JOURNAL OF COMPUTATIONAL PHYSICS 112, 364–369 (1994)

Coagulation Algorithms with Size Binning

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Received February 9, 1993

The Smoluchowski equation describes the time evolution of an aerosol particle size distribution due to aggregation or coagulation. Any algorithm for computerized solution of this equation requires a scheme for describing the continuum of aerosol particle sizes as a discrete set. One standard from of the Smoluchowski equation accomplishes this by restricting the particle sizes to integer multiples of a basic unit particle size (the monomer size). This can be inefficient when particle concentrations over a large range of particle sizes must be calculated. Two algorithms employing a geometric size binning convention are examined: the first assumes that the aerosol particle concentration as a function of size can be considered constant within each size bin; the second approximates the concentration as a linear function of particle size within each size bin. The output of each algorithm is compared to an analytical solution in a special case of the Smoluchowski equation for which an exact solution is known. The range of parameters more appropriate for each algorithm is examined.

THE SMOLUCHOWSKI EQUATION

The standard equation describing aggregation or coagulation in aerosols was first developed by Smoluchowski [1],

$$\frac{\partial n_k}{\partial t} = \frac{1}{2}\sum_{j=1}^{k-1} K_{j,k-j} n_j n_{k-j} - \sum_{j=1}^{\infty} K_{j,k} n_j n_k, \qquad (1)$$

where n_k is the concentration of particles of size k, i.e., particles whose size is an integer k times the size (mass) of the smallest particle, the monomer. This equation, given here in discrete form, assumes that mass is transported through the particle size spectrum by binary interactions between particles. The first sum accounts for the increase in the concentration of k-sized particles due to aggregation of smaller particles, and the second sum accounts for the decrease in the concentration of k-sized particles due to aggregation of k-sized particles with any other particle. Each term in both sums is a product of an interaction rate $K_{j,k}$ (the coagulation kernel) and the total number of interactions per unit volume possible among j- and k-sized particles. The factor of one half in the first sum avoids double counting.

SIZE BINNING

To reduce memory requirements and to increase efficiency, computer models of aggregation employ algorithms in which particles of similar size are grouped into bins. One standard formalism is that employed by Toon *et al.* [2] and Turco *et al.* [3] in which the range of particle sizes encompassed by successive bins increases geometrically, i.e., a characteristic size of particles in bin α is given by

$$S_\alpha = qS_{\alpha-1}, \qquad (2)$$

where q is a constant. (Particle size here is measured in units of monomers, a particle of size α is an aggregate of α monomers.) A similar relationship applies to the high and low size boundaries for bin α, H_α and L_α. A number of con-

0021-9991/94 $6.00

ventions exist for defining H, L, and S. For simplicity, this paper employs the following definitions:

$$L_\alpha = q^\alpha$$
$$H_\alpha = q^{\alpha+1} \tag{3}$$
$$S_\alpha = \frac{H_\alpha + L_\alpha}{2} = \left(\frac{q+1}{2}\right) q^\alpha.$$

With the size of particles in a bin restricted to being greater than the low size boundary and less than or equal to the high size boundary, monomers (particles of unit size) belong in bin number -1. Since $H_{-1} = 1$ and monomers are the smallest particles allowed, bin -1 contains only monomers.

For coagulation models employing size bin structures with $q \geq 2$, the standard Smoluchowski equation cannot be applied in a straightforward fashion. This becomes obvious when one considers the following situation. For interactions between particles in bins α and β (with $\alpha < \beta$), the possible sizes of the resulting particles range from $q^\alpha + q^\beta$ to $q^{\alpha+1} + q^{\beta+1}$. For $q \geq 2$, the lower end of this size range is still within bin β, while the upper end of the range is within size bin $\beta + 1$. The difficulty is in deciding what fraction of the products of these interactions will fall into each of these two size bins.

