Supplemental Information

An Analytic Equation for the Volume Fraction of Condensationally Grown Mixed Particles and Applications to Secondary Organic Material Produced in Continuously Mixed Flow Reactors

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S1. Derivation of probability density function p of volume fraction

The final result of this derivation appears as Equation 5 in the main text.

$$\begin{aligned} p(\varepsilon) &= p(\varepsilon; d) \\ &= \left(\frac{dN}{d\varepsilon} \Big|_d \right) / \left(\int_0^1 \frac{dN}{d\varepsilon} \Big|_d d\varepsilon \right) \\ &= \left(\frac{dN}{dd} \Big|_\varepsilon \frac{dN}{d\varepsilon} \Big|_d \right) / \left(\frac{dN}{dd} \Big|_\varepsilon \int_0^1 \frac{dN}{d\varepsilon} \Big|_d d\varepsilon \right) \\ &= \left(\frac{\partial^2 N}{\partial d \partial \varepsilon} \right) / \left(\int_0^1 \frac{\partial^2 N}{\partial d \partial \varepsilon} d\varepsilon \right) \\ &= f(d, \varepsilon) / \left(\int_0^1 f(d, \varepsilon) d\varepsilon \right) \\ &= \frac{f(d, \varepsilon)}{n(d)} \\ &= -\frac{f(d, z)}{3z^2 n(d)} \end{aligned} \tag{5}$$

Throughout Supplemental Information, equation numbers not preceded by “S” refer to equations in the main text.

S2. Derivation of $f(d, t)$, $f(d, d_0)$, $f(d_0, t)$, $f(d, \varepsilon)$, and $f(d, z)$ for a CMFR

By Equation S5 of Kuwata and Martin (2012) for a CMFR, the distribution function $f(d, t; d_0)$ is as follows:

$$f(d, t; d_0) = \frac{\partial^2 N}{\partial d \partial t} = \begin{cases} \frac{e^{-t/\tau}}{\tau} \frac{(d + \lambda)}{(d_0 + \lambda)} n_0(d_0), & \text{if } t \geq 0 \ \&\& \ d_0 \geq 0 \ \&\& \ d \geq d_0 \\ 0, & \text{if } t < 0 \ || \ d_0 < 0 \ || \ d < d_0 \end{cases} \quad (\text{S1})$$

This equation as written overstates the degrees of freedom because Equation 6 provides additional constraints among d , d_0 , and t . With this constraint in mind, substitution of any of the three variables as a function of the other two means formulations can be written for the bivariate functions $f(d, d_0)$, $f(d, t)$, $f(d_0, t)$ (see next few paragraphs; summary in Table 1). By additional use of Equation 1, as well as the definition of z , we can obtain $f(d, \varepsilon)$ and $f(d, z)$. Derivations of these functions follow in the next paragraphs.

Using $d_0(d, t)$ of Equation 6 to eliminate d_0 from Equation S1 derives the following result for $f(d, t)$:

$$f(d, t) = \frac{\partial^2 N}{\partial d \partial t} = \begin{cases} \frac{e^{-t/\tau}}{\tau} \frac{(d + \lambda)}{(x + \lambda)} n_0(x), & \text{if } x \geq 0 \\ 0, & \text{if } x < 0 \end{cases} \quad (7)$$

for $x = \left((d + \lambda)^2 - 2\beta t \right)^{1/2} - \lambda$. This result appears as Equation S8 in Kuwata and Martin (2012)

and as Equation 7 in the main text. For this equation, the condition $t \geq 0 \ \&\& \ d_0 \geq 0 \ \&\& \ d \geq d_0$ reduces to $d^2 + 2d\lambda - 2\beta t \geq 0$ because (1) $t \geq 0$ is always implied for t taken as an independent variable, (2) $d_0 \geq 0$ results directly in the stated condition of $d^2 + 2d\lambda - 2\beta t \geq 0$ by using the replacement of $d_0(d, t)$ from Equation 6, and (3) $d \geq d_0$ evaluates to hold for $t \geq 0$ and therefore must be true.

