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GROWTH OF ULTRAFINE PARTICLES BY BROWNIAN COAGULATION

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Abstract—Current atmospheric observations tend to support the view that continental tropospheric aerosols (particularly urban aerosols) show multimodal mass distributions in the size range of 0.01–100 μm. The origin of these aerosols is both natural and anthropogenic. Recently, trimodal sub-μm size distributions from combustion measurements at 0.008, 0.035 and 0.15 μm were also observed. Our interest in the present study is the secondary process of growth of sub-μm size aerosols by the coagulation process alone. Using the '*J*-space' (integer-space) distribution method of Salk (Suck) and Brock (1979, *J. Aerosol Sci.* **10**, 581–590), we report an accurate numerical simulation study of the evolution of ultrafine to fine particle size distributions. Comparision with the analytic solution of Scott (1968, *J. atmos. Sci.* **25**, 54–64) was made to test the accuracy of our *J*-space or integer-space distribution method. Our multimodal sub-μm particle size distribution study encompassed the particle size range of 0.001–0.20 μm. Details of particle growth in each mode and interaction between different modes in the multimodal distribution were qualitatively analyzed.

1. INTRODUCTION

Continental tropospheric aerosols and particularly urban aerosols show multimodal mass distributions (Durham *et al.*, 1975; Husar and Whitby, 1973; Seinfeld, 1975). The origin of atmospheric aerosol is two-fold: primary and secondary. Mixing of primary sources can contribute multimodal size distributions. Particles generated from dissimilar secondary processes, i.e. the formation of clusters, nucleation, condensation and coagulation processes may also contribute multimodality in particle size distributions. From a molecular dynamics simulation, Zurek and Schieve (1978) demonstrated a possibility of forming bimodal ultrafine particle size distributions from the homogeneous formation of clusters alone (Brock, 1980). Based on the measurements of Barsic (1977), Whitby (1978) reported that three sub-μm modes could be created from a rich propane flame diluted with unfiltered air. The first two sub-μm size modes located at 0.008 and 0.035 μm were considered to result from the propane flame and the third mode near 0.15 μm was due to the surrounding pre-existing atmospheric aerosols. In general, the ultrafine particles of sub-μm size are generated by gas-to-particle conversion processes which involve homogeneous and heterogeneous nucleation [upon collision with molecules of the same species or with surrounding foreign particles (clusters and aerosols)] under highly inhomogeneous conditions such as in shock waves, nozzle exhausts, flames, etc. (Brock, 1980). The secondary aerosols initiated by the nucleation processes are subject to efficient growth by condensation and coagulation.

Earlier we (Salk(Suck) and Brock, 1979) examined the evolution of atmospheric aerosol particle size-distributions with the mass concentrations of 50–100 $\mu g\,m^{-3}$ and the particle size range of 0.05–10 μm by allowing long (2 h) coagulation simulation time. This study showed that near-constancy (or an asymptotic limit) in both multimodal size distributions and modal positions is achieved after a long time (~ 1 h) for an initial distribution which was considered in the paper. The subject of ultrafine particles is considered to be one of the most challenging and interesting in aerosol science (Brock, 1980). To the best of our knowledge, there exists no study on accurate numerical simulation of the evolution of multimodal particle size distributions which are limited only to the particles of sub-μm sizes. In the present study, only homogeneous coagulational growth by Brownian motion is considered. Fine particles in the size range of 0.1–1 μm are known to readily penetrate to the critical lower lung region (Davies *et al.* 1975). Keeping this in mind, we plan to pay special attention to the interaction of trimodally distributed particles of sub-μm size close to the measurements of Barsic (1977).

Small air borne particles in the form of molecules, ions, neutral clusters and ion clusters are subject to collisions that allow homogeneous and heterogeneous nucleation processes to take place. Understanding the formation of ultrafine aerosols by these processes requires microscopic knowledge of molecular interactions, energies of formation, sticking coefficients and the stability of clusters (Salk(Suck) *et al.*, 1986). In general, charged (ion) clusters are more stable than neutral clusters due to added attractive electrostatic and induction forces (Salk(Suck), 1981). Thus, quasi-stable hydrated ion clusters of relatively large size (e.g. larger than 10 watermolecule clusters) are likely to form at high humidities (Salk(Suck) *et al.*, 1981, 1982, 1983, 1986). At present the detailed kinetics of forming

the ultrafine particles, including such ion clusters, is not well understood. This is the subject which presents much difficulty in explaining the origin of ultrafine particles. For this reason we limit our study only to coagulational growth of ultrafine to fine particles by considering the Brownian-particle approximation, thus ignoring growth by nucleation and condensation.

