

MASTERAEROSOL SIMULATION INCLUDING CHEMICAL
AND NUCLEAR REACTIONS*

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ABSTRACT

The numerical simulation of aerosol transport, including the effects of chemical and nuclear reactions, presents a challenging dynamic accounting problem.

Particles of different sizes agglomerate and settle out due to various mechanisms, such as diffusion, diffusiophoresis, thermophoresis, gravitational settling, turbulent acceleration, and centrifugal acceleration. Particles also change size, due to the condensation and evaporation of materials on the particle.

Heterogeneous chemical reactions occur at the interface between a particle and the suspending medium, or a surface and the gas in the aerosol. Homogeneous chemical reactions occur within the aerosol suspending medium, within a particle, and on a surface. These reactions may include a phase change.

Nuclear reactions occur in all locations. These spontaneous transmutations from one elemental form to another occur at greatly varying rates and may result in phase or chemical changes which complicate the accounting process.

This paper presents an approach for inclusion of these effects on the transport of aerosols. The accounting system is very complex and results in a large set of stiff ordinary differential equations (ODEs). The techniques for numerical solution of these ODEs require special attention to achieve their solution in an efficient and affordable manner.

INTRODUCTION

An aerosol is a suspension of particles in a gas. The particles may be composed of solids and liquids and may consist of several different species. Particles may range in size from 0.001 μm to over 100 μm in diameter. The carrier gas can also consist of several different species.

Many complex physical and chemical processes may be occurring simultaneously within the aerosol, affecting both particle size distribution and overall composition. The processes considered here include both discrete and continuous phenomena. These are particle agglomeration, particle deposition, condensation and evaporation, heterogeneous chemical reactions, homogeneous chemical reactions, homogeneous nucleation, and nuclear reactions.

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A one-volume model is presented which describes the evolution of this physical system as a system of time-dependent ODEs where the basic quantities of interest are the mass of each species at each location. In the next section, a discrete model for the particle size distribution is described. Then, in subsequent sections, mathematical modeling techniques for each process are briefly discussed. Finally, we show how the aerosol simulation can be performed in a multivolume region. The one-volume model is then used as a common building block for several different multivolume simulations. A single volume of aerosol is assumed to be very large with respect to the size of the aerosol particles. Within this volume, it is assumed that particles of each size are of uniform composition and that they are distributed uniformly throughout the volume. It is also assumed that the aerosol gas is evenly mixed and uniformly distributed.

The present formulation is motivated by an application in which a volume of aerosol is a slice of a stream tube that is bounded by a duct. It is assumed that a velocity profile or flow regime (either laminar or turbulent) exists throughout the plane normal to the axial flow direction. This view is not limiting in that coefficients which depend on the surface area of the wall can be easily altered to reflect different geometries.

It is further assumed that the principle of superposition is applicable. That is, the effects of the various mechanisms are additive. Under this assumption, we write the contribution to the differential equation of y at location loc due to process $proc$ as

$$\left. \frac{dy_{loc}}{dt} \right|_{proc}$$

so that

$$\frac{dy_{loc}}{dt} = \sum_{proc} \left. \frac{dy_{loc}}{dt} \right|_{proc} \quad (1)$$

PARTICLE DISTRIBUTION MODEL

In the aerosol simulation, we treat the continuous particle size distribution as a discrete particle distribution using a bar chart approximation. Each bar is then considered to be a particle bin containing the number of particles which are in some average size for that bin.

Suppose there are NUMB bins and NUMC noncondensable gases. And assume there are NUMV condensable substances, which may be in the vapor state, condensed on particles, or condensed on the surface of a wall. Then there are a total of $(\text{NUMB} + 2) \text{NUMV} + \text{NUMC}$ time-dependent mass ODEs in a single volume. For a

simulation with 20 bins, 2 condensable substances and 1 noncondensable gas, there are 133 DEEs.

The concentrations or number of particles of each size determine, in part, the rates for the mass transport by the processes of agglomeration, deposition, and condensation. This requires that the correct particle number evolution be maintained, as well as conservation of mass.