The relationship $f(d, t; d_0)$ defined as $\partial^2 N / \partial d \partial t$ in Equation S1 can be re-expressed to define $f(d, d_0)$ as $\partial^2 N / \partial d \partial d_0$ by obtaining $\partial t / \partial d_0$ from the derivative of Equation 6. The result is as follows:

$$f(d, d_0) = \frac{\partial^2 N}{\partial d \partial d_0} = \begin{cases} -\frac{n_0(d_0)}{\beta\tau} (d + \lambda) \exp\left(-\frac{(d + \lambda)^2 - (d_0 + \lambda)^2}{2\beta\tau}\right), & \text{if } d \geq d_0 \\ 0, & \text{if } d < d_0 \end{cases} \quad (\text{S2})$$

The condition $t \geq 0$ & $d_0 \geq 0$ & $d \geq d_0$ reduces to $d \geq d_0$ for Equation S2 because (1) $t \geq 0$ becomes $(d + \lambda)^2 - (d_0 + \lambda)^2 \geq 0$ by use of $t(d, d_0)$ of Equation 6 and is therefore always true since we require $d \geq d_0$, (2) $d_0 \geq 0$ is always implied for d_0 taken as an independent variable, and (3) $d \geq d_0$ is the stated requirement for Equation S2. Figure S2 shows a density plot of Equation S2 as well as several cross-sections through the density plot.

The function $f(d, d_0)$ defined as $\partial^2 N / \partial d \partial d_0$ is transformed using Equations 1 and S2 into the following expression for $f(d, \varepsilon)$ defined as $\partial^2 N / \partial d \partial \varepsilon$ by use of $\partial d_0 / \partial \varepsilon$, as follows:

$$f(d, \varepsilon) = \frac{\partial^2 N}{\partial d \partial \varepsilon} = \frac{n_0 \left((1 - \varepsilon)^{1/3} d \right)}{3\beta\tau (1 - \varepsilon)^{2/3}} d (d + \lambda) \exp\left(-\frac{(d + \lambda)^2 - \left((1 - \varepsilon)^{1/3} d + \lambda \right)^2}{2\beta\tau}\right) \quad (8)$$

For Equation 8, the condition $t \geq 0$ & $d_0 \geq 0$ & $d \geq d_0$ incorporates the full range of $0 \leq \varepsilon \leq 1$ because (1) $t \geq 0$ becomes $1 + 2\lambda/d - z(z + 2\lambda/d) \geq 0$ by use of $\varepsilon(d, d_0)$ of Equation 1 and $t(d, d_0)$ of Equation 6 and can only be true provided that $0 \leq \varepsilon \leq 1$, (2) $d_0 \geq 0$ becomes $zd \geq 0$ by Equation 6 and is always true for the stated requirement of $0 \leq \varepsilon \leq 1$, and (3) $d \geq d_0$ becomes $1 \geq z$ and thus states the requirement of $0 \leq \varepsilon \leq 1$.

The function $f(d, \varepsilon)$ defined as $\partial^2 N / \partial d \partial \varepsilon$ is transformed from Equation 8 into the following expression for $f(d, z)$ defined as $\partial^2 N / \partial d \partial z$ by use of $\partial \varepsilon / \partial z$, as follows:

$$f(d, z) = \frac{\partial^2 N}{\partial d \partial z} = -\frac{d(d + \lambda)}{\beta\tau} \exp\left(-\frac{(d + \lambda)^2 - (zd + \lambda)^2}{2\beta\tau}\right) n_0(zd) \quad (9)$$

For completeness of the presentation, the function $f(d_0, t)$ defined as $\partial^2 N / \partial d_0 \partial t$ is as follows:

$$f(d_0, t) = \frac{\partial^2 N}{\partial d_0 \partial t} = \frac{n_0(d_0)}{\tau} e^{-t/\tau} \quad (\text{S3})$$

For Equation S3, the condition $t \geq 0 \ \&\& \ d_0 \geq 0 \ \&\& \ d \geq d_0$ incorporates the full range of $0 \leq \varepsilon \leq 1$ because (1) $t \geq 0$ and $d_0 \geq 0$ are always implied for t and d_0 taken as independent variables and (2) $d \geq d_0$ by Equation 6 becomes $t \geq 0$, which is always true. Figure S3 shows a density plot of Equation S3 as well as several cross-sections through the density plot.