Due to the involvement of integration over a wide range of particle sizes, it is of great importance to demonstrate numerical accuracy in solving the non-linear Smoluchowski rate equation. The previous test of our numerical method (Salk(Suck) and Brock, 1979) was indirect as it was based only on the criterion of conservation of total mass during the course of simulation time. Therefore, in the present study, we will present a direct comparison of our numerical results with the analytic solutions of the rate equation obtained by Scott (1968), who assumed simple forms for the coagulation constant.

2. BRIEF REVIEW OF INTEGER-SPACE SMOLUCHOWSKI EQUATION

The following is a brief review based on our earlier study (Salk(Suck) and Brock, 1979). The 'equation of motion' for Brownian-coagulational growth, or the net rate of creating particles of mass m, is written

$$\begin{aligned} \mathrm{d}f(m,t)/\mathrm{d}t = (1/2)\int_0^m K(m^{1/3}-m'^{1/3}, m'^{1/3}) \\ \times f(m-m',t)f(m',t)\,\mathrm{d}m' \\ -f(m,t)\int_0^\infty K(m^{1/3}, m'^{1/3}) \\ \times f(m',t)\,\mathrm{d}m', \end{aligned} \tag{1}$$

where $f(m,t)\mathrm{d}m$ is the number concentration of particles at time t in the range of m to $m+\mathrm{d}m$. In order to cover a wide range of particle size for the numerical solution of the equation above, we write

$$m(J) = m(J_0)\exp[\alpha(J-J_0)], \tag{2}$$

and

$$\Psi(J) = \alpha m(J) f[m(J)], \tag{3}$$

where J is the integer corresponding to J-th particle mass, $m(J)$; J_0, the lowest limit of J, and α, the adjustable parameter which determines the step size increment of particle mass.

The substitutions of (2) and (3) into (1) above transforms the original 'direct space' or 'mass-space' Smoluchowski equation into the 'J-space' or 'integer-space' Smoluchowski equation below

$$\begin{aligned} \mathrm{d}\Psi(J,t)/\mathrm{d}t = \int_{J_0}^{J_h} \kappa'(\tilde{J},J')\Psi(\tilde{J},t)\Psi(J',t)\,\mathrm{d}J' \\ -\Psi(J,t)\int_{J_0}^{\infty}\kappa(J,J')\Psi(J',t)\,\mathrm{d}J', \end{aligned} \tag{4}$$

where J_{max} is the upper limit of J. Here the 'integer space' kernels κ and κ' are defined by

$$\kappa'(\tilde{J},J') = \{m(J)/m(\tilde{J})\}\kappa(J,J'), \tag{5}$$

with

$$\kappa(J,J') = K(m^{1/3}-m'^{1/3}, m'^{1/3}). \tag{6}$$

The non integral value $\tilde{J}$ is

$$\tilde{J} = J + (1/\alpha)\ln\{1-\exp[-\alpha(J-J')]\}. \tag{7}$$

The integer J_h which corresponds to mass, $m/2$ is

$$J_h = J - (\ln 2/\alpha), \tag{8}$$

with $J \geqslant 2$, and the parameter α is obtained from

$$\alpha = \ln 2/n, \tag{9}$$

with $n \geqslant 1$.

3. COMPARISON BETWEEN THE ANALYTIC SOLUTION OF SCOTT AND OUR INTEGER-SPACE NUMERICAL METHOD

For the sake of numerical comparison of Scott's analytic solution with our integer-space (J-space) numerical method, we take a constant value of the coagulation coefficient $K = C$ and the initial distribution of

$$f(v,0) = (N_0/v_0)\mathrm{e}^{-x}, \tag{10}$$

with

$$x = v/v_0, \tag{11}$$

as was selected by Scott (1968). Here v is the particle volume; N_0, the initial number of particles; and v_0, the inital mean volume.

The analytic solution at time t corresponding to the initial distribution (10) above is

$$f(v,t) = 4(N_0/v_0)\mathrm{e}^{-2x/(T+2)}/(T+2)^2, \tag{12}$$

where

$$T = CN_0t. \tag{13}$$

The relationship between mass and volume for spherical particles is

$$m = v\rho = (4/3)\pi r^3\rho. \tag{14}$$

We solve the integer-space Smoluchowski equation (4) numerically as follows; the numerical solution of the integer space integration was obtained by the Adams–Moulton 4–5 method with Gill starter. Necessary interpolation for $\Psi(\tilde{J})$ in (4) was made by the method of cubic spline interpolation. The numerical integration for the integrals in (4) was made using Gauss–Legendre quadrature method.

