]. Therefore, the TEMOM has potentials to couple with computational fluid dynamics to solve complicated particulate problems. In order to apply the moment model to the entire size regime, the Harmonic solution is utilized [17].

The present study is focused on complicated binary H_2SO_4–H_2O system, which requires at least two components interacting to form particles, but needs low saturation ratio [18,19]. Up to now, the investigation on binary nucleation mechanism of sulfuric acid–water (H_2SO_4–H_2O) system has been excessively done and two different versions of the classic theory available for this issue has been proposed in the literatures [20,21]. However, both these two theories require large quantities of computing time as they predict the formation of newly particles by nucleation. In order to save consumed time, it is necessary to use parametrized model to predict the process of nanoparticle formation. In this field, Kulmala et al. [22] first performed parameterizations for the binary nucleation rate as a function of temperature, relative humidity and acidity using thermodynamically consistent theory. They observed the computational time needed using parametrized model was reduced by a factor of 25 when compared to the classic theory. Later, Vehkamäki et al. developed Kulmala et al.'s work and further applied it in a wider condition [23,24]. Current studies showed binary models based on Vehkamäki et al. may overestimated the binary homogenous nucleation rate by around three orders of magnitude [2,25–28]. However, in some cases such as engineering exhausts, Vehkamäki and co-workers' model may be preferential and in fact it has been successfully used for predicting the evolution of particulates in diesel exhaust plumes [29–31]. There are also other studies on particle formation and evolution in exhaust plumes using different nucleation models [32,33]. Here, we introduce Vehkamäki and co-workers' model [23] into TEMOM model and emphasisly investigated the fundamentals of competition between nucleation, coagulation and condensation at the engineering atmosphere.

Our paper is set out as follows. In Section 2 we set out the derivation of TEMOM model involving binary homogeneous nucleation and growth of water–sulfuric acid nanoparticles, and in Section 3 this model is used to investigate competing processes as binary nucleation, condensation and coagulation are simultaneously considered. In Section 4, the investigation is focused on how background particles influence the nucleation process and the dynamics of critical nucleus.

2. Basic equations

In this work, we consider a number density function defined in terms of particle volume, v. The general particle dynamics equation for coagulation derived from Smoluchowski mean-field theory can be represented in the following continuous integro-differential form [5]:

$$\frac{\partial N(v,t)}{\partial t} = \frac{1}{2}\int_{v^*}^{v} \beta(v-v_1,v_1)N(v-v_1,t)N(v_1,t)\,dv_1 - N(v,t)\int_{v^*}^{\infty}\beta(v,v_1)N(v_1,t)\,dv_1 + \frac{\partial G(v,t)N(v,t)}{\partial v} + J(v^*)\delta(v-v^*) \quad (1)$$

The first two terms on the right-hand side (RHS) represent the increase and decrease of particles in $[v, v+dv]$ by Brownian coagulation; the third term of RHS accounts for the loss or gain of particles by condensation at rate $G(v,t)$; the last term of RHS represents the formation of new particles of critical volume v^* at rate J by binary homogeneous nucleation of water–sulfuric acid vapors. $N(v,t)$ is the distribution function of particle size based on the particle volume v at time t, and $\beta(v,v_1)$ is the frequency for coagulation between two particles with volumes v and v_1. In Eq. (1), the nucleation term, condensation term as well as coagulation term must be modeled using various approximation or hypothesis based on physical/chemical nature.

2.1. Binary homogeneous nucleation

For the classic theory of binary homogeneous nucleation, nucleation is the formation of supercritical stable clusters which can be identified by finding the maximum of the formation free energy with respect to number of water and acid molecules [1,28]. Many recent modern studies indicated that the sulfuric acid tends to gather water molecules around to form hydrates [1,23,24,28,34]. These hydrates are considered to stabilize the vapor and reduce the nucleation rates by a factor 10^3–10^8 [23]. Taking into account the effect of hydrates on nucleation rate and using the thermody-