S3. Derivation of probability density function $p(\varepsilon; d)$ for a CMFR

The probability density function $p(\varepsilon)$ at a diameter d is obtained by combining Equations 4, 5, and 9, as follows:

$$\begin{aligned} p(\varepsilon; d) &= -\frac{f(d, z)}{3z^2 n(d)} \\ &= -\frac{\frac{n_0(zd)}{3\beta\tau z^2} d(d+\lambda) \exp\left(-\frac{(d+\lambda)^2 - (zd+\lambda)^2}{2\beta\tau}\right)}{\int_1^0 \frac{n_0(z^*d)}{\beta\tau} d(d+\lambda) \exp\left(-\frac{(d+\lambda)^2 - (z^*d+\lambda)^2}{2\beta\tau}\right) dz^*} \\ &= \frac{n_0(zd) \exp\left(\frac{(zd+\lambda)^2}{2\beta\tau}\right)}{3z^2 \int_0^1 n_0(z^*d) \exp\left(\frac{(z^*d+\lambda)^2}{2\beta\tau}\right) dz^*} \end{aligned} \quad (10)$$

S4. Derivation of probability density function $p(\varepsilon; d)$ for a CMFR for $n_0(d)$ described by a single Dirac delta function

$$\begin{aligned}
 p(\varepsilon; d) &= \frac{N \delta(zd - d_0) \exp\left(\frac{(zd + \lambda)^2}{2\beta\tau}\right)}{3z^2 \int_0^1 N \delta(z^*d - d_0) \exp\left(\frac{(z^*d + \lambda)^2}{2\beta\tau}\right) dz^*} \\
 &= \frac{\delta(zd - d_0) d \exp\left(\frac{(zd + \lambda)^2}{2\beta\tau}\right)}{3z^2 \int_{-d_0}^{d-d_0} \delta(x) \exp\left(\frac{(x + d_0 + \lambda)^2}{2\beta\tau}\right) dx} \text{ for } x = z^*d - d_0 \text{ and } dx = d dz^* \quad (11) \\
 &= \frac{\delta(zd - d_0) d}{3z^2} \exp\left(\frac{(zd + \lambda)^2 - (d_0 + \lambda)^2}{2\beta\tau}\right)
 \end{aligned}$$

As a check on this result, we should get unity:

$$\begin{aligned}
 \int_0^1 p(\varepsilon; d) d\varepsilon &= \int_0^1 \delta(zd - d_0) d \exp\left(\frac{(zd + \lambda)^2 - (d_0 + \lambda)^2}{2\beta\tau}\right) dz \\
 &= \int_0^1 \delta(x) \exp\left(\frac{(x + d_0 + \lambda)^2 - (d_0 + \lambda)^2}{2\beta\tau}\right) dx \text{ for } x = z^*d - d_0 \text{ and } dx = d dz^* \quad (S4) \\
 &= \exp\left(\frac{(d_0 + \lambda)^2 - (d_0 + \lambda)^2}{2\beta\tau}\right) \\
 &= 1
 \end{aligned}$$

S5. Derivation of probability density function $p(\varepsilon; d)$ for a CMFR for $n_0(d)$ described by multiple Dirac delta functions

$$\begin{aligned}
 p(\varepsilon; d) &= \frac{\exp\left(\frac{(zd + \lambda)^2}{2\beta\tau}\right) \sum_{j=1}^k N_j \delta(zd - d_{0,j})}{3z^2 \sum_{j=1}^k \int_0^1 N_j \delta(z^*d - d_{0,j}) \exp\left(\frac{(z^*d + \lambda)^2}{2\beta\tau}\right) dz^*} \\
 &= \frac{d \exp\left(\frac{(zd + \lambda)^2}{2\beta\tau}\right) \sum_{j=1}^k N_j \delta(zd - d_{0,j})}{3z^2 \sum_{j=1}^k \int_{-d_{0,j}}^{d-d_{0,j}} N_j \delta(x) \exp\left(\frac{(x + d_{0,j} + \lambda)^2}{2\beta\tau}\right) dx} \quad \text{for } x = z^*d - d_{0,j} \text{ and } dx = d dz^* \\
 &= \frac{\frac{d}{3z^2} \sum_{j=1}^k N_j \delta(zd - d_{0,j})}{\sum_{j=1}^q N_j \exp\left(\frac{(d_{0,j} + \lambda)^2 - (zd + \lambda)^2}{2\beta\tau}\right)} \tag{12}
 \end{aligned}$$