Figure 1 shows a comparison between the Scott's analytic (exact) solution (solid curves), namely Equation (12) and our numerical results (dashed curves) over a wide range of particle size, from 0.001 to 100 $\mu\mathrm{m}^3$, at time $t = 0$, 1200, 2400, 3600 s. The constant value chosen for the coagulation coefficient is $2.0 \times 10^{-9}\ \mathrm{cm}^3\,\mathrm{s}^{-1}$. The initial number of particles N_0 is $10^6\ \mathrm{cm}^{-3}$, and the initial mean volume v_0, $5 \times 10^{-13}\ \mathrm{cm}^3$. Agreement between the exact and nu-

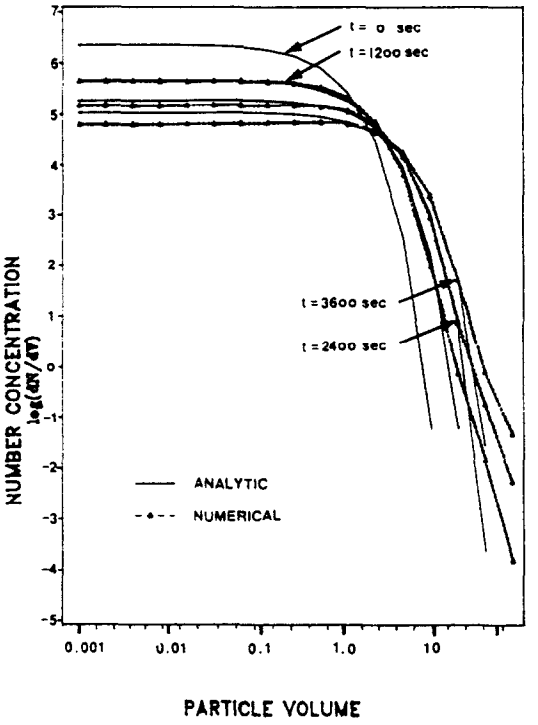

Fig. 1. Comparison between exact and numerical results. The evolution of $[dN/d(\ln V)]$ number concentration vs particle volume at $t = 0, 1200, 2400$ and 3600 s. Δ represents numerical and solid line, exact values.

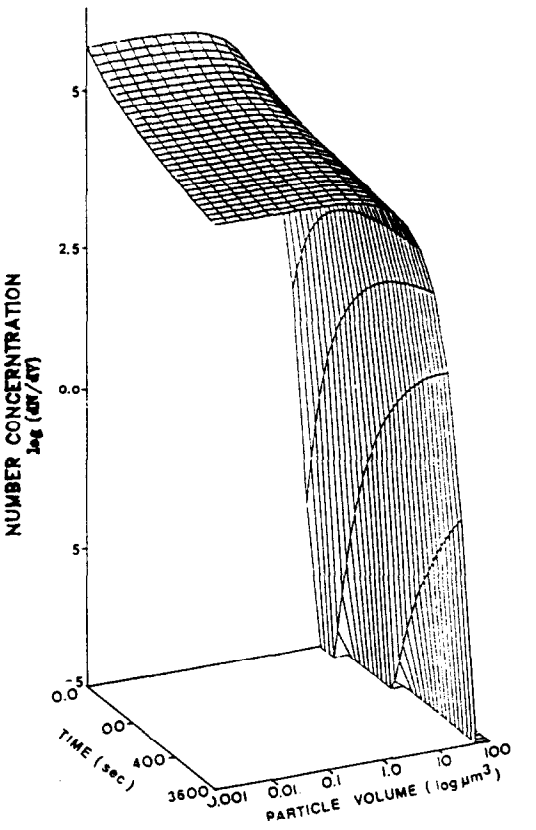

Fig. 2. The evolution of $[dN/d(\ln V)]$ number concentration as a function of volume and time.

merical solutions is remarkably good even after the long time simulation of $t = 3600$ s. The percent error in the size range of 0.001–1.0 μm^3 at $t = 3600$ s was found to be less than 4.4%. Some disagreement found near the upper limit of the particle size is insignificant as the number concentrations of particles close to this limit were found to be negligibly small. Figure 2 is a three-dimensional plot of the same particle size distribution as a function of volume v and time t in order to show a comprehensive picture of the evolution of the particle size distribution.

