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Electronic Supporting Information for

Accurate and fast numerical algorithms for tracking particle size distributions during nanoparticle aggregation and dissolution

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Additional Supporting Information (Files uploaded separately)

MATLAB code for the Sectional Method, Direct Simulation Monte Carlo, the Direct Quadrature Method of Moments, and the Extended Quadrature Method of Moments

Introduction

Supporting Methods (Text S1.i - S1.7) provide a more complete treatment of the models used in this work. Supporting Figures, as referenced in the main text, include the following: results of the model calibration to determine aggregation and dissolution rates (Figure S1); results for additional test cases such as dissolution to equilibrium and dissolution and aggregation for multiple particle sizes (Figure S2-S5); initial particle size distributions associated with various test cases (Figure S6, Figure S8), and additional error analyses for the "aggregation only" case (Figure S7) and the size-unresolved mass balance model for dissolution to equilibrium (Figure S9).

Additional Supporting Information includes MATLAB code for our implementation of the Sectional Method, Direct Simulation Monte Carlo, the Direct Quadrature Method of Moments with ratio constraints, and the Beta Extended Quadrature Method of Moments. The code is parameterized for the test cases presented in Figure 2 and Figures S2-S4 to allow rapid reproduction of these results by interested readers.

Text S1. Supporting Methods

Symbols

k_B	Boltzmann constant
R	Gas constant
μ	Viscosity of water
Т	Temperature
V _{sol}	Solution volume
S _{tot}	Total initial NP surface area in solution
\overline{V}	Molar volume of $Me_x O_x$
γ	Particle surface free energy
$ ho_p$	Density of Me_xO_x
D _{Me} ion	Me^+ diffusion coefficient in water ("ion" used in place of "+" to avoid any confusion of the metal ion charge with the addition operator)
$a_{Me_x^0x/Me_{ion}}$	Stoichiometric coefficient for Me_xO_x dissolution to form Me^+
h	Particle boundary layer thickness (Nernst-Brunner modified Noyes Whitney)
$[Me_{ion}]_t$	Metal ion concentration at time t
$[Me_{ion}]_{eq}$	Metal ion concentration at equilibrium
$[Me_xO_x]_t$	Me_xO_x concentration at time t
t	Time
r	Particle radius
m	Particle mass
D _{geom,0}	"Characteristic diameter" of primary NPs: Surface-weighted geometric mean diameter
$\hat{D}_{i,agg}$	"Characteristic diameter" of aggregates
I otal Mass Balance	
M _{NP,tot}	I otal NP mass in solution
ⁿ mb	Dissolution rate constant, total mass balance model
ĸ _{S,mb}	Surface-area normalized reaction rate, total mass balance model
Population Balance (all)	
^f (m)	Particle size distribution (function of mass)
<i>m</i> .	SM: representative bin size for bin <i>i</i>
	Moment methods: abscissa associated with quadrature point <i>i</i>
Wi	Weight associated with quadrature point <i>i</i> (moment methods)
m_{avg}	Average primary particle mass
r_{avg}	Average primary particle radius
n	Number of quadrature points (moment methods)
X _{geom,i}	Geometric mean number of primary particles in aggregates of size <i>i</i>
μ_k	<i>k</i> th moment of the particle size distribution
N	Total particle number concentration at time t (N_0 = initial concentration)
Α	Dissolution rate, <i>dm/dt</i>
k _{S,pb}	Surface-area normalized reaction rate, population balance
K	Proportionality constant for permeable aggregates colliding due to Brownian motion

K D_f Fractal dimension of the aggregate Collision rate due to Brownian motion β Attachment efficiency α Dissolution flux φ Sectional Method N_i Nu

- Number concentration of particles in bin *i*

m _{rat}	Ratio used to select bin sizes
q	Exponent used to select bin sizes
m _{i,lo}	Mass at the lower boundary of size bin <i>i</i>
m _{min}	Minimum particle mass
m _{max}	Maximum particle mass
n _{bins}	Number of size bins
Direct QMOM	
a _i	Derivative of weight associated with quadrature point <i>i</i> with respect to <i>t</i>
b _i	Derivative of weighted abscissa associated with quadrature point <i>i</i> with respect to <i>t</i>
\bar{S}_k	Source term for NP processes
Extended QM	UNI Number of accordery quedroture points
<u>П2</u>	Number of secondary quadrature points
σ_{β}	Unner hound on a
$\beta_{\beta,max}$	$\frac{\partial p_{\beta}}{\partial t} = \frac{\partial p_{\beta}}{\partial t}$
m_{i_1,i_2}	Weight associated with secondary quadrature point i_1, i_2
<i>m</i> _{i1,i2}	Abscissa associated with secondary quadrature point i_1 , i_2
<i>P</i> _{<i>i</i>₁,<i>i</i>₂}	
λ_i	First parameter of the beta distribution associated with primary quadrature point <i>i</i>
μ_i	Second parameter of the beta distribution associated with primary quadrature point <i>i</i>
μ_k	Transformed moment set
μ_k^*	Transformed star moment set
p_k^*	Canonical star moment set
p_k^*	Transformed canonical star moment set
$\frac{\underline{H}_{2k}}{\underline{H}_{2k+1}}, \overline{H}_{2k}$	Hankel determinants of the transformed star moment set
J _i	Difference between predicted and known value of the 2 <i>n</i> th moment for a given estimate of σ_{β}
Е	First parameter of the weight function w used to find the secondary quadrature points
ζ	Second parameter of the weight function w used to find the secondary quadrature points
J	Jacobi matrix used to find the secondary quadrature points
	Diagonals of the Jacobi matrix J
b_j	Co-diagonals of the Jacobi matrix J
Direct Simulation Monte Carlo	
f _{safety}	Safety factor to ensure only one aggregation event occurs during a time step
t _{coag,i}	Average time to coagulation for particle <i>i</i>
P _{ij}	Probability of collision between particles <i>i</i> and <i>j</i>
Analytical Solutions	
μ_{ln}	Location parameter of the lognormal distribution at time $t (\mu_{ln,0} = \text{initial condition})$
σ_{ln}	Scale parameter of the lognormal distribution at time t ($\sigma_{ln,\theta}$ = initial condition)

S1.i. Introduction to Supporting Methods:

In recognition of the complexity and diversity of these methods, and the reader's need to assess their most fundamental features without getting bogged down, we use a set of notations that (we hope) is as simple as possible. In so doing, we have deviated from the more rigorous formulations found in many of the original works. In addition, we emphasize model development for a simple batch reactor and the practical identification and treatment of common errors that arise during their execution, rather than (e.g.) theory, the mathematical derivations of these methods, or the execution of their many permutations and extensions. The Methods in the main text are a reduced version of those that follow.

S1.1. Total Mass Balance

Conventional mass balance differs from population balance as described in Section S1.2 in that the particle size distribution (and/or its statistical properties) are not resolved or tracked over time. Instead, only the total mass concentration of each species of interest (here, the metal oxide and its ions) is tracked.

In a simple batch reactor (complete dispersion, no advection), and in the absence of dissolution, aggregation has no effect on the total NP mass. When dissolution does occur, the following simple first-order linear inhomogeneous differential equation¹ has been used to describe dissolution.²

$$\frac{d[Me_{ion}]_t}{dt} = k_{mb}([Me_{ion}]_{eq} - [Me_{ion}]_t)$$

Analytical solution: $[Me_{ion}]_t = [Me_{ion}]_e \notin 1 e^{-k_m \frac{b}{b}}$ (S1)

In Equation S1, $[Me_{ion}]_t$ is the mass concentration of the ion in solution at time t, $[Me_{ion}]_{eq}$ is the ion concentration in solution at equilibrium, and k_{mb} is an empirical rate constant determined by data fitting. In a batch reactor model, $[Me_xO_x]_t$ can be calculated directly once $[Me_{ion}]_t$ is known because the total metal concentration remains constant. Since an analytical solution is available, simulation runtimes are trivial. As a matter of historical interest, we note that Equation S1 is the original 1897 form of the Noyes Whitney equation before its modification by Nernst and Brunner to the form used most often today (see Section S1.2.b).³

As written, Equation S1 is not a function of particle size. The size dependence of k_{mb} may be determined by data fitting. The size dependence of the equilibrium solubility, $[Me_{ion}]_{eq'}$ is either determined by data fitting or estimated using the Ostwald-Freundlich relation, a theoretical model that attributes the observed increase in solubilities as particle radii (*r*) decrease to an increase in surface curvature.

$$\frac{[Me_{ion}]_e}{[Me_{ion}]_e} \left(\begin{array}{c} e \\ b \\ u \end{array} \right) = e^{2\gamma V /_R T r}$$
(S2)

where γ is the surface free energy, V is the molar volume, R is the gas constant, and T is the temperature. Equation S2 may over-estimate the equilibrium solubility of NPs.⁴⁻⁷ Since our analysis is purely theoretical and questions about the appropriateness of these models for NPs can only be answered with experiments, we use Equation S2 in this work (applying it in both mass balance and population balance models).