Defining $X^\gamma_{\alpha,\beta}$ to be the number of possible interactions between particles in bins α and β that would form particles in the bin γ size range, the Smoluchowski equation is replaced by the equation

$$\frac{\partial C_\beta}{\partial t} = \sum_{\alpha=-1}^{\beta-1} K_{\alpha,\beta-1} X^\beta_{\alpha,\beta-1} - \sum_{\alpha=-1}^{\beta-1} K_{\alpha,\beta} X^{\beta+1}_{\alpha,\beta} - 2K_{\beta,\beta} X^{\beta+1}_{\beta,\beta}$$
$$- K_{\beta,\beta} X^\beta_{\beta,\beta} - \sum_{\gamma=\beta+1}^{\infty} K_{\beta,\gamma} (X^\gamma_{\beta,\gamma} + X^{\gamma+1}_{\beta,\gamma}), \tag{4}$$

where C_β is the concentration of particles within size bin β. The first term in this equation gives the increase in C_β due to interactions of bin $\beta - 1$ particles with particles from bin $\beta - 1$ and all smaller size bins. The second term gives the loss of particles from bin β to bin $\beta + 1$ in interactions between bin β particles and particles in all smaller bins. The third term gives the loss of particles from bin β to bin $\beta + 1$ due to interactions between two particles in bin β. The factor of two in the third term accounts for both bin β particles being removed in each interaction. The fourth term accounts for the loss of one particle per interaction when two bin β particles combine to form another bin β particle. The final term gives the loss of particles from bin β due to interactions of bin β particles with particles of all larger bins. Double counting in interactions between particles from the same bin is taken into account in the values of the X coefficients.

The values of the X coefficients can be calculated by assuming a size distribution function $N(s)$ within each size bin, where $N(s)\,ds$ is the concentration of particles whose size is between s and $s + ds$. The X coefficient values are then found by integrating the product of the size distribution functions over the appropriate ranges of sizes. For example, to calculate the number of interactions of clusters from bins α and β ($\alpha < \beta$) that will form clusters in bin $\beta + 1$, integrate the number of possible interactions in each interval, $N(s)\,N(s')\,ds'\,ds$, over the range of size combinations that will give a new particle with size greater than H_β, i.e., over the range where $s \leq H_\alpha$, $s' \leq H_\beta$, and $s + s' > H_\beta$. Figure 1 illustrates the regions over which to integrate for the cases where the new particle belongs in bin β or in bin $\beta + 1$. The integrals acquired are

$$X^\beta_{\alpha,\beta} = \int_{L_\alpha}^{H_\alpha} \int_{L_\beta}^{H_\beta - s} N(s)\,N(s')\,ds'\,ds \tag{5}$$

$$X^{\beta+1}_{\alpha,\beta} = \int_{L_\alpha}^{H_\alpha} \int_{H_\beta - s}^{H_\beta} N(s)\,N(s')\,ds'\,ds \tag{6}$$

$$X^\alpha_{\alpha,\alpha} = \tfrac{1}{2} \int_{L_\alpha}^{H_\alpha - L_\alpha} \int_{L_\alpha}^{H_\alpha - s} N(s)\,N(s')\,ds'\,ds \tag{7}$$

$$X^{\alpha+1}_{\alpha,\alpha} = \tfrac{1}{2} \int_{L_\alpha}^{H_\alpha} \int_{L_\alpha}^{H_\alpha} N(s)\,N(s')\,ds'\,ds - X^\alpha_{\alpha,\alpha}, \tag{8}$$

where $\alpha < \beta$. The unique definition of bin -1 (monomers only) requires a slightly different derivation of some X coefficient values, as

$$X^\alpha_{-1,\alpha} = \int_{L_\alpha}^{H_\alpha - 1} C_{-1} N(s)\,ds \tag{9}$$

$$X^{\alpha+1}_{-1,\alpha} = \int_{H_\alpha - 1}^{H_\alpha} C_{-1} N(s)\,ds \tag{10}$$

$$X^0_{-1,-1} = \tfrac{1}{2}(C_{-1})^2 \tag{11}$$

$$X^{-1}_{-1,-1} = 0, \tag{12}$$

where C_{-1} is the monomer concentration, the concentration of particles in bin -1.

CONSTANT $N(s)$ ALGORITHM

The simplest approximation for $N(s)$, the zero-order approximation, is achieved by assuming that the size distribution function within each bin is constant with respect to particle size. If C_α is the concentration of particles in bin α, then

$${}^0N(s) = \frac{C_\alpha}{H_\alpha - L_\alpha} \quad \text{for} \quad L_\alpha < s \leq H_\alpha \quad \text{and} \quad \alpha \geq 0. \tag{13}$$