The index change $k \rightarrow q$ in the last line for the denominator corresponds to the index of the last element of $\{d_{0,1}, d_{0,2}, \dots, d_{0,k}\}$ that satisfies $d - d_{0,j} > 0$, i.e., because the integral of the Dirac delta function must pass through zero for the term in the sum to survive.

The cumulative distribution function $c(\varepsilon)$ is then given as follows

$$\begin{aligned}
c(\varepsilon; d) &= \int_0^\varepsilon p(\varepsilon; d) d\varepsilon \\
&= \frac{d \sum_{j=1}^k \int_0^\varepsilon z^{-2} N_j \delta(zd - d_{0,j}) \exp\left(\frac{(zd + \lambda)^2}{2\beta\tau}\right) d\varepsilon}{3 \sum_{j=1}^q N_j \exp\left(\frac{(d_{0,j} + \lambda)^2}{2\beta\tau}\right)} \\
&= \frac{d \sum_{j=1}^k \int_z^1 N_j \delta(z^* d - d_{0,j}) \exp\left(\frac{(z^* d + \lambda)^2}{2\beta\tau}\right) dz^*}{\sum_{j=1}^q N_j \exp\left(\frac{(d_{0,j} + \lambda)^2}{2\beta\tau}\right)} \\
&= \frac{\sum_{j=1}^k \int_{zd-d_{0,j}}^{d-d_{0,j}} N_j \delta(x) \exp\left(\frac{(x+d_{0,j} + \lambda)^2}{2\beta\tau}\right) dx}{\sum_{j=1}^q N_j \exp\left(\frac{(d_{0,j} + \lambda)^2}{2\beta\tau}\right)} \quad \text{for } x = z^* d - d_{0,j} \text{ and } dx = d dz^* \\
&= \frac{\sum_{j=r}^q N_j \exp\left(\frac{(d_{0,j} + \lambda)^2}{2\beta\tau}\right)}{\sum_{j=1}^q N_j \exp\left(\frac{(d_{0,j} + \lambda)^2}{2\beta\tau}\right)}
\end{aligned} \tag{13}$$

The index changes $k \rightarrow q$ and $1 \rightarrow r$ in the last line for the numerator are required because the integral of the Dirac delta function must pass through zero for the term in the sum to survive: (1) $k \rightarrow q$ since $d - d_{0,j} > 0$ (else $\int g(x) \delta(x) dx = 0$) and (2) $1 \rightarrow r$ since $zd - d_{0,j} < 0$ (else $\int g(x) \delta(x) dx = 0$).

S6. Derivation of probability density function $p(\varepsilon; d)$ for a CMFR for $n_0(d)$ described by

Gauss functions

$$\begin{aligned}
 p(\varepsilon; d) \Big|_{\text{Gauss}} &= \frac{\exp\left(\frac{(zd + \lambda)^2}{2\beta\tau}\right) \sum_{|q|=1}^{\infty} \frac{N_q}{\sqrt{2\pi\sigma_q^2}} \exp\left(-\frac{(zd - \hat{d}_{0,q})^2}{2\sigma_q^2}\right)}{3z^2 \sum_{|q|=1}^{\infty} \frac{N_q}{\sqrt{2\pi\sigma_q^2}} \int_0^1 \exp\left(\frac{(z^*d + \lambda)^2}{2\beta\tau} - \frac{(z^*d - \hat{d}_{0,q})^2}{2\sigma_q^2}\right) dz^*} \\
 &= z^{-2} \xi \exp\left(\frac{y^2(zd)}{2\gamma_0}\right) \sum_{|q|=1}^{\infty} \frac{N_q}{\sqrt{2\pi\sigma_q^2}} \exp\left(-\frac{y^2(zd, 0, \hat{d}_{0,q})}{2\sigma_q^2}\right)
 \end{aligned} \tag{15}$$

for the normalization factor ξ give in the main text.

