Appendix A: Population Balance Equations (PBEs) for the various population classes in the bivariate PBE model are as follows.

For $\overline{n}_A(i)$:

$$\frac{d\overline{n}_A(i)}{dt} = -k_c\overline{n}_A(i) + \frac{k_c}{2}\sum_{j=0}^{\infty}\sum_{k=0}^{\infty}\overline{n}_A(j)\overline{n}_A(k)E(i,j+k) + k_c\sum_{j=n^*}^{\infty}\sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\overline{n}_{SA}(j,k)\overline{n}_A(l)\tilde{E}(i,k+l)$$
$$+k_c\sum_{j=n^*}^{\infty}\sum_{k=0}^{\infty}\sum_{l=1}^{\infty}\overline{n}_{SA}(j,k)\overline{n}_B(l)\tilde{E}(i,k-l) + k_c\sum_{j=n^*}^{\infty}\sum_{k=0}^{\infty}\sum_{l=1}^{\infty}\sum_{m=0}^{\infty}\overline{n}_{SA}(j,k)\overline{n}_{CA}(l,m)\tilde{E}(i,k+m)$$
$$+k_c\sum_{j=n^*}^{\infty}\sum_{k=0}^{\infty}\sum_{l=1}^{\infty}\sum_{m=1}^{\infty}\overline{n}_{SA}(j,k)\overline{n}_{CB}(l,m)\tilde{E}(i,k-m) + k_c\sum_{j=n^*}^{\infty}\sum_{k=1}^{\infty}\sum_{l=0}^{\infty}\overline{n}_{SB}(j,k)\overline{n}_A(l)\tilde{E}(i,l-k)$$
$$+k_c\sum_{j=n^*}^{\infty}\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}\sum_{m=0}^{\infty}\overline{n}_{SB}(j,k)\overline{n}_{CA}(l,m)\tilde{E}(i,m-k) + k_c\sum_{j=0}^{\infty}\sum_{k=1}^{\infty}\overline{n}_A(j)\overline{n}_B(k)E(0,k;i,j-k)$$
$$+k_c\sum_{j=1}^{\infty}\sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\overline{n}_{CA}(j,k)\overline{n}_A(l)E(0,j;i,k+l) + k_c\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}\sum_{l=0}^{\infty}\overline{n}_{CB}(j,k)\overline{n}_A(l)E(0,j+k;i,l-k)$$
$$+k_c\sum_{j=1}^{\infty}\sum_{k=0}^{\infty}\sum_{l=1}^{\infty}\overline{n}_{CA}(j,k)\overline{n}_B(l)E(0,j+l;i,k-l)$$
$$+\frac{k_c}{2}\sum_{j=1}^{\infty}\sum_{k=0}^{\infty}\sum_{l=1}^{\infty}\sum_{m=0}^{\infty}\overline{n}_{CA}(j,k)\overline{n}_{CA}(l,m)E(0,j+l;i,k+m)$$
$$+k_c\sum_{j=1}^{\infty}\sum_{k=0}^{\infty}\sum_{l=1}^{\infty}\sum_{m=1}^{\infty}\overline{n}_{CA}(j,k)\overline{n}_{CB}(l,m)E(0,j+l+m;i,k-m) \qquad \text{(A1)}$$

where, $k_c = \beta_d q_d N_{drop}$. The first term in the right hand side is the death term due to collision of $\overline{n}_A(i)$ with all other drops, where as the other terms are birth terms of $\overline{n}_A(i)$ due to coalescence-exchange of different pairs.

A similar PBE can be written for $\overline{n}_B(i)$ by interchanging $\overline{n}_A(i)$ with $\overline{n}_B(i)$, $\overline{n}_{CA}(i,j)$ with $\overline{n}_{CB}(i,j)$ and $\overline{n}_{SA}(i,j)$ with $\overline{n}_{SB}(i,j)$ everywhere in equation A1. $\frac{d\overline{n}_A(i)}{dt}$ and $\frac{d\overline{n}_B(i)}{dt}$ are integrated for i = 1 to Z_{max}, with a total of Z_{max} equations for each population.