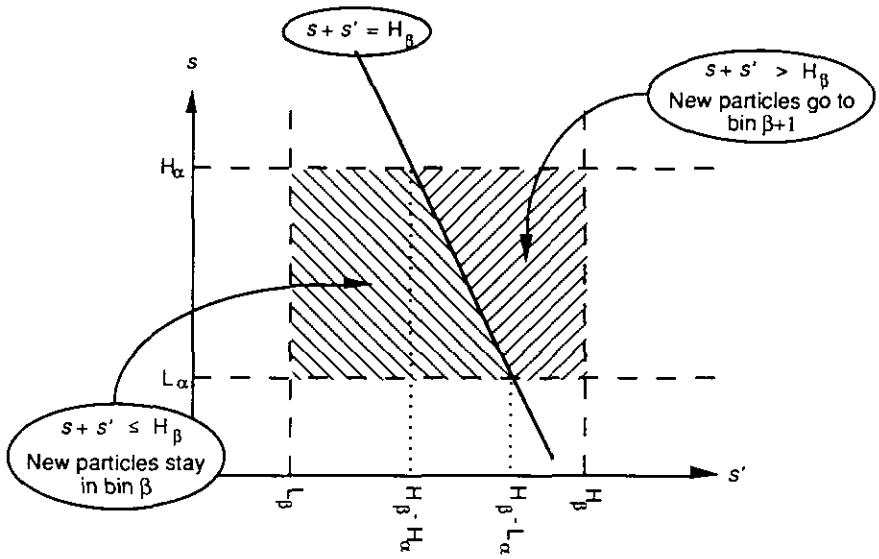

FIG. 1. The limits of integration appropriate for calculating X coefficients can be determined through this and other similar graphical representations.

The prefixed superscript 0 indicates the zero-order approximation. Substituting Eq. (13) into the equations above gives the X coefficients for the zero-order case:

$$ {}^0X^{\beta}_{\alpha,\beta} = C_\alpha C_\beta \left(1 - \frac{1}{2}\frac{H_\alpha + L_\alpha}{H_\beta - L_\beta}\right) \tag{14} $$

$$ {}^0X^{\beta+1}_{\alpha,\beta} = \frac{C_\alpha C_\beta}{2}\frac{H_\alpha + L_\alpha}{H_\beta - L_\beta} \tag{15} $$

$$ {}^0X^{\alpha}_{\alpha,\alpha} = \frac{(C_\alpha)^2}{4}\left(\frac{H_\alpha - 2L_\alpha}{H_\alpha - L_\alpha}\right)^2 \tag{16} $$

$$ {}^0X^{\alpha+1}_{\alpha,\alpha} = \frac{(C_\alpha)^2}{2}\left[1 - \frac{1}{2}\left(\frac{H_\alpha - 2L_\alpha}{H_\alpha - L_\alpha}\right)^2\right] \tag{17} $$

$$ {}^0X^{\alpha}_{-1,\alpha} = C_{-1}C_\alpha\left(1 - \frac{1}{H_\alpha - L_\alpha}\right) \tag{18} $$

$$ {}^0X^{\alpha+1}_{-1,\alpha} = \frac{C_{-1}C_\alpha}{H_\alpha - L_\alpha}. \tag{19} $$

This zero-order approximation is similar to the technique employed by Toon *et al.* [2] and Turco *et al.* [3].

LINEAR $N(s)$ ALGORITHM

A first-order approximation may be obtained by assuming the particle size distribution to be a linear function of particle size within each bin, i.e.,

$$ {}^1N(s) = A_\alpha s + B_\alpha \qquad \text{for} \quad L_\alpha < s \leqslant H_\alpha, \tag{20} $$

where the prefixed superscript 1 indicates the first-order approximation. This approximation requires the definition of an additional variable to describe the contents of each size bin, such as M_α, the total mass concentration of particles within size bin α. Defining the mass unit to be the monomer mass, the total number concentration and total mass concentration of particles in each bin are given by the equations

$$ C_\alpha = \int_{L_\alpha}^{H_\alpha} {}^1N(s)\, ds \tag{21} $$

$$ M_\alpha = \int_{L_\alpha}^{H_\alpha} {}^1N(s)\, s\, ds. \tag{22} $$

Substituting Eq. (20) into these two integrals yields the values for the coefficients A_α and B_α,

$$ A_\alpha = \frac{12M_\alpha - 6C_\alpha(H_\alpha + L_\alpha)}{(H_\alpha - L_\alpha)^3} \tag{23} $$

$$ B_\alpha = \frac{4C_\alpha(H_\alpha^2 + H_\alpha L_\alpha + L_\alpha^2) - 6M_\alpha(H_\alpha + L_\alpha)}{(H_\alpha - L_\alpha)^3}. \tag{24} $$