In subsequent sections, the rates for mass transport are developed using n_j , the number of particles in bin j per unit aerosol volume for

$j=1,2,\dots,NUMB$. The mass is tracked as mad_{loc}^i , the mass of type i at location loc per unit volume of aerosol, for $loc=j=1,\dots,NUMB$. When $loc=a$, the location is the aerosol carrier gas, and when $loc=w$, the location is the wall. In general, the n_j 's are not carried directly, since they are completely determined by the volume of a typical particle in bin j and the densities and masses of the constituents of the particle.

If the particle bin sizes are all fixed, the principle of particle number evolution fails. To properly conserve mass and particle number evolution, it is necessary to model the largest, or overspill, bin as a control volume containing particles of various sizes. In this case, the particle number concentration equation must be carried explicitly. This model is constructed to allow aerosol process to continue to occur within this bin. Details with an error analysis of the floating overspill bin are described in Reference 1.

AGGLOMERATION

Particles in an aerosol agglomerate when they come into contact with each other. Agglomeration mechanisms include diffusion, settling, turbulence, and acceleration. These mechanisms are controlled by the flow regime.

Variation in the particle number concentration causes particle agglomeration by diffusion. This mechanism is modeled using Fick's first law of diffusion.

Particles with different velocities have the potential to collide. In viscous flow, where the viscous forces greatly exceed inertial forces, the drag force on a particle is proportional to the particle diameter. Therefore, forces applied to particles of different sizes can result in different particle velocities and agglomeration.

For gravitational settling, the terminal velocity for an aerosol particle is obtained from the appropriate force balance equation. The resulting settling velocity is proportional to the particle diameter. Particle agglomeration by turbulent motion is caused by the velocity gradient which exists in a turbulent eddy. Two particles in such an eddy may have different velocities, due to the difference in the position of their centers. A second turbulent agglomeration mechanism is due to local acceleration in a turbulent eddy. As the aerosol is accelerated, a drag force is created by the difference between the velocities of the accelerated flow and the particle. Two particles of different sizes will momentarily have different velocities. Other forces acting on the aerosol include general accelerations, such as centrifugal acceleration of an aerosol in a duct going around a bend.

There are contributions to the particle number equations and the mass equations which include the effects of all particle agglomeration mechanisms. Particles are removed from bin l and bin k according to

$$\frac{dn}{dt} \Big|_{\text{agglomeration of } l \text{ and } k} = -K_{lk}^a n_l n_k \quad (2)$$

where j is l or k and where K_{lk}^a is the appropriate agglomeration coefficient. New particles are formed

at the rate $K_{lk}^a n_l n_k$. Note that the above rate is proportional to n^2 ; for other contributions, such as deposition or condensation, the rate will be proportional only to n .

The newly formed particle does not necessarily coincide with one of the fixed size particles in the discrete distribution. Particle number evolution for this process reduces the number of particles in the system; two particles agglomerate into one. This principle and conservation of mass are applied to the resultant particle, as discussed in Reference 1. The result of the l, k agglomeration is either redistributed between two bins which bracket the size of the resultant particle or put into the overspill bin.

Each l, k agglomeration may contribute only to one low bin/high bin redistribution or to the overspill bin. On the other hand, an arbitrary bin j may be the low bin or high bin for several different l, k agglomerations; and the overspill bin may similarly receive particles and mass from several different l, k agglomerations. In general then,

$$\frac{dn_j}{dt} \Big|_{\text{agglomeration}} = - \sum_{l=1}^{NUMB} K_{lj}^a n_l n_j - K_{jj}^a n_j n_j + \sum_{sym=low}^{high} \sum_{l=1}^{NUMB} \sum_{k=l}^{NUMB} f_{lk}^{sym} K_{lk}^a n_l n_k \quad (3)$$

where sym may also equal os (overspill) when j is os . The fractions f_{lk}^{low} , f_{lk}^{high} and f_{lk}^{os} are defined to preserve particle number evolution and to conserve mass in the redistribution process. Note that most of the terms in the multiple summations are zero, so only the nonzero terms are calculated. This is done by developing an analytic expression for f in terms of the sizes of the agglomerating particles and the sizes of the different bins.