In Equation S2, we used the initial surface-weighted geometric mean radius as the characteristic particle size for the distribution. In general, the surface-weighted geometric mean diameter, $D_{geom,0}$ (where 0 indicates "primary" or unaggregated particles, and not *t*=0) was calculated at every time step as shown.

$$D_{geom,0} = exp \left[\frac{\sum_{i=1}^{n} W_i D_i^2 \ln D_i}{\sum_{i=1}^{n} W_i D_i^2} \right]$$
(S3)

where D_i is the particle diameter associated with a given size class (in the SM) or quadrature point (in the QMOM) and W_i is the particle number concentration associated with that size class $({}^{W_i=N_i})$ or quadrature point $({}^{W_i=w_i})$.⁸

Eq. S3 was used wherever a measure of the primary particle size was needed. This measure has several advantages over more traditional estimates of particle diameter including the (number-weighted) mean and the geometric mean. The geometric mean of a skewed distribution is a better estimate of its central tendency than its average. For reactive NPs, the surface-weighted diameter is more relevant than the number-weighted diameter because of the controlling influence of surface area on dissolution kinetics. In addition, the surface-weighted diameter does not rely on the zeroth moment (the total number concentration) and is thus robust to numerical errors introduced by approximation of the dissolution flux.

S1.2. Population Balance: General Principles

Although definitions vary (e.g., population balance is often defined simply as an implementation of the "population balance equation," Equation S4),^{9, 10} population balance may be defined most generally as a means of modeling particle populations in which the continuity equation describes the distribution of particle properties (so-called "internal coordinates") across the population in addition to tracking changes in the average or total properties of the population (e.g., mass concentration) across space and time ("external coordinates").¹¹ The internal coordinate of greatest interest in population balance is nearly always particle size, and we focus exclusively on this property here.

By tracking changes in the particle size distribution over time and space, rather than merely tracking the total particle mass (Section S1.1), population balance models are able to track changes in the number concentration, surface area concentration, and primary and/or aggregate particle sizes in addition to the total NP and ion mass concentrations. Additionally, population balance allows the modeler to explicitly account for size-dependent differences in dissolution and aggregation rates across the population at each time step. However, the mathematical complexity, data requirements, and runtime demands of population balance methods are, unsurprisingly, substantially greater than that of total mass balance models. Modelers should not use this method unless it is truly necessary.¹²

The particle size distribution is described differently in different population balance methods. The three most popular alternatives are sectional methods, moment methods, and Monte Carlo methods.^{10, 13-15} In the sectional method (SM), the size domain is divided into sections or "bins" such that the particle size distribution is treated like a histogram. Moment methods conserve computational resources relative to the SM by only tracking the evolution of the lower-order statistical moments of a particle size distribution instead of tracking the entire distribution.^{10, 16} As described in Section S1.2.d, the moments capture most of the essential features of the distribution and can also, in some cases, be used to reconstruct it. Monte Carlo methods explicitly model the behavior of a finite sub-population of particles^{10, 15} and thus may require high runtimes relative to moment methods to achieve a given accuracy.¹³ MC simulation is generally considered too computationally expensive for incorporation with computational fluid dynamics code,^{11, 17} but it is a reasonable alternative for batch reactor-type systems (e.g.,

laboratory studies).¹⁴ Importantly, there are an impressive number of variants upon, and alternatives to, these three major approaches.

We compare two moment methods in this work: The Direct Quadrature Method of Moments (DQMOM)^{11, 18} and the Extended Quadrature Method of Moments (EQMOM).¹⁹ Differences between these methods, their application to NPs, and their advantages over "classical" QMOM¹⁶ are described in detail below (Sections S1.5 and S1.6). We chose DQMOM because it is extremely fast and relatively simple to implement. We chose EQMOM because it is specifically designed to deal with the "dissolution flux problem" described in the main text and Section S1.2.e.iii, which is crippling for most moment-based approaches.

S1.2.a. The population balance equation for dissolution and aggregation

The following population balance equation (PBE) may be used to describe a change in the particle size distribution, f, over time, t, due to dissolution and aggregation^{9, 10, 16, 20-22}

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{diss} + \left(\frac{\partial f}{\partial t}\right)_{agg}$$

$$\left(\frac{\partial f}{\partial t}\right)_{diss} = -\frac{\partial(Af)}{\partial m}$$

$$\left(\frac{\partial f}{\partial t}\right)_{agg} = \frac{1}{2} \int_{0}^{m} \alpha(m - m', m') \beta(m - m', m') f(m - m') f(m') dm'$$

$$- f(m) \int_{0}^{\infty} \alpha(m, m') \beta(m, m') f(m') dm'$$
(S4)

where *m* (particle mass) is our chosen size coordinate, A=dm/dt is the dissolution rate law described in Section S1.2.b.^{9, 16, 23} β is the frequency of particle-particle collisions (#/m³) that may lead to an aggregation event, and α is the probability that two particles will remain attached upon collision. a is alternatively called the "sticking coefficient" or "attachment efficiency," and is a major focus of current NP fate research.²⁴⁻²⁶ Several other terms may be included in the PBE if

other processes (e.g., aggregate breakage, settling) are of interest. Note, however, that $\overline{(\overline{\partial t})}$ agg applies equally to both NP homoaggregation, modeled in this work, and heteroaggregation (e.g., as demonstrated by Therezien et al.).²⁷

The first term on the right-hand side of the equation for $\left(\frac{\partial f}{\partial t}\right)_{agg}$ describes the formation of new aggregates of size *m* via the aggregation of primary (unaggregated) particles or aggregates of size (m-m') with those of size m' (the coefficient, 1/2, simply eliminates double-counting). The third term describes the loss of particles of size m due to the aggregation of particles of size m with those of any other size. Note that both terms are simply second-order rate laws in which the aggregation rate, described by the product $\alpha\beta$, is assumed to be linearly proportional to the number concentrations of particles of each size.

S1.2.b. Dissolution rate

We use the 1900 variant on Eq. S1 (the original Noyes Whitney equation) by Brunner and Tolloczko³ to describe the size-dependent dissolution of NPs. In this form, k_{mb} is replaced with the product of a surface area-normalized rate, $k_{S,mb}$, and S_{tot} , the total surface area of all particles in solution.

$$\frac{d[Me_{ion}]_t}{dt} = k_{S,mb}S_{tot}([Me_{ion}]_{eq} - [Me_{ion}]_t)$$
(S5)

Thus this expression simply states that particle dissolution is surface-area dependent and proceeds by exponential decay until equilibrium is achieved.

To use Equation S5 in population balance, we must rewrite the right-hand side in terms of our internal coordinate, particle mass. We must also rewrite the entire expression in terms of the mass loss of a single particle of a given size, rather than the gain in the ion concentration due to dissolution of all particles. A derivation follows in which we assume spherical particles, ignore the dependence of the total number concentration on time, and assume that the particle population is monodisperse. These assumptions are not applied elsewhere in our work; they are simply a convenience that allows us to find an appropriate form of Equation S5 for use in our model.

 $a_{Me_xO_x/Me_{ion}}$ is the stoichiometric coefficient for Me_xO_x dissolution (g Me_xO_x lost / g Me_{ion} formed), $M_{NP,tot}$ is the total NP mass in solution, V_{sol} is the solution volume, and N_0 is the initial total particle number concentration.

$$\begin{aligned} \frac{d[Me_{ion}]_{t}}{dt} &= k_{S,mb} S_{tot} ([Me_{ion}]_{eq} - [Me_{ion}]_{t}) \\ \frac{dM_{NP,tot}}{dt} &\approx a_{Me_{x}} v_{x/Me_{ion}} V_{sol} k_{S,mb} S_{tot} ([Me_{ion}]_{t} - [Me_{ion}]_{eq}) \\ \frac{dm_{i}}{dt} &\approx \frac{a_{Me_{x}} v_{x/Me_{ion}} V_{sol} k_{S,mb} S_{tot}}{N_{0} V_{sol}} ([Me_{ion}]_{t} - [Me_{ion}]_{eq}) \\ \frac{dm_{i}}{dt} &\approx \frac{a_{Me_{x}} v_{x/Me_{ion}} V_{sol} k_{S,mb} (N_{0} V_{sol} 4\pi r_{i}^{2})}{N_{0} V_{sol}} ([Me_{ion}]_{t} - [Me_{ion}]_{eq}) \\ \frac{dm_{i}}{dt} &\approx a_{Me_{x}} v_{x/Me_{ion}} V_{sol} k_{S,mb} 4\pi \left(\frac{3}{4\rho_{p}\pi}\right)^{2/3} m_{i}^{2/3} ([Me_{ion}]_{t} - [Me_{ion}]_{eq}) \\ A_{i} &= \frac{dm_{i}}{dt} = k_{S,pb} m_{i}^{2/3} ([Me_{ion}]_{t} - [Me_{ion}]_{eq}) \end{aligned}$$

As an alternative to Equation S5, many authors have proposed the Nernst-Brunner modified Noyes Whitney equation, a second modification of Equation S1.⁴⁻⁷

$$\frac{d[Me_{ion}]_t}{dt} = \frac{D_{Me_{ion}}S_{tot}}{hV_{sol}} ([Me_{ion}]_{eq} - [Me_{ion}]_t)$$
(S7)

(S6)

 $D_{Me_{ion}}$ is the rate of ion diffusion in water and *h* is the thickness of a boundary layer around the surface of the particles through which ions must diffuse for dissolution to occur.