Since both C_α and M_α are needed to describe the contents of size bin α, the time dependence of each must be defined. The time dependence of C_α is given by Eq. (4), but a similar equation for M_α requires definition of another set of coefficients. Where the equation for C_α required the coefficients $X^{\gamma}_{\alpha,\beta}$, the equation for M_α requires the four coefficients $U^{\alpha\to\beta}_{\alpha,\beta}$, $U^{\alpha\to\beta+1}_{\alpha,\beta}$, $U^{\beta\to\beta+1}_{\alpha,\beta}$, and $U^{\alpha\to\alpha+1}_{\alpha,\alpha}$, where $\alpha < \beta$. These U coefficients represent the total mass of particles (in units of the monomer mass) per unit volume that could be transported from one bin to another as indicated by the superscripts through all possible interactions between particles in the subscripted size bins. The following equation

describes the time dependence of the size-binned mass concentration:

$$\frac{\partial M_\beta}{\partial t} = \sum_{\alpha=-1}^{\beta-2} K_{\alpha,\beta-1}(U^{\alpha\to\beta}_{\alpha,\beta-1} + U^{\beta-1\to\beta}_{\alpha,\beta-1}) + K_{\beta-1,\beta-1}U^{\beta-1\to\beta}_{\beta-1,\beta-1} + \sum_{\alpha=-1}^{\beta-1} K_{\alpha,\beta}U^{\alpha\to\beta}_{\alpha,\beta} - \sum_{\alpha=-1}^{\beta-1} K_{\alpha,\beta}U^{\beta\to\beta+1}_{\alpha,\beta} - K_{\beta,\beta}U^{\beta\to\beta+1}_{\beta,\beta} - \sum_{\gamma=\beta+1}^{\infty} K_{\beta,\gamma}(U^{\beta\to\gamma}_{\beta,\gamma} + U^{\beta\to\gamma+1}_{\beta,\gamma}). \quad (25)$$

The first term in Eq. (25) gives the increase in bin β mass from interactions between bin $\beta-1$ particles and particles from all smaller bins. The mass transferred to bin β in this term is from both of the interacting bins. The second term gives the increase in bin β mass due to interactions between two particles in bin $\beta-1$. The third term gives the mass transferred to bin β from all smaller bins when they interact with particles in bin β. Term four gives the loss of mass from bin β to bin $\beta+1$ from interactions of bin β with all smaller bins. Term five gives the loss of mass from bin β to bin $\beta+1$ in interaction between two bin β particles. The final term gives the loss of mass from bin β due to interactions between bin β particles and particles from all larger bins. The values of the U coefficients are found from the following integrals ($\alpha<\beta$), in a manner similar to the derivations of the X coefficients:

$$U^{\alpha\to\beta+1}_{\alpha,\beta} = \int_{L_\alpha}^{H_\alpha}\int_{H_\beta-s}^{H_\beta} {}^1N(s)\,{}^1N(s')\,s\,ds'\,ds \quad (26)$$

$$U^{\beta\to\beta+1}_{\alpha,\beta} = \int_{L_\alpha}^{H_\alpha}\int_{H_\beta-s}^{H_\beta} {}^1N(s)\,{}^1N(s')\,s'\,ds'\,ds \quad (27)$$

$$U^{\alpha\to\beta}_{\alpha,\beta} = \int_{L_\alpha}^{H_\alpha}\int_{L_\beta}^{H_\beta-s} {}^1N(s)\,{}^1N(s')\,s\,ds'\,ds \quad (28)$$

$$U^{\alpha\to\alpha+1}_{\alpha,\alpha} = \tfrac{1}{2}\int_{L_\alpha}^{H_\alpha-L_\alpha}\int_{H_\alpha-s}^{H_\alpha} {}^1N(s)\,{}^1N(s')(s+s')\,ds'\,ds + \tfrac{1}{2}\int_{H_\alpha-L_\alpha}^{H_\alpha}\int_{L_\alpha}^{H_\alpha} {}^1N(s)\,{}^1N(s')(s+s')\,ds'\,ds \quad (29)$$