DEPOSITION

Particles in the aerosol can be deposited on a solid or liquid surface by several different mechanisms. These mechanisms include diffusion, thermophoresis, gravitational settling, turbulent acceleration, and centrifugal acceleration. Diffusiophoresis and Stefan flow are mechanisms related to condensation and evaporation and are discussed later.

Particles which contact a surface, such as the wall of a duct, stick to the surface. This keeps the number concentration of particles low near the surface and creates a number concentration gradient, so particles diffuse toward the surface. If the temperature of the surface is different from that of the aerosol, a thermal gradient exists near the surface. If the

surface is cooler than the aerosol, this gradient drives particles toward the wall in the process called thermophoresis. An effective force is exerted on the particles, since the gas on the hot side has greater molecular movement than the gas on the cold side. This results in a net momentum transfer to the particle in the direction of the surface. Other forces which add to deposit particles are gravity, acceleration in turbulent eddies, and centrifugal acceleration due to a change in flow direction.

Each of these mechanisms removes particles from the aerosol according to the contribution

$$\left. \frac{dn_j}{dt} \right|_{\text{deposition}} = -K_j^d n_j \quad (4)$$

where K_j^d is the appropriate deposition coefficient.

CONDENSATION AND EVAPORATION

Under suitable conditions, condensation and/or evaporation of condensable substances may occur. Particles change size continuously due to these processes. The principles of particle number evolution and conservation of mass are applied for these processes within the discrete particle distribution model. In particular, there is no change in the number of particles, although the size of a particle increases or decreases.

It is assumed that each condensable vapor behaves as an ideal gas and has a saturation vapor pressure, p_i^{sat} . For condensation or evaporation on surfaces which are relatively flat with respect to the gas molecule size, the saturation vapor pressure is dependent only on temperature. Condensation and evaporation are controlled by the difference between the partial pressure, p_i^{par} , and the saturation pressure. If $p_i^{\text{par}} > p_i^{\text{sat}}$, condensation of mass type i will occur; and if $p_i^{\text{par}} < p_i^{\text{sat}}$, evaporation will occur, provided that condensate is available to evaporate. The rate at which condensable gas molecules migrate to and from the condensing surface is controlled by diffusion, assuming the surface is large compared to the molecular mean free path. Fick's first law is applied to determine this rate for condensation and evaporation.

The change of mass of a condensable in the vapor is also proportional to the particle diameter and the potential $p_i^{\text{par}} - p_i^{\text{sat}}$. The rate at which the diameter of a particle changes can be determined, if the density of the condensate and the volume of the spherical shell are known. This rate equation can be integrated to determine the time it takes for one particle to change to the next particle size.

The rate at which particles are removed from bin j by condensation of vapor i upon particles in bin j is a contribution of the form

$$\left. \frac{dn_j}{dt} \right|_{\text{condensation of mass type } i} = -K_j^{c,i} n_j \quad (5)$$

where $K_j^{c,i}$ is the bin condensation coefficient.

Particles are added to bin $j+1$ at the same rate. Similarly, for evaporation, particles are removed

from bin j and added to bin $j-1$ at the rate $K_j^{e,i} n_j$, where $K_j^{e,i}$ is the bin evaporation coefficient.

For condensation, vapor is removed from the gas mixture and added to the mass inventory in bin $j+1$. For evaporation, condensate is removed from the inventory or mass in bin j and returned to the aerosol. When j is the largest bin, particles are not removed by condensation. Mass inventory is changed by adding the condensate. To preserve the particle number evolution, no particles can be added; hence, this largest bin cannot be a fixed size particle bin but is the floating overspill bin in which the average size particle changes. Many details of the condensation/evaporation model are given in References 1 and 2.