If we apply the same logic we applied to Equation S5 and assume that *h* approximately equals the particle radius, which is generally the case below 30 microns in size,^{28, 29} we get Equation S8, which is equivalent to the Maxwellian flux expression used in many atmospheric chemistry models (compare to Eq. 12.9, p. 591, in ref 20). When mass is the internal coordinate,

$$A_{i} = \frac{dm_{i}}{dt} = K2\pi D_{Me_{ion}} \left(\frac{6m_{i}}{\rho_{p}\pi}\right)^{1/3} \left([Me_{ion}]_{t} - [Me_{ion}]_{eq}\right)$$
(S8)

Here, *K* is a coefficient that arises during the conversion and should approximately (if not exactly) equal the stoichiometric coefficient.

Equation S6 has many advantages over Equation S8 for our purposes, and will thus be used in this work. First, Equation S8 assumes that the rate-limiting step of dissolution is the diffusion of metal ions away from the particle surface. However, for metals and metal sulfides, the rate-limiting step is more likely to be the rate of surface oxidation. Second, the empirical form (Equation S6) is preferable to the theoretical form (Equation S8) until the theoretical form has been extensively tested against experimental data. Third, Equation S8 may be unusable in cases where the radius, rather than the particle mass, is chosen as the internal coordinate, since dr/dt will approach infinity as r approaches zero.

The effect of aggregation on dissolution is poorly understood at present. In order to bound its effect, we consider two extreme cases. In the first, our "base case," we maximize the dissolution rate by assuming that aggregation has no effect. This approach is in general agreement with experimental results, for which small particles have been shown to dissolve faster than large particles even when they form larger aggregates.³⁰ We proceed as follows: The model is run once for a "dissolution only" case in order to determine the average primary (unaggregated) particle mass at each time step, $m_{avg}(t)$. It is then run a second time for the case of simultaneous dissolution and aggregate size by the geometric mean number of primary particles in the aggregate, X_i , to determine the overall dissolution rate of the aggregate. To minimize error in $D_{geom,0}(t)$, we assume a monodisperse primary particle population.

In the second case, which provides a conservative lower bound on the dissolution rate, we assume that aggregation leads to complete fusion of the particles, forming compact, solid spherical particles whose dissolution behavior is determined by the aggregate mass, m_i .

S1.2.c. Collision rate

In this work, we treat α (the probability of attachment upon collision) as a known constant with a fixed value between 0 and 1. Collisions, which determine the collision rate (β), are assumed to result from Brownian motion.

One advantage of choosing mass as our size coordinate is that the mass of every newly formed aggregated can be calculated exactly from the masses of the colliding species. In contrast, the radius of the aggregate must be estimated from the unknown geometry of the aggregate. However, even if mass is our size coordinate, we must make an assumption about the porosity of the aggregates and its effect on their collision rates. We use the following expression for the collision rate between aggregates of size m_i and m_j

$$\beta_{i,j} = \frac{2k_B T}{3\mu} \left(m_i^{1/D_f} + m_j^{1/D_f} \right) \left(m_i^{-1/D_f} + m_j^{-1/D_f} \right)$$
(S9)

where ${}^{D}f$ is the fractal dimension of the aggregates.^{31, 32} We assume ${}^{D}f = 1.8$ (for all particle sizes), which is approximately correct for aggregates formed by Brownian diffusion.^{21, 32} More detailed and theoretically rigorous rate laws exist,³³⁻³⁶ but a simple approach is suited to an illustrative analysis performed in the absence of experimental data.

The characteristic aggregate diameters reported in our results (e.g., Figure 2), are estimated from the characteristic primary particle diameters at time t, $D_{geom,0}(t)$, as shown in Equation S10. In the absence of dissolution, $D_{geom,0}(t) = D_{geom,0}(0)$.³³

$$D_{i,agg} = D_{geom,0} (X_{geom,i})^{1/D_f}$$
(S10)

S1.2.d. Statistical moments of a distribution

The statistical moments, $\mu_{k'}$ of a particle size distribution, f(m), are given as ¹⁶

$$\mu_k = \int m^k f(m) dm \tag{S11}$$

It is easily seen that μ_0 (the "zeroth moment") is the total particle number concentration. By the same logic, the moment sequence k = 0, 1/3, 2/3, 1 creates a sequence of values that are directly proportional to the total particle number concentration (k = 0), the sum of all particle radii (divided by μ_0 to find the average particle size, k = 1/3), the surface area concentration (k = 2/3), and the total mass concentration of the particle population (k = 1). By tracking this moment sequence over time, we are then able to track any dose metric of practical interest with ease.

If radius were our internal coordinate, the moment sequence needed to calculate the metrics described above would be k = 0, 1, 2, 3.

If the particle size distribution is described exactly by a particular distribution (e.g., exponential, lognormal), its moments can often be calculated directly from the parameters of the distribution using known formulas. The EQMOM relies on this relationship between moments and distribution parameters. They can also be used in the EQMOM and the DQMOM to determine the initial (t = 0) moments of a known distribution.

S1.2.e. Introduction to Moment Methods

S1.2.e.i. The Quadrature Approximation

In classical quadrature-based moment methods, Equation S11 (the moment equation) is replaced with a discrete approximation using an "*n*-point Guassian quadrature rule."¹⁶

$$\mu_{k} = \int m^{k} f(m) dm = \sum_{i=1}^{n} m_{i}^{k} w_{i}$$
(S12)

In effect, the continuous function f(m) is replaced with a particular discrete approximation defined by its "quadrature points," or the set of *n* "abscissas" and "weights" (m_i , w_i). The strength of *n*point Gaussian quadrature is that it allows the quadrature points to be calculated from the lowerorder moments of the distribution, thus solving the so-called "closure problem" that characterizes moment methods.¹⁶

S1.2.e.ii. Numerical Solution: The Moment Evolution Equations and Matrix Inversion

In classical QMOM, the population balance equation used in the SM (Equation S4) is replaced with a continuity equation (the "moment evolution equation") that combines Equation S4 with the $d\mu_{\nu}$

derivative of Equation S11 to instead balance the moments of the distribution, dt. The moment evolution equations for the processes of dissolution and aggregation are as follows:¹⁶

$$\frac{d\mu_{k}}{dt} = \left[\frac{d\mu_{k}}{dt}\right]_{diss} + \left[\frac{d\mu_{k}}{dt}\right]_{agg}$$

$$\left[\frac{d\mu_{k}}{dt}\right]_{diss} = k \int_{0}^{\infty} m^{k-1} A(m) f(m) dm$$

$$\left[\frac{d\mu_{k}}{dt}\right]_{agg} =$$

$$\frac{1}{2} \int_{0}^{\infty} \int_{0}^{\infty} \alpha(m,m') \beta(m,m') [(m+m')^{k} - m^{k} - (m')^{k}] f(m) f(m') dm dm'$$
(S13)

The quadrature approximation of Equation S13 is

$$\frac{d\mu_k}{dt} \approx k \sum_{i=1}^n m_i^{k-1} A_i w_i + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n \alpha_{ij} \beta_{ij} [(m_i + m_j)^k - m_i^k - m_j^k] w_i w_j$$
(S14)

Classical QMOM proceeds as follows: (1) Quadrature points are estimated from the moments calculated during the previous time step (or the initial conditions) using a matrix inversion algorithm such as Product-Difference (described shortly). The moments of the distribution are then evolved from one time step to the next using (e.g., the Euler approximation of) Equation S14.