S7. Derivation of probability density function $p(\varepsilon; d)$ for a CMFR for $n_0(d)$ described by triangular functions

$$\begin{aligned}
p(\varepsilon; d)|_{\wedge} &= \frac{\exp\left(\frac{(zd + \lambda)^2}{2\beta\tau}\right) \sum_j N_j \begin{cases} m_{j1}zd + b_{j1} & d_{j1} \leq zd \leq d_{j2} \\ m_{j2}zd + b_{j2} & d_{j2} < zd \leq d_{j3} \\ 0 & \text{otherwise} \end{cases}}{3z^2 \sum_j N_j \int_0^1 \exp\left(\frac{(z^*d + \lambda)^2}{2\beta\tau}\right) \begin{cases} m_{j1}z^*d + b_{j1} & d_{j1} \leq z^*d \leq d_{j2} \\ m_{j2}z^*d + b_{j2} & d_{j2} < z^*d \leq d_{j3} \\ 0 & \text{otherwise} \end{cases} dz^*} \\
&= \frac{\exp\left(\frac{(zd + \lambda)^2}{2\beta\tau}\right) \sum_j N_j \begin{cases} m_{j1}zd + b_{j1} & d_{j1} \leq zd \leq d_{j2} \\ m_{j2}zd + b_{j2} & d_{j2} < zd \leq d_{j3} \\ 0 & \text{otherwise} \end{cases}}{3z^2 \sum_j N_j \left(\int_{\min(1, d_{j1}/d)}^{\min(1, d_{j2}/d)} \exp\left(\frac{(z^*d + \lambda)^2}{2\beta\tau}\right) (m_{j1}z^*d + b_{j1}) dz^* \right. \\
&\quad \left. + \int_{\min(1, d_{j2}/d)}^{\min(1, d_{j3}/d)} \exp\left(\frac{(z^*d + \lambda)^2}{2\beta\tau}\right) (m_{j2}z^*d + b_{j2}) dz^* \right)} \\
&= z^{-2} \xi \exp\left(\frac{y^2(zd)}{2\gamma_0}\right) \sum_j N_j \begin{cases} m_{j1}zd + b_{j1} & d_{j1} \leq zd \leq d_{j2} \\ m_{j2}zd + b_{j2} & d_{j2} < zd \leq d_{j3} \\ 0 & \text{otherwise} \end{cases} \tag{21}
\end{aligned}$$

for the normalization factor ξ given in the main text.

S8. Generalized form of probability density function $p(\varepsilon; d)$ for any steady-state flow reactor

$$\begin{aligned}
 p(\varepsilon; d) &= \left. \frac{\partial c(\varepsilon)}{\partial \varepsilon} \right|_d \\
 &= \left. \frac{\partial c}{\partial d_0} \right|_d \left. \frac{\partial d_0}{\partial \varepsilon} \right|_d \\
 &= \frac{f(d, d_0)}{n(d)} \left. \frac{\partial d_0}{\partial \varepsilon} \right|_d \\
 &= \frac{f(d, d_0)}{\int_d^0 f(d, d_0^*) dd_0^*} \left. \frac{\partial d_0}{\partial \varepsilon} \right|_d \\
 &= \frac{f(d, d_0)}{\int_0^d f(d, d_0^*) dd_0^*} \frac{d}{3z^2} \text{ using } dd_0/d\varepsilon = -d^3/3d_0^2 = -d/3z^2 \text{ and } d_0 = zd = d(1-\varepsilon)^{1/3} \\
 &= \frac{d n_0(d_0) p_t(t) \frac{dt}{dd}}{3z^2(\varepsilon) \int_0^d n_0(d_0^*) p_t(t) \frac{dt}{dd^*} dd_0^*} \text{ using } f(d, d_0) dd = n_0(d_0) p_t(t) dt \\
 &= \frac{d n_0(d_0) p_t \left(\int_{d_0}^d I^{-1}(d^*) dd^* \right)}{3z^2(\varepsilon) \int_0^d n_0(d_0^*) p_t \left(\int_{d_0}^d I^{-1}(d^*) dd^* \right) dd_0^*} \text{ using } t = \int_{d_0}^d I^{-1}(d^*) dd^* \text{ and } \frac{dt}{dd} = I^{-1}(d) \\
 &= \frac{n_0(zd)}{3z^2} \frac{p_t \left(\int_{zd}^d I^{-1}(d^*) dd^* \right)}{\int_0^1 \left(n_0(z^* d) p_t \left(\int_{z^* d}^d I^{-1}(d^*) dd^* \right) dz^* \right)} \text{ using } d_0 = zd \text{ and } dd_0 = d dz
 \end{aligned} \tag{A1}$$