Recently assuming a constant value of the coagulation coefficient, Mulholland and Baum (1980) studied the effect of particle coagulation on an aerosol with a truncated Junge initial size distribution for arbitrary particle size and time by obtaining the exact analytical solution to the Smoluchowski equation. Their solution exhibited a cross-over from the Junge form to an asymptotic exponential form and persistence to retain a similar structure at later times. However, the use of a constant value for the coagulation coefficient for a wide range of particle size may not accurately represent a realistic picture of the evolution of particle size distribution. In the next section we choose the widely used (accepted) Fuchs' interpolation formula (Fuchs, 1964; Wagner and Kerker, 1980) for the coagulation coefficient in the transition regime in order to numerically simulate the coagulational growth of multimodally distributed fine particles in the size range of 0.001–0.2 μm. The procedure we follow could be used to check the distribution evolution predicted by Mulholland and Baum (1980) but we have not done this to date.

4. EVOLUTION OF TRI-MODAL FINE PARTICLE SIZE DISTRIBUTIONS: NUMERICAL SIMULATION

The measurements of Barsic (1977) showed that three different modes of fine particle size distributions at 0.008, 0.035 and 0.15 μm could be generated from propane–air combustion in a controlled humidity environment as mentioned earlier. This study revealed that the number concentration of the generated aerosols (containing sulphur, hydrocarbons and traces of many metals) from a propane diffusion flame strongly depends on the relative humidity of the air (Barsic, 1977; Whitby, 1978).

In the present numerical simulation of particle growth dynamics, the initial particle size distributions were taken to be log-normal for each mode, with the selection of mass concentrations close to often observed values (20–200 $\mu g\,m^{-3}$). Parameter values necessary for the use of the Fuch's coagulation coefficient are chosen to be $\rho = 1.0\,g\,cm^{-2}$ for the density of the hydrated aerosols, $\eta = 1.8 \times 10^{4}\,g\,cm^{-1}\,s^{-1}$ for the viscosity of the gas, and $l = 6.5 \times 10^{-4}$ cm for the mean free path. Other details are given in the paper of

Salk(Suck) and Brock (1979). The initial trimodal mass density distribution is shown by circles in Fig. 3. The initial aerosol mass distribution that we chose here has reasonably well separated modal positions of 0.006, 0.03 and 0.15 μm, and the geometric standard deviation of 2.2. The increase of concentration in the second Aitken particle mode of the mass density distribution ($dM/d\ln R$ with R as the particle diameter) was predicted to be extremely fast, that is, the first few seconds as shown in Fig. 3. This period of time is somewhat comparable to the human breathing period and thus coagulation may be an important factor in determining the fate of ultrafine particles inhaled into the lungs. See the curves designated by □ (2 s) and Δ (4 s). The particle size shift of the second mode is seen to be relatively slow compared to that of the first mode. The third accumulation mode showed an appreciable increase in the magnitude of the concentration, but not a noticeable change in particle size shift. The appreciable increase in the concentration of the second and third mode means that ultrafine particles (say, 0.006 μm) in the multimodal distributions grow extremely fast to a noticeable size of 0.01 μm, within a few seconds, by interaction with the larger particles. Undoubtly this growth will be further enhanced by condensation of water vapor molecules on the surface of the ultrafine particles under a high humidity condition. Thus our numerical values shown in Fig. 3 are to be interpreted as lower limits in the growth of ultrafine particles for the initial distributions considered here, as only coagulational growth was taken into consideration.

5. CONCLUSION

Our objectives for the present paper were twofold; a stringent numerical test of an accurate simulation procedure and a realistic simulation of the evolution of a sub-μm particle size distribution by coagulational growth alone. We have demonstrated that a highly accurate numerical solution of the integer-space (or J-space) Smoluchowski equation is now feasible; we found good agreement with the exact (analytic) solution of Scott (1968). Secondly, using a more realistic coagulation coefficient (Fuchs' interpolation formula) compared to the constant value used for the coagulation coefficient in the previous sections, we have studied the evolution of a multimodal mass density distribution of sub-μm size particles and found that rapid (that is, within a few seconds) growth of the ultrafine particles indeed occurs as a result of coagulational growth alone and that under a high humidity condition, this growth represents only a lower limit due to the omission of nucleational and condensational growth. In view of the current lack of a realistic simulation study for growth dynamics (kinetics) of utralfine particles, we hope that our present study gives deeper insight into the growth rate of ultrafine particles for the case of multimodal sub-μm particle size distributions.