Although the DQMOM and the EQMOM differ from the classical QMOM in their description of the particle size distribution and their treatment of its dynamic evolution, the algorithms for all three methods require the implementation of a matrix inversion procedure in which the lower-order moments of the distribution are used to determine its quadrature points. In this work, we employ the Product-Difference algorithm.^{10, 16} The modified Wheeler algorithm (MATLAB code provided in Appendix A of ref 37, "Adaptive 1-D quadrature algorithm") is a popular alternative that readily identifies and handles numerical problems resulting from the use of too many quadrature points (where *n* should not exceed 5-10).¹⁹ However, we found that its use of an iterative approach to determine an ideal number of quadrature points was unnecessary for successful implementation of the DQMOM and unnecessarily complicated our implementation of the EQMOM.

S1.2.e.iii. The Dissolution Flux Problem

As particles dissolve completely, the cross the lower boundary of the size domain. This creates an efflux of particles from the system, φ , which may be calculated as shown:¹⁹

$$\varphi = A(0)f(0)$$

(S15)

Classical moment methods only track six or fewer quadrature points, and these points will not generally lie close enough to the lower boundary to allow an accurate prediction of f(0). We will refer to this as the "dissolution flux" problem of classical moment methods. Although it could be a crippling problem when modeling reactive NPs, which readily dissolve completely, it does not seem to be of great concern to the population balance modeling community at large; in fact, it appears to only be the focus of a few recent works (in which it is generally described in terms of evaporating sprays and thus referred to as the "evaporation flux" problem). In this work, we test three proposed solutions to the problem: The Direct Quadrature Method of Moments with and without ratio constraints and the Extended Quadrature Method of Moments.

S1.3. Population Balance #1: The Sectional Method

S1.3.a. Binning approach

In the sectional method (SM), particles are distributed to "sections" (bins) based on their size. In this work, we apply the binning method and numerical solution proposed by Hounslow et al.²³ and extended by Lister et al. ⁹ This method differs from sectional methods used to date in the nanoparticle fate literature^{27, 28, 38-40} in that it uses a geometric series to define a set of expanding bin sizes, rather than defining bins of equal size. Two benefits of such a method are that (1) it allows the modeler to capture a particle size distribution spread over many orders of magnitude (e.g., nanometer to micron size range)^{4, 5, 7} with a relatively small number of bins, and that (2) the highest model resolution (and computational burden) is placed on the smallest particles, for which aggregation and dissolution occur more rapidly, numerical error is more likely to arise, and the dissolution flux (introduced in Section S1.2.e.iii) must be estimated.

The grid of bin sizes is defined as follows: A ratio, m_{rab} is chosen such that the representative particle size at the lower boundary of each bin i+1, $m_{i+1,lo}$, is related to the size of the lower boundary of next smallest bin, bin *i*, by the non-negative integer *q*, as shown.

$$m_{rat} = m_{i+1,lo}/m_{i,lo} = 2^{1/q} \quad q \ge 1 \tag{S16}$$

Note that, when q = 1 ($m_{rat} = 2$), the representative size in each bin is twice the size of the previous bin.²³ In practice, higher q's result in a higher resolution to the size distribution. However, little to no benefit is generally observed for $q \ge 7$.

The representative lower boundary size of each bin can then be expressed in terms of the lower boundary of the entire size distribution, m_{min} .⁴¹

$$m_{i,lo} = (m_{rat}^{l})m_{min} \tag{S17}$$

The total number of bins needed to describe the size distribution is ²²

$$n_{bins} = 1 + \frac{ln_{im}^{m}(m_{max}/m_{min})}{ln_{im}^{m}(m_{rat})}$$
(S18)

In this work, we set m_{min} to be the approximate mass of a single Me_xO_x molecule (the molecular weight of the molecule of interest divided by Avogadro's number).

For the purpose of calculating the moments of the distribution, the central estimate of the representative size of each bin, m_{i} is estimated for a given moment of the distribution, k, as follows^{23, 41}

$$m_{i} = \frac{m_{rat}^{k+1} - 1}{(k+1)(m_{rat} - 1)} m_{i,lo}^{k}$$
(S19)

S1.3.b. Numerical solution for dissolution

We rewrote the Second Order Finite Difference approximation by Hounslow et al. and Kostoglou and Karabelas (described subsequently) in order to describe particle dissolution under an arbitrary rate law A_i (Section S1.2.b) as opposed to growth.^{23, 41}

$$\binom{dN_i}{dt}_{diss} = \frac{1}{m_{i,lo}} (aA_{i-1}N_{i-1} + bA_iN_i + cA_{i+1}N_{i+1})$$
where

$$a = -\frac{2m_{rat}}{(1+m_{rat})(m_{rat}^2 - 1)}$$

$$b = -\frac{2}{1+m_{rat}}$$

$$c = \frac{2m_{rat}}{(1+m_{rat})(m_{rat}^2 - 1)}$$
(S20)

 N_i is the number of particles in bin *i* at time *t*.

For dissolution, we used partially implicit time integration via Gauss-Seidel iteration with Type I (zero concentration) boundary conditions.⁴² We also tested an explicit alternative and a partial step procedure, fourth-order Runge-Kutta. Explicit methods were too unstable; Runge-Kutta was slow and provided no noticeable improvement in accuracy.

S1.3.c. Numerical solution for aggregation

For aggregation, we use the formulation by Lister et al. (Eq. 35 in ref 9), which captures all possible particle re-binning events that may occur on the geometric grid described by Equation S17 during an aggregation event between two particles of any size.

$$\begin{pmatrix} \frac{dN_i}{dt} \end{pmatrix}_{agg} = \sum_{j=1}^{i-Q(q)-1} \alpha_{i-1,j} \beta_{i-1,j} N_{i-1} N_j \frac{2^{\frac{j-i+1}{q}}}{2^{\frac{1}{q}}-1}$$

$$+ \sum_{k=2j}^{q} \sum_{i-Q(q-k+1)-k}^{i-Q(q-k+1)-k} \alpha_{i-k,j} \beta_{i-k,j} N_{i-k} N_j \frac{2^{\frac{j-i+1}{q}}-1+2^{-\frac{k-1}{q}}}{2^{\frac{1}{q}}-1}$$

$$+ \frac{1}{2} \alpha_{i-q,i-q} \beta_{i-q,i-q} N_{i-q}^{2}$$

$$+ \sum_{k=2j}^{q} \sum_{i-Q(q-k+1)-k+1}^{i-Q(q-k+1)-k+1} \alpha_{i-k+1,j} \beta_{i-k+1,j} N_{i-k+1} N_j \frac{-2^{\frac{j-i}{q}}+2^{\frac{1}{q}}-2^{-\frac{k-1}{q}}}{2^{\frac{1}{q}}-1}$$

$$-\sum_{j=1}^{i-Q(q)} \alpha_{i,j} \beta_{i,j} N_i N_j \frac{2^{\frac{j-1}{q}}}{2^{\frac{1}{q}}-1}$$

$$-\sum_{j=i-Q(q)+1}^{\infty} \alpha_{i,j} \beta_{i,j} N_i N_j$$

 $Q(q) = \sum_{l=1}^{q} l.$ where $P(q) = \sum_{l=1}^{q} l.$ For aggregation, we use explicit time integration and the Euler method. As with dissolution, an alternative solution that used fourth-order Runge-Kutta provided no clear benefit and was discarded.

S1.4. Population Balance #2: Direct Simulation Monte Carlo

In the Monte Carlo approach, a large number of NPs (10^3-10^4) are randomly selected from the initial particle size distribution, which is then evolved in time according to their rates of dissolution and aggregation. For purposes of calculating statistics of the distribution such as the raw fractional moments, the sub-population is treated as a representative sample.

For dissolution, each particle in the sample population simply loses mass at the rate suggested by its dissolution rate law (Eq. S6). For the "dissolution only" case, a fixed time step was used.

Cases that included aggregation had a variable time step. We employed the Direct Simulation Monte Carlo approach of Zhao et al. (2007).¹⁵ At each time point, the length of the next time step, Δt , was chosen dynamically such that at most one aggregation event would occur during the time step:

$$\Delta t = f_{safety} \cdot min(t_{coag,i}), \ t_{coag,i} = \frac{V_{sol}}{\sum_{j \neq i} \alpha \beta_{ij}}$$
(S22)

where f_{safety} is a safety factor below 1 (e.g., $f_{safety} = 0.01$) that ensures the time step always remains below the shortest time in which aggregation occurs; $t_{coag,i}$ is the average time to coagulation for particle *i*; and V_{sol} , α , and β_{ij} are (as defined previously) the solution volume, the size-independent attachment efficiency, and the collision rate between particles *i* and *j*, respectively.