The foregoing equation in red begins with Equation 2 of Kuwata and Martin (2012) and is further developed as follows:

$$\begin{aligned}
\frac{\partial}{\partial d_0} \left[n(d; d_0) dd \right] &= \frac{\partial}{\partial d_0} \left[\left(\int_0^\infty n(d; d_0) dd \right) p_t(t; d_0) dt \right] \\
\frac{\partial}{\partial d_0} \left[\left. \frac{\partial N}{\partial d} \right|_{d_0} dd \right] &= \frac{\partial}{\partial d_0} \left[\left(\int_0^\infty \left. \frac{\partial N}{\partial d} \right|_{d_0} dd \right) p_t(t; d_0) dt \right] \\
\frac{\partial^2 N}{\partial d \partial d_0} dd &= \left(\frac{\partial}{\partial d_0} \int_0^\infty \left. \frac{\partial N}{\partial d} \right|_{d_0} dd \right) p_t(t) dt \\
\frac{\partial^2 N}{\partial d \partial d_0} dd &= \left(\int_0^\infty \frac{\partial^2 N}{\partial d \partial d_0} dd \right) p_t(t) dt \\
\frac{\partial^2 N}{\partial d \partial d_0} dd &= \left(\int_0^\infty f(d, d_0) dd \right) p_t(t) dt \\
f(d, d_0) dd &= n_0(d_0) p_t(t) dt
\end{aligned}$$

The use of this equation requires that p_t must not depend on d_0 for the shown derivatives to hold.

The foregoing equation in blue appears as Equation 1 in Kuwata and Martin (2012).

List of Supplemental Figures

Figure S1. Organic volume fraction plotted in false color as a function of grown particle diameter and seed particle diameter (Equation 1).

Figure S2. Distribution function $f(d, d_0)$. (a) Density plot of $f(d, d_0)$ as a function of grown particle diameter d and seed particle diameter d_0 (Equation S2). Parameter values are as for Figure 1. Contours of constant particle residence time ranging from $0(\times 10^3)$ to $16(\times 10^3)$ s are shown. (b) Cross-sections through $f(d, d_0)$ for fixed d and variable d_0 . The sections are shown for five grown particle diameters d ranging from 50 to 450 nm. (c) Cross-sections through $f(d, d_0)$ for fixed d_0 and variable d . The sections are shown for seven seed particle diameters d_0 ranging from 20 to 80 nm.

Figure S3. Distribution function $f(d_0, t)$. (a) Density plot of $f(d_0, t)$ as a function of seed particle diameter d_0 and particle residence time t (Equation S3). Parameter values are as for Figure 1. Contours of constant grown particle diameter are shown. (b) Cross-sections through $f(d_0, t)$ for fixed d_0 and variable t . The sections are shown for seven seed particle diameters ranging from 20 to 80 nm. (c) Cross-sections through $f(d_0, t)$ for fixed t and variable d_0 . The sections are shown for eleven particle residence times ranging from 0 to 20000 s.

Figure S4. Comparison of $p(\epsilon; d)$ calculated by the analytical equation of this study (Equation 15; black line) to that calculated by a numerical sectional model of Smith et al. (2011; 2012) (red dashed line). The parameters listed in Figure 3 are used to described the number-diameter distribution of the seed particles. Parameter values τ , β , and λ are as for Figure 1. The sectional model differs from the analytical model

for lowest organic volume fractions because of bin resolution of the sectional model near the seed particle diameter.

Figure S1

Figure S2

Figure S3

Figure S4