$$U^{\alpha\to\alpha+1}_{-1,\alpha} = C_{-1}\int_{H_\alpha-1}^{H_\alpha} {}^1N(s)\,s\,ds \quad (30)$$

$$U^{-1\to\alpha+1}_{-1,\alpha} = C_{-1}\int_{H_\alpha-1}^{H_\alpha} {}^1N(s)\,ds = {}^1X^{\alpha+1}_{-1,\alpha} \quad (31)$$

$$U^{-1\to0}_{-1,-1} = 2\,{}^1X^{0}_{-1,-1} \quad (32)$$

$$U^{-1\to-1}_{-1,-1} = 0. \quad (33)$$

Substituting the first-order relationship for $N(s)$ into the equations for the X and U coefficients yields the coefficients needed for the first-order approximation. The calculations are straightforward and similar to those for the zero-order X coefficients given above. With the zero-order X coefficients given as an illustration, the first-order X and U coefficients will not be listed here, in the interest of brevity.

There is an undesirable artifact of the linear $N(s)$ or first-order approximation. The effect arises when the average size (M_β/C_β) of the particles within a bin β is smaller than the mean of the allowable particle sizes for that bin ($[H_\beta+L_\beta]/2$). When this occurs, the linear approximation of $N(s)$ has a negative value at $s=H_\beta$, and so Eqs. (4) and (25) may indicate a flow of negative particles and/or negative mass into the next larger (and possibly unoccupied) bin (bin $\beta+1$). Since negative mass is not physically possible, this must not be allowed. The correction is fairly simple: in interactions between bin β and a smaller bin α, if the X and U coefficients call for transport of negative mass or negative particles into bin $\beta+1$, redirect all transport calculated for bin $\beta+1$ into bin β instead and set all transport into bin $\beta+1$ to zero. The negative mass and particles must be redirected rather than simply deleted in order to conserve mass. On the positive side, this artifact minimizes the number of bins containing extremely small fractions of particles, reducing the computer memory allocation and computation time by a significant amount that would otherwise be required to track this insignificantly small fraction of the particle population.

ALGORITHM COMPARISONS

The constant $N(s)$ and linear $N(s)$ algorithms for aggregation/coagulation may be evaluated by calculating with each algorithm the time evolution of a system of particles from an initially monodisperse distribution, employing a constant coagulation kernel, $K_{j,k}=K$. These calculated evolutions may then be compared to the analytical solution of the Smoluchowski equation for these conditions. Thorough derivation of this analytical solution may be found in a number of publications [4]. The solution is

$$n_j(t) = \frac{N_0(t/\tau)^{j-1}}{(1+t/\tau)^{j+1}}, \quad (34)$$

where N_0 is the initial concentration of monomers, n_j is the concentration of particles of size j, t is the time elapsed, and $\tau=2/(KN_0)$ is the characteristic time for coagulation. Another useful equation gives the total number of clusters or particles of all sizes at any given time:

$$N_c(t) = \frac{N_0}{1+t/\tau}. \quad (35)$$

The conditions used in the evaluation trials were an initial monodisperse aerosol of 10^7 particles per cubic centimeter, and a constant coagulation kernel of 5×10^{-10} m^3/particle · s, appropriate for water droplets of about 6 nm in radius in room-temperature air. Three different size bin scales (q values) were run for each algorithm, $q = 2$, $q = 4$, and $q = 6$. The comparison to the analytical solution was made by calculating the number of particles of integer size according to Eq. (34) and summing these through the range of each size bin to determine the total number of particles within each bin. The root-mean-square (RMS) deviation of the output of each algorithm from these analytically determined size bin values was then calculated at several time intervals. These deviations were normalized by dividing by the total number of particles from Eq. (35). The normalized RMS deviations are plotted against time in Figs. 2, 3, and 4.