Aggregation is treated probabilistically. Particle *i* undergoes aggregation during a time step if

rand() <
$$\frac{1 - exp[in]}{2 * t_{coag,i}}$$
 (S23)

where rand() is a random number between 0 and 1. Particle *j*, the particle that aggregates with particle *i* during the time step (i.e., the mass of particle *j* is added to that of particle *i*, and particle *j* is removed from the sample) is found using the "inverse method," which sums the probabilities of collision between particles *i* and *j*, P_{ij} , according to Eq. S24 until it reaches a particle *j* for which the summation exceeds a new random value rand().

select j' for which

$$rand() > \sum_{\substack{j=1\\j\neq i}}^{j} P_{ij} \qquad P_{ij} = \frac{\alpha_{ij}\beta_{ij}}{\sum_{j\neq i}\alpha_{ij}\beta_{ij}}$$
(S24)

If the number of particles in the sample drops below half of its original value, the entire population is doubled (by exact replication of the current sample) to prevent errors that arise as the number of particles in the sample trends towards zero. The solution volume is doubled when the sample is doubled, a so-called "stepwise constant-volume" approach.

S1.5. Population Balance #3: The Direct Quadrature Method of Moments (DQMOM) DQMOM approximates the particle size distribution as a sum of *i* Dirac delta functions with *n* weights w_i at locations (abscissas) $m_{i,i} = 1 \dots n$.

$$f(m) = \sum_{i=1}^{n} w_i \delta(m - m_i)$$
(S25)

In the univariate case (i.e., when only one internal coordinate is considered), this representation is mathematically identical to the quadrature point approximation used in classical QMOM (Equation S12).¹¹ In the DQMOM, however, the continuity equation (Equation S4) is re-written in terms of the derivatives of the weights and abscissas of the distribution so that the quadrature points may be evolved *directly* at each time step. This approach contrasts with that of classical QMOM, for which the continuity equation is expressed in terms of the derivatives of the moments such that quadrature points must be recalculated from the moment set at each time step (e.g., using a matrix inversion procedure, see Section S1.2.e.ii). Direct QMOM is, unsurprisingly, much faster than the classical approach.¹¹

S1.5.a. Numerical solution of the DQMOM

Marchisio and Fox (2005) derive the DQMOM formulation for the Williams spray equation, a specific implementation of the PBE (Equation S4) that accounts for non-homogeneous flow.^{11, 18} We focus here on implementation of their method in a simple batch reactor model (no-flow, homogeneous). Based on ref 18, we propose two means of addressing the dissolution flux problem.

Let a_i and b_i describe the evolution of weights and weighted abscissas over time

$$a_i = \frac{\partial w_i}{\partial t}, b_i = \frac{\partial (w_i m_i)}{\partial t}$$
(S26)

 a_i and b_i may then be found by solving the following system of equations, where S_k is a placeholder for functions that describe the evolution of the particle size distribution over time due to specific processes (compare to Equation S14).³¹

$$S_k = (1-k)\sum_{i=1}^n m_i^k a_i + k\sum_{i=1}^n m_i^{k-1} b_i$$

$$\bar{S}_k = S_{k,diss} + S_{k,agg}$$

$$S_{k,diss} = k \sum_{i=1}^{n} m^{k-1} A_{i} w_{i}$$

$$S_{k,agg} = \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \alpha_{ij} \beta_{ij} [(m_{i} + m_{j})^{k} - m_{i}^{k} - m_{j}^{k}] w_{i} w_{j}$$
(S27)

Equation S27 is solved with linear algebra as described in the Appendix of ref 11.

We use the Euler method in conjunction with a_i and b_i to update the weights and abscissas from one time step to the next. The moments may be determined from the set (m_i, w_i) at any time step by simple application of the quadrature approximation (Equation S12).

S1.5.b. Error in the DQMOM

Two sources of error in DQMOM are of special importance: The matrix defined by the coefficients on the left-hand side of Equation S27 may be ill-conditioned, or it may be singular.

An "ill-conditioned" matrix is one for which error is introduced during matrix inversion because the solution to the linear equation is highly sensitive to round-off error in the coefficient matrix. Poorly conditioned matrices have higher condition numbers than well-conditioned matrices, where the condition number is defined as the ratio of the largest singular values of the matrix to the smallest. In numerical methods, ill-conditioning causes numerical instability.

We found that ill-conditioning occurred readily during NP aggregation because it causes a rapid increase in the values of the abscissas used to calculate the coefficient matrix. We solved this problem by re-scaling the abscissas at each time step using the scale factor introduced in Section 2.4 of ref 18, $\max(m_i), i = 1...n$. In our case, re-scaling was not needed in the absence of aggregation. Furthermore, we found that this simple re-scaling procedure made the stability of the DQMOM comparable to that of the EQMOM and the SM. Thus we did not attempt more rigorous approaches such as singular value decomposition and/or iterative solution methods.^{18, 31}

When the condition number of a matrix is infinite, the matrix is *singular*. In the DQMOM, singularity reflects a lack of independence in the moment sequence, which occurs when two or more abscissas are identical (i.e., the distribution has zero variance). In this case, the system of equations does not have a unique solution.¹¹ In our experience, this rare but fatal error often results from initial conditions¹⁰ and can generally be eliminated by reducing the number of quadrature points; *n* should not, in any case, exceed 5 or $6.^{31}$ Alternatively, the problem can usually be solved by perturbing non-distinct abscissas (keeping weights the same) or by averaging the values of a_i and b_i found at neighboring points.¹¹

S1.5.c. Estimating dissolution flux with ratio constraints

As described in Section S1.2.e.iii, a flux term must be added to Equation S27 when NPs are able to undergo complete dissolution.

$$S_{k} = (1-k)\sum_{i=1}^{n} m_{i}^{k} a_{i} + k\sum_{i=1}^{n} m_{i}^{k-1} b_{i} + \delta_{k0}\varphi$$
(S28)

Here, φ is the dissolution flux and δ_{k0} equals one for k=0 and zero for any other value of k.

Equation S28 assumes that the lower boundary of the particle size distribution occurs at zero. In fact, the DQMOM is implemented on a semi-infinite domain, [0, Inf), rather than the finite domain $[m_{min}, m_{max}]$ used in the SM and (Beta) EQMOM. However, we found that the SM and the EQMOM were insensitive to our choice of m_{min} . Thus any error arising from the use of a different lower boundary in the DQMOM had no appreciable effect on model predictions.

The EQMOM (described below) tackles the dissolution flux problem head-on, reconstructing the particle size distribution at each time step in order to evaluate it. Since no reconstruction is available in the DQMOM, we are left with a system of equations that has one too many unknowns. As suggested by ref 18, however, we can approximate a solution by adding two more constraints to Equation S28. These "ratio constraints," which are applied only when calculating the influence of dissolution on the weights and abscissas, simply state that the change in the particle size distribution due to dissolution will be smooth.

$$\frac{d}{dt} \left(\frac{w_i}{w_{i+1}} \right) = 0, \ \frac{d}{dt} \left(\frac{m_i}{m_{i+1}} \right) = 0 \tag{S29}$$

The ratio constraints for the weights (see Section 2.3 of ref 18 for the derivation) provide a new system of equations which can be solved for i=1,...,n-1 (e.g., via matrix inversion) to find b_i .

$$w_{i+1}m_{i+1}b_{i}^{*} - w_{i}m_{i}b_{i+1}^{*} = E_{i}$$

$$E_{i} = w_{i}w_{i+1}(m_{i}A_{i+1} - m_{i+1}A_{i})$$
where $b_{i}^{*} = b_{i} - w_{i}A_{i}$
(S30)

Once b_i is known, a_i is found using Equation S31

$$a_{i} = \frac{w_{i}k\sum_{i=1}^{n}m_{i}^{k-1}(b^{*})}{(k-1)\sum_{i=1}^{n}m_{i}^{k}w_{i}}$$
(S31)

Any value of *k* other than 1 may be used in Equation S31.

Finally, solving Equation S28 for k=0 gives an approximation of the dissolution flux

$$\varphi = -\sum_{i=1}^{n} a_i \tag{S32}$$

 φ cannot be negative. If the procedure described above results in $\varphi < 0$, it is set to zero along with a_i and b_i^* .

In traditional DQMOM (Equation S27), scaling factors are only applied to the abscissas to ensure numerical stability (Section S1.5.b). When the dissolution flux term is added, weights

must be rescaled as well. We use the scaling factor $\sum_{i}^{n} w_{i}$ as suggested by ref 18.

Because the ratio constraints assume that the particle size distribution transforms smoothly over time, it is expected to perform poorly for highly monodisperse particle

populations. In such cases, traditional DOMOM may work better. The following simple procedure is employed: Whenever an abscissa crosses the lower size boundary, its corresponding weight is set to zero. The abscissa itself remains unchanged.