Physically, the mass of type i at each location may have only nonnegative values. This constrains the variables used in the system of ODEs. Numerically, the time step can be restricted so that each variable remains positive; however, this technique can result in unnecessarily small time steps. For evaporation of a condensate, there is a discontinuity in the first derivative at the point of dryout. When a variable becomes negative in the solution of the system of ODEs, a root-finding method is used to locate the point in time at which it is zero. Then the problem is restarted at that time, using the interpolated values.

Condensation and evaporation may also occur at other surfaces, such as a wall. This creates a secondary hydrodynamic flow known as Stefan Flow. A secondary diffusion process of the carrier gas occurs to maintain constant total pressure near the wall. The partial pressure gradient of the condensing or evaporating material must be balanced by a partial pressure gradient of the other gases in the opposite direction. Stefan Flow provides the source of material by transporting gas toward the wall for condensation and away from the wall for evaporation. For condensation, Stefan Flow results in another particle deposition mechanism. In addition, these two diffusion effects may act to drive particles either to or from the surface in a process called diffusiphoresis. Particles will be driven toward the surface if the more massive molecules in a mixture are diffusing in that direction while less massive molecules are diffusing in the opposite direction. This also results in particle deposition.

HETEROGENEOUS CHEMICAL REACTIONS

Heterogeneous chemical reactions are reactions that occur at the interfaces between the vapor and either the surfaces of the particles or the surface of a wall. These reactions may include both a phase change and a change in the chemical form in which a particular element is present. The phase changes effectively result in particle size changes, as in condensation and evaporation. These reactions are controlled by diffusion and thermodynamic relationships which determine the rates at which these reactions proceed.

The rate at which reactions proceed toward the equilibrium point is described by the product of a mass transfer coefficient (or deposition velocity), the appropriate area of the surface at which the reaction is taking place, and a driving potential as a difference between the actual value and a mad_i^{cont} value. This latter value is a controlling value which determines the equilibrium point of the reaction. The

equilibrium value changes with time. In addition, some heterogeneous chemical reactions may be strongly biased toward one direction.

Mass is transferred to or from the aerosol according to

$$\frac{d}{dt} \text{mass}_a^k \Big|_{\text{heterogeneous reaction at loc}} = -K_{\text{loc}}^{TR,k} \quad (4)$$

where $K_{\text{loc}}^{TR,k}$ is the coefficient of the heterogeneous reaction for mass type k at location loc . More details of this model are given in Reference 3.

HOMOGENEOUS CHEMICAL REACTIONS

Homogeneous chemical reactions occur throughout the volume of the aerosol, within a particle, or within mass deposited on a wall. Although such reactions are controlled by various thermodynamic rate parameters, the rates of reaction are assumed to be very high because of the high potential for the various chemical constituents to be in close contact. The model is then based on the equilibrium state appropriate for the local thermodynamic conditions. As local thermodynamic conditions change, the equilibrium point also changes. The basic parameter used to determine this point is the thermodynamic convenience function (property) called Gibbs free energy.

With the Second Law of Thermodynamics, and Gibbs free energy, the equilibrium point for a reaction occurring in the presence of other reactions at a constant total pressure and a constant temperature can be determined. The classical formulation results in a large system of nonlinear algebraic equations which must be solved. To solve these equations for a realistic situation requires extensive storage and considerable computational time, making inclusion of a full homogeneous reaction model into an aerosol code impractical. However, the inclusion of such a model would give the equilibrium point for each constituent at each temperature and pressure during the aerosol transient.

When two states of the same constituent exist in equilibrium, the partial pressure of the vapor is the saturation value at the temperature and total pressure of the mixture. This observation suggests an alternative approach to model these reactions. A composite partial pressure relationship (as a function of temperature and pressure) can be used to represent the composite behavior of each element of interest. Then the condensation model previously discussed could be used as a mass transfer mechanism to keep the amount of mass at each location at the equilibrium point.