With $q = 2$, the average particle size for any size bin is twice the average size of the next smaller bin. This is the highest size resolution possible with these size-binning algorithms, since the formalism breaks down for $q < 2$. Figure 2 shows that both algorithms yield RMS deviations from the analytical solution of less than 2% of the total particle count throughout the first 3500 s of the simulation. With errors in this range, both algorithms should be considered quite good, although the constant $N(s)$ algorithm is slightly better for times less than about 3200 s, and the linear $N(s)$ algorithm appears to be better after 3200 s. These simulations were not continued beyond 3500 s because of the large memory allocation and run times required for the high size resolution simulations. The curves in Fig. 2 are similar in shape to those in Figs. 3 and 4, indicating that the RMS deviation for the constant algorithm would probably continue to increase with time after 3200 s, while that for the linear algorithm would probably remain at approximately 1% or lower. With $q = 4$, Fig. 3 shows a much lower deviation from the analytical solution for the linear $N(s)$ algorithm, approximately one-tenth the deviation of the constant $N(s)$ algorithm. The $q = 6$ case is similar, with the difference between the two algorithms being slightly greater. The similarity in the shape of the RMS deviation curves on

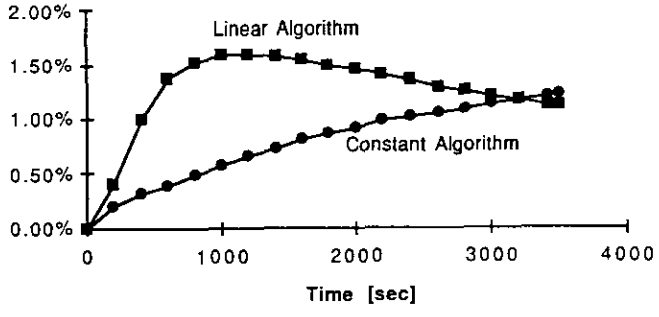

FIG. 2. Algorithm comparisons at high size resolution. Here the particle size in each size bin is twice that in the previous bin.

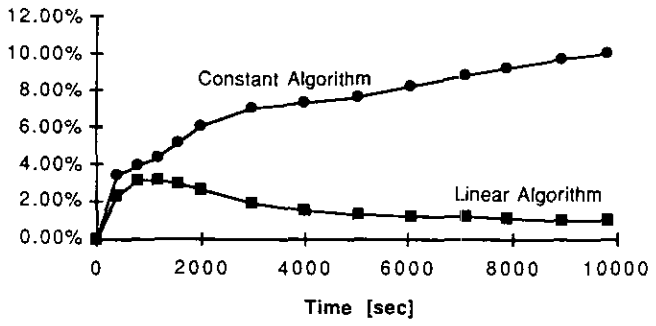

FIG. 3. Algorithm comparisons at moderate size resolution. Here the particle size in each size bin is four times that in the previous bin.

Figs. 2, 3, and 4 indicate that, if the $q = 2$ case were continued beyond 3200 s, the RMS deviation for the constant algorithm would probably continue to increase with time, while that for the linear algorithm would probably remain at approximately 1% or lower.

Probably the most surprising finding in this research involves the calculation time required for these two algorithms. Because of its mathematical simplicity compared to the linear $N(s)$ algorithm, one would expect the constant $N(s)$ algorithm to run more quickly, but the difference in run time between algorithms is quite small. The run time required is more dependent on the number of size bins tracked and the frequency of output to disk.

CONCLUSIONS

Simulations of aggregation or coagulation in which a large range in particle size is expected can be run more efficiently if the particle concentrations may be calculated for ranges of particle sizes, or size bins. Lower size resolutions (larger size bins) require fewer calculations and smaller memory allocations. For a formalism of size bins with geometrically increasing size, various algorithms may be developed based on differing assumptions about the dependence of particle concentration on particle size within

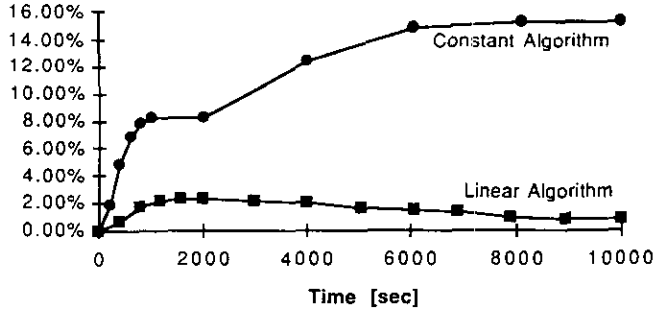

FIG. 4. Algorithm comparisons at lower size resolution. Here the particle size in each size bin is six times that in the previous bin.

the bins. Assuming concentration to be a linear function of size within each bin yields a more mathematically complicated set of calculations for each size bin than does assuming constant concentration within each bin. However, for extended duration simulations (~ 3 h in the test cases) the linear algorithm is an order of magnitude more accurate than the constant algorithm and requires roughly the same amount of computer run time.

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