S1.5.d. Initial conditions

The DQMOM uses an efficient and relatively simple approach to transform the weights and abscissas of the particle size distribution over time in response to aggregation and dissolution. However, it does not specify the initial value of the set (w_i, m_i) . At t = 0, we express the locations and weights of the initial quadrature points in terms of the lower order moments of the distribution and solve using a matrix inversion procedure (the Product Difference algorithm, see Section S1.2.e.ii).

S1.6. Population Balance #4: (Beta) Extended Quadrature Method of Moments (EQMOM)

As its name suggests, the Extended Quadrature Method of Moments is an extension of classical OMOM (Section S1.2.e). In both methods, the particle size distribution is approximated by a set of quadrature points, which are calculated from the lower-order moments of the distribution at each time step using a matrix inversion algorithm, and the moments are evolved directly at each time step.

In the classical QMOM and the DQMOM, the PSD is represented by a sum of Dirac delta functions. In the EQMOM, each abscissa m_i is instead assumed to describe the central tendency of a new statistical distribution, $\delta_{\sigma_{\beta}}(m,m_i)$. The entire distribution is thus described by a weighted sum of probability density functions (pdfs) as shown:

$$f(m) = \sum_{i=1}^{n} w_i \delta_{\sigma_\beta}(m, m_i)$$
(S33)

 $\delta_{\sigma_{\beta}}(m,m_i)$ takes a pre-specified form. We employ the Beta distribution (Beta EQMOM) in this work;¹⁹ provides details for both Beta and Gamma EQMOM.

When $\delta_{\sigma_{\beta}}(m,m_i)$ represents a Beta distribution, f(m) may be rewritten as follows:

$$f(m) = \sum_{i=1}^{n} w_i \frac{m^{\lambda_i^{-1}} (1-m)^{\mu_i^{-1}}}{B(\lambda_i, \mu_i)}$$
(S34)

where $\lambda_i = m_i / \sigma_\beta$ and $\mu_i = (1 - m_i) / \sigma_\beta$ are the parameters of the distribution and σ_β is a measure of the spread of each Beta distribution around each "primary" abscissa. Note that every primary abscissa is assumed to have the same σ_{β} . When $\sigma_{\beta} = 0$, EOMOM is equivalent to the DOMOM and (in the univariate case) the classical QMOM. Otherwise, σ_{β} is used to find a set of "secondary" quadrature points, each of which is distributed around the first. Thus EQMOM employs two nested quadrature steps at each time step.

Unlike the primary quadrature step, which only estimates 4-6 quadrature points with accuracy, the secondary quadrature step is highly efficient and accurate up to any number of quadrature points. As such the EOMOM provides two relatively accurate approximations of the PSD: Equation S34 and the discrete "dual quadrature approximation," Equation S43 (below). As described in Section S1.6.f, Equation S34 can be used to (1) reconstruct the particle size distribution from its quadrature points and (2) estimate the particle efflux from the system due to complete dissolution.

S1.6.a. First coordinate transformation

The Beta EQMOM defines the particle size distribution on the domain [0, 1], rather than upon the finite interval $[m_{min}, m_{max}]$.^{13, 43} At each time step, the first step in the BEQMOM is thus to perform the following coordinate transformation on the moment set calculated during the previous time step⁴³

$$\tilde{\mu}_{k} = \frac{1}{(m_{max} - m_{min})^{k}} \sum_{j=0}^{k} \frac{k!}{j!(k-j)!} (-m_{min})^{k-j} \mu_{k}$$
(S35)

A few notes are in order regarding our choice of moments. In the DQMOM and the SM, we solve for the fractional moments of the distribution. In contrast, for simplicity, we tracked only the integer moments in EQMOM. Fractional moments (e.g., as shown in Figure 2) were estimated *ex post facto* from the reconstructed distribution at each time step using Equation S11 and Equation S34.

The matrix inversion algorithm used in classical QMOM (e.g., Product-Difference) requires the first 2n moments of the distribution (where *n* is the number of quadrature points). The EQMOM requires one additional moment (2n+1) in order to find σ_{β} . The DQMOM and the SM do not rely on a matrix inversion procedure, so any choice of moments will do.

S1.6.b. Set-up for primary quadrature

EQMOM uses an iterative procedure to simultaneously select σ_{β} and determine the set of primary quadrature points. This step begins with an initial guess for σ_{β} , such as its theoretical lower bound of zero (see Section S1.6.c for details on the bounds of σ_{β}).

The parameters of a beta distribution have a known relationship to its moments:

$$\mu_{k} = \frac{m_{i} + (k-1)\sigma_{\beta}}{1 + (k-1)\sigma_{\beta}}\mu_{k-1}, k > 0$$
(S36)

Let us call the set of (transformed) moments that could be estimated from the primary quadrature points of the distribution the "star moments:"

$$\tilde{\mu}_{k}^{*} = \sum_{i=1}^{n} m_{i}^{k} w_{i}$$
(S37)

Equation S36 suggests that the (transformed) moment set of the distribution, which is known from the previous time step, can be expressed as a function of the 2n (transformed) star moments of the distribution and a set of k coefficients, γ_k , which are solely a function of σ_β (see ref 19 for the derivation).

$$\tilde{\mu}_{k} = \gamma_{k} \tilde{\mu}_{k}^{*} + \gamma_{k-1} \mu_{k-1}^{*} + \dots + \gamma_{1} \tilde{\mu}_{1}^{*} \text{ for } k \ge 1$$
(S38)

For example, $\tilde{\mu}_0 = \tilde{\mu}_0^*$

 $\tilde{\mu}_1 = \tilde{\mu_1^*}$

$$\begin{split} \tilde{\mu}_{2} &= \frac{1}{1 + \sigma_{\beta}} (\tilde{\mu}_{2}^{*} + \sigma_{\beta} \tilde{\mu}_{1}^{*}) \\ \tilde{\mu}_{3} &= \frac{1}{(1 + 2\sigma_{\beta})(1 + \sigma_{\beta})} (\tilde{\mu}_{3}^{*} + 3\sigma_{\beta} \tilde{\mu}_{2}^{*} + 2\sigma_{\beta}^{2} \tilde{\mu}_{1}^{*}) \\ \tilde{\mu}_{4} &= \frac{1}{(1 + 3\sigma_{\beta})(1 + 2\sigma_{\beta})(1 + \sigma_{\beta})} (\tilde{\mu}_{4}^{*} + 6\sigma_{\beta} \tilde{\mu}_{3}^{*} + 11\sigma_{\beta}^{2} \tilde{\mu}_{2}^{*} + 6\sigma_{\beta}^{3} \tilde{\mu}_{1}^{*}) \end{split}$$

In order to find the star moments, μ_k^* (k=0, 1, ..., 2*n*-1), this system of equations is written in matrix form and solved via matrix inversion. The star moment set itself is then inverted using a classical QMOM algorithm such as Product-Difference in order to find the set of *n* primary quadrature points suggested by the initial choice of σ_β . Finally, these quadrature points are used in Equation S37 to estimate the 2*n*th star moment, $\tilde{\mu}_{2n}^*$.

The "goodness of fit" between the true distribution and the distribution suggested by our choice of σ_{β} is described by $\tilde{\mu}_{2n} - \tilde{\mu}_{2n}^{*}$, or Equation S39. Let us call this difference $J_i(\sigma_{\beta})$.

$$J_{i}(\sigma_{\beta}) = \tilde{\mu_{2n}} - \gamma_{2n}\tilde{\mu_{2n}} - \gamma_{2n-1}\tilde{\mu_{2n-1}} - \dots - \gamma_{1}\tilde{\mu_{1}}^{*}$$
(S39)

The best choice for σ_{β} is the value for which $J_i(\sigma_{\beta})=0$. We use a root-finding algorithm to find the smallest σ_{β} which meets this condition.