A simple composite saturation partial pressure relationship can be obtained by considering only the condensation stoichiometric relations of the elements in their dominant constituent form (if known). A more accurate relationship can be based on the results of the equilibrium calculations from chemical equilibrium systems programs. The approach taken in our aerosol simulation is to use the latter method, when such results are available. Otherwise, the simpler method is used.

HOMOGENEOUS NUCLEATION

Homogeneous nucleation is the formation of particles from a supersaturated vapor without the

assistance of condensation sites. Gas molecules may form a cluster; whether or not colliding molecules of the vapor stay together as a cluster depends on thermodynamic principles. If the cluster remains, it will provide a site upon which condensation can occur. After sufficient condensation has occurred on a cluster, the resulting aerosol particle will grow until it can be added to the smallest bin. From the simplest point of view, then, homogeneous nucleation may move saturated vapor to the smallest particle bin.

NUCLEAR REACTIONS

Nuclear reactions are spontaneous transmutations from one elemental form to another which may occur in any location and may also result in phase changes. Nuclear reactions are also called radioactive decay. Beta decay is the process of an isotope of one element transmuting to another element with the same mass number and is the only decay process considered here. This decay from one element to another can affect chemical reactions by the availability and state of the elements involved. The rate at which beta decay of an isotope occurs is a function of the number of nuclei of that isotope and is practically independent of all physical and chemical conditions.³

Consider a decay chain of the form $\dots \rightarrow E_{i-1}^m \rightarrow E_i^m \rightarrow E_{i+1}^m \rightarrow \dots$, where E_i is a generic element with atomic number i and m is the mass number of the chain. The differential equation describing the number of atoms of E_i^m is given by

$$\frac{d}{dt} (\#E_i^m) = -\lambda_{i,m} (\#E_i^m) + \lambda_{i-1,m} (\#E_{i-1}^m) + S (\#E_i^m) \quad (7)$$

where $\lambda_{i,m}$ is the decay rate coefficient for the decay of E_i^m to E_{i-1}^m and S is a source term.

The fission of a radioactive material, such as U^{235} , produces a large number of radioactive fragments, each with a different yield or probability. For fission of U^{235} , the yield as a function of atomic number is a nearly symmetrical bimodal distribution. The two peaks with yields $>1\%$ include the elements Se through Rh (atomic numbers 34 through 45) and Sn through Sm (atomic numbers 50 through 62.)

Each radioactive fragment will undergo beta decay until a stable isotope results. There is at most one such decay chain or sequence of beta decays for each mass number. An element may appear in several decay chains as different isotopes. For example, from the fission of U^{235} there are 10 fragments with yields greater than 1% which involve isotopes of Cs. Thus, 10 ODEs are required to track the isotopes of Cs.

For a particular problem, there may be only a few basic radioactive elements of interest. The model must include all decay chains for isotopes of all elements which occur in those decay chains involving isotopes of the elements of primary interest. Five of the volatile fission products of U^{235} are Sr, Ru, Te, I, and Cs. The decay chains with yields greater than 1% which contain these five elements include 20 other elements also. If there were 10 isotopes of each, then 250 ODEs would be required to track the five elements of interest.

This number of equations would be required at each location of interest in each volume.

The simulation proceeds in two steps to reduce the number of equations. First, the isotopes of each element are grouped as a composite; then, some of these elements are grouped as pseudo-elements. In this model, sufficient information is retained and processed as side calculations to produce estimates of the masses for each isotope of each element.

To develop the composite model of each element from the isotopes of interest, each chain of interest is altered slightly, if necessary, so that it is adequately represented by Equation (7). For any one chain, the molecular weight is the same for all elements in that chain and so

$$\frac{d}{dt} \text{mad}_{loc}^{i,m} = -\lambda_{i,m} \text{mad}_{loc}^{i,m} + \lambda_{i-1,m} \text{mad}_{loc}^{i-1,m} + S_{\text{mad}_{loc}^{i,m}} \quad (8)$$

The composite mass of the element is represented as the sum of mass of its isotopes. The equation for the composite element is Equation (8) without the identification of isotope m , where the λ 's are now composite decay rate coefficients which are time-dependent. By forming the composite model for all isotopes of each element, the number of equations for each location for the fission of U^{235} is reduced to 25. Therefore, modeling the aerosol particles with 20 bins still requires over 500 ODEs for each volume.