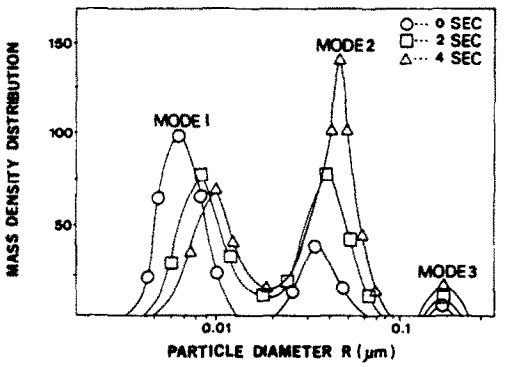

Fig. 3. The evolution of multimodal fine particle mass density distribution [$dM/d(\ln R)$] as a function of particle diameter R. o represents $t = 0$ s; □, $t = 2$ s and Δ, $t = 4$ s.

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REFERENCES

Barsic N. A. (1977) Size distributions and concentrations of fine particles produced by propane air combustion in a controlled humidity environment. Ph.D. Thesis, University of Minnesota.

Brock J. R. (1980) The kinetics of ultrafine particles. In *Topics in Current Physics, V16, Aerosol Microphysics I* (edited by Marlow W. H.), pp. 15–59. Springer, New York.

Davies C. N., Lever M. J. and Rothenberg S. J. (1977) Experimental studies of the deposition of particles in the human lung. In *Inhaled Particle IV*, Part 1 (edited by Walton W. H.), pp. 151–162. Pergamon Press, Oxford.

Durham J. L., Wilson W. E., Ellstad T. G., Willeke K. and Whitby K. T. (1975) Comparison of volume and mass distributions for Denver aerosols. *Atmospheric Environment* **9**, 717–722.

Fuchs N. A. (1964) *Mechanics of Aerosols*, p. 294. Pergamon Press, Oxford.

Husar R. B. and Whitby K. T. (1973) Growth mechanisms and size spectra of photochemical aerosols. *Envir. Sci. Technol.* **7**, 241–248.

Mulholland G. W. and Baum H. R. (1980) Effect of initial size distribution, *J. Aerosol Sci.* **10**, 581–590.

Salk(Suck) S. H. (1981) Change of free energy in heteromolecular nucleation: electrostatic energy contribution. *J. chem. Phys.* **75**, 5090–5096.

Salk(Suck) S. H. and Brock J. R. (1979) Evolution of atmospheric aerosol particle size distribution. *J. Aerosol Sci.* **10**, 581–590.

Salk(Suck) S. H., Chen T. S., Emmons R. W., Hagen D. E. and Kassner J. L., Jr. (1982) Role of ions in heteromolecular nucleation: free energy change of hydrated ion clusters. In *Heterogeneous Atmospheric Chemistry Geophysical Monograph Series* Vol. 26, pp. 28–31.

Salk(Suck) S. H., Hagen D. E. and Kassner, J. L., Jr. (1983) Study of pre-nucleation ion clusters. *J. chem. Phys.* **79**, 4502–4506.

Salk(Suck) S. H., Kassner, J. L., Jr. Thurman R. E., Yue P. C. and Anderson R. A. (1981) Theoretical prediction of ion clusters relevant to the atmosphere. *J. atmos. Sci.* **38**, 1272–1277.

Salk(Suck) S. H., Lutrus C. K. and Hagen D. E. (1986) Stability of water clusters in assoication with pre-existing aerosols under high humidity conditions. *Atmospheric Environment* (to be published).

Salk(Suck) S. H., Middleton P. B. and Brock J. R. (1977) On the mutimodality of density functions of pollutant aerosols. *Atmospheric Environment* **11**, 251–255.

Scott W. T. (1968) Analytic studies of cloud droplet coalescence. *J. atmos. Sci.* **25**, 54–64.

Seinfeld J. H. (1975) *Air Pollution*, pp. 89–82. McGraw-Hill, New York.

Wagner P. E. and Kerker M. (1980) Coagulation of aerosols by Brownian motion. *J. Colloid. Int. Sci.* **73**, 244–247.

Whitby K. T. (1978) Size distribution and physical properties of combustion aerosols. In *Conference on Carbonaceous Particles in the Atmosphere*, p. 31. Berkeley, California.

Zurek W. and Schieve W. (1978) Molecular dynamics study of clustering—I. *J. chem. Phys.* **68**, 840–846.