S1.6.c. Procedure to find σ_{β}

 σ_{β} is bounded on the interval $[0, \sigma_{\beta,max}]$, where $\sigma_{\beta,max}$ is either chosen arbitrarily¹³ or is calculated from the Hankel determinants of the distribution, which are defined as follows for all integer moments *k*:

$$\underline{H}_{2k} = \begin{vmatrix} \tilde{\mu}_{0}^{*} & \cdots & \tilde{\mu}_{k}^{*} \\ \vdots & \ddots & \vdots \\ \tilde{\mu}_{k}^{*} & \cdots & \tilde{\mu}_{2k}^{*} \end{vmatrix}, \overline{H}_{2k+1} = \begin{vmatrix} \tilde{\mu}_{0}^{*} - \tilde{\mu}_{1}^{*} & \cdots & \tilde{\mu}_{k}^{*} - \mu_{k+1}^{*} \\ \vdots & \ddots & \vdots \\ \tilde{\mu}_{k}^{*} - \tilde{\mu}_{k+1}^{*} & \cdots & \tilde{\mu}_{2k}^{*} - \mu_{2k+1}^{*} \end{vmatrix},$$

$$\underline{H}_{2k+1} = \begin{vmatrix} \tilde{\mu}_{1}^{*} & \cdots & \tilde{\mu}_{k+1}^{*} \\ \vdots & \ddots & \vdots \\ \tilde{\mu}_{k+1}^{*} & \cdots & \tilde{\mu}_{2k+1}^{*} \end{vmatrix}, \overline{H}_{2k} = \begin{vmatrix} \tilde{\mu}_{1}^{*} - \tilde{\mu}_{2}^{*} & \cdots & \tilde{\mu}_{k}^{*} - \mu_{k+1}^{*} \\ \vdots & \ddots & \vdots \\ \tilde{\mu}_{k}^{*} - \tilde{\mu}_{k+1}^{*} & \cdots & \tilde{\mu}_{2k-1}^{*} - \tilde{\mu}_{2k}^{*} \end{vmatrix}$$
(S40)

The Hankel determinants (Eq. 1.4.3, p. 20 in ref 43) are first used in Equation S41 (Eq. 1.4.5, p. 20 in 43) to find the "canonical" moments, p_k^* , corresponding with the (transformed) star moment set $\tilde{\mu}_k^*$. $\sigma_{\beta,max}$ is then expressed in terms of the canonical moments (Equation S42):

$$\tilde{p}_{k}^{*} = \frac{\underline{H}_{2k+1}\overline{H}_{2k}}{\underline{H}_{2k+1}\overline{H}_{2k} + \overline{H}_{2k+1}\underline{H}_{2k}} \quad \text{where } \underline{H}_{-1} = \overline{H}_{-1} = \overline{H}_{0} = \overline{H}_{0} = 1$$
(S41)

$$\sigma_{\beta,max} = \begin{pmatrix} \tilde{p}_{2}^{*}(1-\tilde{p}_{3}^{*}) \\ 1-\tilde{p}_{1}^{*}-2*\tilde{p}_{2}^{*}-\tilde{p}_{1}^{*}\tilde{p}_{2}^{*}+2\tilde{p}_{2}^{*}\tilde{p}_{3}^{*} \\ 0.99999*\frac{\tilde{p}_{2}^{*}}{1-\tilde{p}_{2}^{*}} if \tilde{p}_{3}^{*} = \frac{\tilde{p}_{1}^{*}+\tilde{p}_{2}^{*}-\tilde{p}_{1}^{*}\tilde{p}_{2}^{*}}{1+\tilde{p}_{2}^{*}} \\ \frac{\tilde{p}_{2}^{*}\tilde{p}_{3}^{*}}{\tilde{p}_{1}^{*}+\tilde{p}_{2}^{*}-\tilde{p}_{1}^{*}\tilde{p}_{2}^{*}-2\tilde{p}_{2}^{*}\tilde{p}_{3}^{*}} if \tilde{p}_{3}^{*} < \frac{\tilde{p}_{1}^{*}+\tilde{p}_{2}^{*}-\tilde{p}_{1}^{*}\tilde{p}_{2}^{*}}{1+\tilde{p}_{2}^{*}} \\ \end{cases}$$
(S42)

The coefficient 0.99999 is added in the second case to ensure that the $\sigma_{\beta,max}$ remains finite when $\tilde{p}_2^* = 1$ (Dr. Frédérique Laurent-Nègre, personal correspondance).

Recall that the purpose of the search procedure is to find the smallest value of σ_{β} such that $J_i(\sigma_{\beta}) = 0$. Once the bounds on σ_{β} are known, they can be narrowed using an unbounded search procedure such as the secant method until a new interval is found for which $J_i(\sigma_{\beta,min})$ and $J_i(\sigma_{\beta,max})$ straddle the *y*-axis. Since $J_i(0)$ is, by definition, positive, this search procedure generally reduces $\sigma_{\beta,max}$ until $J_i(\sigma_{\beta,max}) < 0$. At this point, we may switch to a bounded search procedure such as Ridder's method in order to rapidly converge on a solution.

We found that it sometimes helped to start our search procedure with a non-zero but low lower bound such as 10^{-50} . However, the reader should be aware that this approach may require other small changes to the search procedure; $J_i(0)$ is guaranteed to be non-negative, but no such guarantee applies to an arbitrarily selected non-zero lower bound.

In practice, the value of σ_{β} chosen by the search procedure may lead to a "unrealizable" or invalid star moment set, or one for which one or more abscissas fall outside of the size domain. The star moment set is realizable if its lowest Hankel determinant (Equation S40) is positive (see Appendix B in ref 19 for details). If our moment set was found to be unrealizable, we simply discarded that estimate in favor of the smallest value of σ_{β} tried during the search procedure for which a realizable star moment set was generated, as suggested by ref 13.

S1.6.d. Secondary quadrature and the second coordinate transformation

We have now successfully discovered σ_{β} and a set of primary quadrature points and can proceed to find the secondary quadrature points of the distribution.

By performing a second (simpler) coordinate transformation on the transformed moment set to define it on the domain [-1,1] instead of [0,1], we can express the beta distribution as a Jacobi polynomial that is orthogonal with respect to the following weight function $w(t) = (1-t)^{\varepsilon}(1+t)^{\zeta}$ where $\varepsilon = \mu_i - 1$ and $\zeta = \lambda_i - 1$.¹⁹ The quadrature points associated with Jacobi polynomials can then be calculated with high accuracy and low computational demands. Details are provided by ref 44 (Chapter 3). This algorithm closely mirrors the Product-Difference and modified Wheeler (matrix inversion) algorithms as described by refs 10, 16, 37.

Briefly, ε and ζ are used in the following recurrence relation to determine a_j and b_j , the diagonals and co-diagonals of the Jacobi matrix, J (Eq. 3.143a p.84 of ref 44):

$$a_j = \frac{\zeta^2 - \varepsilon^2}{(2j + \varepsilon + \zeta)(2j + \varepsilon + \zeta + 2)}$$

$$b_{j} = \frac{4j(j+\varepsilon)(j+\zeta)(j+\varepsilon+\zeta)}{(2j+\varepsilon+\zeta-1)(2j+\varepsilon+\zeta)^{2}(2j+\varepsilon+\zeta+1)}$$
$$\begin{bmatrix} a_{0} & \sqrt{b_{1}} \\ \sqrt{b_{1}} & a_{1} & \sqrt{b_{2}} & \ddots \\ & \ddots & \ddots \\ & & \sqrt{b_{N-1}} & a_{N-\frac{1}{2}} & \sqrt{b_{N}} \\ & & & \sqrt{b_{N}} & a_{N} \end{bmatrix}$$

The i^{th} abscissa associated with each secondary quadrature point is the i^{th} eigenvalue of the Jacobi matrix. The i^{th} weight, w_i , is the squared value of the first component of the i^{th} eigenvector.

Once secondary weights and abscissas are determined for each primary quadrature point to create the two-dimensional set of secondary quadrature points, $\binom{w_{i_1,i_2}, m_{i_1,i_2}}{w_{i_1,i_2}}$, we perform another coordinate transformation to once again define them on the domain [0,1].

We can now calculate the so-called "dual quadrature" representation of the particle size distribution:

$$f(m) = \sum_{i_1=1}^{n_1} \sum_{i_2=1}^{n_2} \rho_{i_1, i_2} \delta(m - m_{i_1, i_2})$$
where $\rho_{i_1, i_2} = w_{i_1} w_{i_1, i_2}$
(S43)

Note that $\delta(m - m_{i_1, i_2})$ is the Dirac delta function as seen in Equation S25, and not the continuous alternative seen in Equation S33, $\delta_{\sigma_\beta}(m, m_i)$.