The second composite submodel groups several elements as pseudo-elements. For each sequence of elements, those not of primary interest are grouped as a composite pseudo-element (pE). After grouping isotopes, there are two major "chains" for the elements with yields over 1%.

Se → Br → Kr → Rb → Sr → Y → Zr → Nb → Mo → Tc
→ Ru → Rh,

and

Sb → Te → I → Xe → Cs → Ba → La → Ce → Pr → Nd
→ Pm → Sm.

These are rewritten as

pE₁ → Sr → pE₂ → Ru → pE₃,

and

pE₄ → Te → I → pE₅ → Cs → pE₆,

where pE_{*i*} is a pseudo-element from grouping several elements. For example, pE₁ is Se through Rb.

This effectively reduces the 25 ODEs to 11 ODEs, provided the grouping of elements as pseudo-elements approximates the information reasonably well. The full details of this nuclear reaction simulation are discussed in Reference 2.

SIMULATION ALGORITHMS

The aerosol transport model thus far developed applies only to one specific volume. Based on this model, a multivolume algorithm for the transport of an aerosol can be constructed. At least three stream-tube-type alternatives are possible in concept which include mass interchange between volumes.

The first alternative is to couple adjacent volumes via the appropriate advection terms. This is undoubtedly the most accurate way to go, but the number of ODEs to be solved simultaneously is large. For example, for 11 materials, 20 bins, and 10 regions, over 2400 coupled ODEs require solution. Nevertheless, this alternative must be developed as a quality control mechanism to be used to assess the acceptability of other alternatives.

The second alternative is to be less precise with respect to the advection terms. For example, for a system modeled with several consecutive volumes, the simulation would proceed by assuming flow from volume 1 to 2, then from 2 to 3, etc. The mad_{loc}^i values in volume 1 would be advanced a set increment in time.

This advancement would require the history of mad_{loc}^i into the first volume during the time period. Calculations would include outflow of mad_{loc}^i to the second region during this time period. These outflow data would then be used as inflow data to perform the same task for the second volume, etc., until the calculations for all volumes are completed through the current time period. The time would then be advanced, and the process repeated. One major problem with this approach is that it may be difficult to save every bit of outflow data for later use as inflow data. In addition, adjacent volumes would likely use different internal time steps to solve the resulting stiff set of ODEs, which would then require interpolation within the input data.

The real advantage of the second alternative is that many fewer ODEs have to be solved at any one time. For the example cited, about 242 ODEs would have to be solved, instead of 2400.

The third alternative is to switch from the Eulerian reference frame of the other alternatives to a Lagrangian frame. As the aerosol volume moves downstream, the local wall inventory is advected out and the upstream wall inventory is advected in. As the aerosol volume goes around a corner, the elbow deposition mode is turned on; when the volume has passed the corner, the elbow deposition mode is turned off, etc. This third alternative has several applications. An important application is aerosol transport at relatively high velocities.

SOLUTION OF EQUATIONS

The application of the simulation model discussed requires the numerical solution of a large number of coupled ODEs, and the resulting equations are very stiff. These ODEs are solved by using an implementation of the stiff methods of Gear⁴ for systems of differential equations with a sparse Jacobian.

SUMMARY

The simulation of a transporting aerosol, including chemical and nuclear reactions, is most difficult. Within this paper we have given an overview of one possible way to approach this simulation with special emphasis on: (a) handling the difficulties that occur in simulating continuous and discrete processes in a particle bin framework; (b) approximating complex chemical reactions, using results of detailed chemical equilibrium codes and a condensation type of mass mover; (c) approximating as

many as 150 nuclear reaction ODEs per location with only about 10 ODEs. (d) handling several different ODE solution problems; and (e) developing the overall simulator for one volume which can be used by several different drivers.

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