S1.6.e. Evolution of the moments

Ref 19 use the dual quadrature approximation to derive expressions for the moment evolution $d\mu_k$

equations, dt. The equations for dissolution and aggregation closely parallel the moment evolution equations used in classical QMOM (Equation S14) and the source terms used in DQMOM (Equation S27). Note that the first coordinate transformation must be reversed before evolving the moments from one time step to the next in order to place the moment set back on its true domain, $[m_{min}, m_{max}]$.

$$\begin{bmatrix}
\frac{d\mu_{k}}{dt}\\
\frac{d}{dt}
\end{bmatrix}_{agg} = \frac{1}{2} \sum_{i_{1}=1}^{n_{1}} \sum_{i_{2}=1}^{n_{2}} \sum_{j_{1}=1}^{n_{1}} \sum_{j_{2}=1}^{n_{2}} \rho_{i_{1}i_{2}} \rho_{j_{1}j_{2}} [(m_{i_{1}i_{2}} + m_{j_{1}j_{2}})^{k} - m_{i_{1}i_{2}}^{k} - m_{j_{1}j_{2}}^{k}] \alpha_{i_{1}i_{2}j_{1}j_{2}} \beta_{i_{1}i_{2}j_{1}j_{2}} \beta_{i_{1}i_{2}j_{2}} \beta_{i_{1}i_{2}} \beta_{i_{1}i_{2}} \beta_{i_{1}i_{2}j_{2}} \beta_{i_{1}i_{2}} \beta_{i_{1}i_{2}} \beta_{i_{1}i_{2}}} \beta_{i_{1}i_{2}} \beta_{i_{1}i_{2}} \beta_{i_{1}i_{2}} \beta_{i_{1}i_{2}} \beta_{i_{1}i_{2}}} \beta_{i_{1}i_{2}} \beta_{i_{1}i_{2}} \beta_{i_{1}i_{2}} \beta_{i_{1}i_{2}} \beta_{i_{1}i_{2}} \beta_{i_{1}i_{2}} \beta_{i_$$

S1.6.f. Calculation of the dissolution flux

Equation S34 allows us to reconstruct the particle size distribution from its primary quadrature points at each time step. Evaluating Equation S34 at m_{min} also allows us to use Equation S15 to approximate the dissolution flux. Of course, for our numerical solution, we must estimate the dissolution flux over a time step rather than at a particular time. To do so, we take the integral of Equation S34 over the range of particle sizes expected to dissolve completely within that time step (calculated using Equation S6).

The dissolution flux may also be approximated as the sum of the weights (particle number) associated with each quadrature point that crosses the lower boundary during a time step. However, this approach is significantly slower than the integral approach because it requires far more secondary abscissas per primary abscissa for accuracy. For example, upwards of 1000 abscissas could be required, as opposed to the (e.g.) $5 \le n_2 \le 80$ suggested when using the integral approximation.¹⁹

S1.7. Analytical Solutions

Consider a lognormal distribution such as we have at the start of our simulation. The following are some useful properties of this distribution (and some of their applications in this work).

Probability density function (used in the analytical solution):

$$f(m,t) = \frac{N}{\sigma_{ln}m\sqrt{2\pi}}e^{-\frac{(\ln m - \mu_{ln})^2}{2(\sigma_{ln}^2)}}$$
(S46)

Cumulative distribution function, where erfc() is the complementary error function (used in the Sectional Method to bin the initial NP population):

$$F(m,t) = \frac{N}{2} erfc \left(-\frac{\ln m - \mu_{ln}}{\sigma_{ln}\sqrt{2}} \right)$$
(S47)

Fractional moments (used to initialize the moments in the EQMOM and DQMOM):

$$\mu_k(t) = N e^{k\mu_{ln} + \frac{1}{2}k^2 \sigma_{ln}^2}$$
(S48)

Williams et al. (1982) provide the following analytical solution for a particle size distribution dm

with any known initial functional form n_0 dissolving according to the rate law $\frac{dm}{dt} = F_d m^d$, where F_d and d are arbitrary constants:⁴⁵

$$f(m,t) = \left[1 - \frac{(1-d)F_d t}{m^{1-d}}\right]^{\frac{d}{1-d}} f_0(\left[m^{1-d} - (1-d)F_d t\right]^{1/(1-d)})$$
(S49)

In our case, under sink conditions (i.e., $[Me^+]_{t=0}$), d = 2/3 and $F_d = -k_{S,pb}[Me^+]_{eq}$ (see Equation S6).

Park et al. (2000) provide an analytical solution for aggregation of an initially lognormal particle size distribution according to the rate law given in Equation S9. In this case, the distribution is assumed to remain lognormal (of the form given by Equation S46).⁴⁶ Parameters

change over time according to Equation S50, where
$$K = \alpha \frac{2k_B T}{3\mu} \text{ (see Equation S9), } \sigma_d(t) = e^{\sigma_{ln}/3}$$

and $v_d(t) = e^{\mu_{ln}}$.
$$ln^2 \sigma_d = \frac{1}{9} ln \left[2 + \frac{X}{Y} \right]$$
$$v_d = v_{d,0} \frac{\exp\left(9 \ln^2 \sigma_{d,0}/2\right) Y}{\left[2 + \frac{X}{Y}\right]}$$
$$N = N_0 \frac{1}{Y}$$
where
$$X = \exp\left(9 \ln^2 \sigma_{d,0}\right) - 2$$
$$Y = 1 + \left\{1 + \exp\left(9 \ln^2 \sigma_{d,0}/D_f^2\right)\right\} K N_0 t$$
(S50)

Equation S49 and Equation S50 were then used in the appropriate expressions (e.g., the moment definition equation, Equation S11) in order to calculate values of interest (values plotted in Figure 2 of the main text).

Integral expressions were only evaluated over the particle size domain. Thus, in essence, particle flux during dissolution was accounted for simply by omitting from the solution the portion of the size distribution that fell below the lower size boundary.



Figure S1. Model results (dot-dashed blue line, from the Sectional Method) compared to experimental data (yellow dots) for the calibration procedure used to provide an order-of-magnitude estimate of the ZnO NP dissolution rate and aggregation rate for all test cases.Data are from an experiment with moderately hard water (MHW) at 25°C (compare to Fig. 3b and Fig. 1c in the cited work).² Model inputs: Mean (52 nm), standard deviation (9 nm), equilibrium ion concentration (2.04 mg/L), and initial concentration (20 mg/L). We assume that the hydrodynamic diameter of the particles is 60% of their collision diameter, given here as the characteristic diameter.²¹



Figure S2. Model results for dissolution of 100 g/m^3 of a lognormal population of NPs (low skew) with different initial particle sizes under sink conditions (ion concentration in bulk solution is set to zero). Solid grey = Analytical Solution, Dot-dashed blue = Sectional Method (SM), Dashed orange = Direct Quadrature Method of Moments (DQMOM) with ratio constraints, Dashed yellow = DQMOM without ratio constraints, Dotted red = Extended Quadrature Method of Moments (EQMOM), Solid green = Direct Simulation Monte Carlo (DSMC).



Figure S3. Model results for dissolution of 100 g/m³ of a lognormal population of NPs (low skew) with different initial particle sizes for dissolution to equilibrium(ion concentration in bulk solution increases until equilibrium is reached, at which point dissolution stops). Dot-dashed blue = SM, Dashed orange = Direct DQMOM with ratio constraints, Dashed yellow = DQMOM without ratio constraints, Dotted red = EQMOM, Solid green = DSMC. No analytical solution is available for this case.



Figure S4. Model results for aggregation of 100 g/m³ of a lognormal population of NPs (low skew) with different initial particle sizes. Dot-dashed blue = SM, Dashed orange = DQMOM with ratio constraints, Dotted red = EQMOM, Solid green = DSMC. Analytical solution not shown.



Figure S5. Error in the EQMOM (dotted red), the DQMOM without ratio constraints (dashed orange), the SM (dot-dashed blue), and DSMC (solid green) compared to the analytical solution (solid grey) for estimates of the evolution of the (normalized) number concentration during dissolution. Worst-case scenario ("sink conditions") are assumed in order to maximize possible error. The error calculation is not normalized. Error remains below 9% for the EQMOM, which also largely captures the nature of the dissolution curve.



Figure S6. Initial particle size distributions in the Sectional Method for the error analysis shown in Figure 4. Distributions were normalized by the bin width so that they could be overlain on the continuous distribution as shown.



Figure S7. Effect of the resolution of the size coordinate on error in the SM for aggregation of \sim 50±10 nm NPs. Error is given relative to the analytical solution (solid grey).Unlike the numerical solution for dissolution, which can use an arbitrary binning scheme, the numerical solution for aggregation requires the geometric binning scheme defined in Equation 2 (main text). Thus *q* could not be reduced below 1 and the number of bins could not be reduced below 47.



Figure S8. Initial particle size distributions used in the analysis presented in Figure 5 (main text) transformed to be in terms of the internal coordinate, particle mass. Size distributions expressed in terms of mass are more skewed than distributions expressed in terms of diameter. The solid black curve represents the initial size distribution for 50 ± 10 nm NPs in our "base case."



Figure S9. First-order linear inhomogenous equation (Equation 27, main text) fit for the case of dissolution to equilibrium (compare to Figure 5). The equilibrium ion concentration was calculated from the Ostwald-Freundlich relation using the initial surface-weighted geometric mean diameter. Benchmark curves (solid grey) in (a) represent the SM validated against the EQMOM and the DQMOM. In (b), curves represent the DQMOM validated against the EQMOM.

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