For $\overline{n}_{CA}(i,j)$:

$$\frac{d\overline{n}_{CA}(i,j)}{dt} = -k_n(i)\overline{n}_{CA}(i,j) - k_c\overline{n}_{CA}(i,j) + k_c\sum_{k=0}^{\infty}\sum_{l=1}^{\infty}\overline{n}_A(k)\overline{n}_B(l)E(i,l;j,k-l)$$

$$+k_c\sum_{k=1}^{\infty}\sum_{l=0}^{\infty}\sum_{m=0}^{\infty}\overline{n}_{CA}(k,l)\overline{n}_A(m)E(i,k;j,l+m)$$

$$+k_c\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}\sum_{m=0}^{\infty}\overline{n}_{CB}(k,l)\overline{n}_A(m)E(i,k+l;j,m-l)$$

$$+k_c\sum_{k=1}^{\infty}\sum_{l=0}^{\infty}\sum_{m=1}^{\infty}\overline{n}_{CA}(k,l)\overline{n}_B(m)E(i,k+m;j,l-m)$$

$$+\frac{k_c}{2}\sum_{k=1}^{\infty}\sum_{l=0}^{\infty}\sum_{m=1}^{\infty}\sum_{n=0}^{\infty}\overline{n}_{CA}(k,l)\overline{n}_{CA}(m,n)E(i,k+m;j,l+n)$$

$$+k_c\sum_{k=1}^{\infty}\sum_{l=0}^{\infty}\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\overline{n}_{CA}(k,l)\overline{n}_{CB}(m,n)E(i,k+m+n;j,l-n)$$

$$+k_c\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}\sum_{m=1}^{\infty}\overline{n}_{CB}(k,l)\overline{n}_B(m)E(i,k;0,l+m)$$

$$+\frac{k_c}{2}\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\overline{n}_{CB}(k,l)\overline{n}_{CB}(m,n)E(i,k+m;0,l+n) \quad \text{(A2)}$$

The first two terms in the right hand side are the death terms due to nucleation and collision of $\overline{n}_{CA}(i,j)$ with all other drops respectively. The other terms are birth terms of $\overline{n}_{CA}(i,j)$ due to coalescence-exchange of different pairs. The last two terms are included only when $j = 0$. Similarly a PBE can be written for $\overline{n}_{CB}(i,j)$ also. $\frac{d\overline{n}_{CA}(i,j)}{dt}$ is integrated for $i = 1$ to Z_{max} and $j = 0$ to Z_{max}, with a constraint of $(i+j) \leq Z_{max}$. For $\frac{d\overline{n}_{CB}(i,j)}{dt}$ equations, i varies from 1 to Z_{max} again, but j varies from 1 to Z_{max} only. The number of equations to be solved for the former population class is $\left(Z_{\max}^2 + Z_{\max}\right)/2$, while for the latter class it is $\left(Z_{\max}^2 - Z_{\max}\right)/2$.

For $\overline{n}_{SA}(i,j)$:

$$\frac{d\overline{n}_{SA}(i,j)}{dt} = k_n(i)\overline{n}_{CA}(i,j) - k_c\overline{n}_{SA}(i,j) + k_c\sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\overline{n}_{SA}(i,k)\overline{n}_A(l)\tilde{E}(j,k+l)$$
$$+k_c\sum_{k=1}^{i-n^*}\sum_{l=0}^{\infty}\overline{n}_{SA}(i-k,l)\overline{n}_B(k)\tilde{E}(j,l-k)$$
$$+k_c\sum_{k=1}^{i-n^*}\sum_{l=0}^{\infty}\sum_{m=0}^{\infty}\overline{n}_{CA}(k,l)\overline{n}_{SA}(i-k,m)\tilde{E}(j,l+m)$$
$$+k_c\sum_{k=1}^{i-n^*}\sum_{l=1}^{i-k-n^*}\sum_{m=0}^{\infty}\overline{n}_{CB}(k,l)\overline{n}_{SA}(i-k-l,m)\tilde{E}(j,m-l)$$
$$+k_c\sum_{k=1}^{i-n^*}\sum_{m=1}^{i-k-n^*}\sum_{l=0}^{\infty}\overline{n}_{CA}(k,l)\overline{n}_{SB}(i-k-m,m)\tilde{E}(j,l-m)$$
$$+\frac{k_c}{2}\sum_{k=0}^{\infty}\sum_{l=n^*}^{\infty}\sum_{m=0}^{\infty}\overline{n}_{SA}(i,k)\overline{n}_{SA}(l,m)\tilde{E}(j,k+m)$$
$$+k_c\sum_{k=0}^{i-n^*}\sum_{l=0}^{\infty}\sum_{m=n^*}^{\infty}\sum_{n=1}^{\infty}\overline{n}_{SA}(i-k,l)\overline{n}_{SB}(m,n)\tilde{E}(k,n;j,l-n)$$
$$+k_c\sum_{k=1}^{i-n^*}\sum_{l=0}^{\infty}\overline{n}_{SB}(i-k,k)\overline{n}_A(l)\tilde{E}(j,l-k)$$
$$+k_c\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}\overline{n}_{SB}(i,k)\overline{n}_B(l)\tilde{E}(0,k+l)$$
$$+k_c\sum_{k=1}^{i-n^*}\sum_{l=1}^{\infty}\sum_{m=1}^{\infty}\overline{n}_{CB}(k,l)\overline{n}_{SB}(i-k,m)\tilde{E}(0,l+m)$$
$$+\frac{k_c}{2}\sum_{k=1}^{\infty}\sum_{l=n^*}^{\infty}\sum_{m=1}^{\infty}\overline{n}_{SB}(i,k)\overline{n}_{SB}(l,m)\tilde{E}(0,k+m) \quad \text{(A3)}$$

The first term in the right hand side is the birth term of $\overline{n}_{SA}(i,j)$ due to nucleation of $\overline{n}_{CA}(i,j)$. The second term accounts for death due to collision of $\overline{n}_{SA}(i,j)$ with all other drops. The remaining terms are birth terms for $\overline{n}_{SA}(i,j)$ due to coalescence-exchange of different pairs. The last three terms in the right hand side of the above equation are included only when $j = 0$. Similarly a PBE can be written for $\overline{n}_{SB}(i,j)$ also. $\frac{d\overline{n}_{SA}(i,j)}{dt}$ is integrated for $i = n^*$ to Z_{max} and $j = 0$ to Z_{max}, with a constraint of $(i+j) \leq Z_{max}$. For

$\frac{d\overline{n}_{SB}(i,j)}{dt}$ equations, i varies from n^* to Z_{max} again, but j varies from 1 to Z_{max}. The number of equations to be solved for the former population class is $\left(Z_{\max}^2 + n^{*2} - 2Z_{\max}n^* + 3Z_{\max} - 3n^* + 2\right)/2$, while for the latter class it is $\left(Z_{\max}^2 + n^{*2} - 2Z_{\max}n^* + Z_{\max} - n^*\right)/2$.

Therefore the total number of equations to be solved in the bivariate model is: $2Z_{\max}^2 + n^{*2} - 2Z_{\max}n^* + 4Z_{\max} - 2n^* + 1$.

Appendix B: The univariate PBE model and moment equations are as follows.

$$\frac{d\overline{n}_A(i)}{dt} = -k_c\overline{n}_A(i)\overline{n}_B(i) - k_c\overline{n}_A(i)\sum_{j=0}^{\infty}\overline{n}_A(j) + \frac{k_c}{2}\sum_{j=0}^{\infty}\sum_{k=0}^{\infty}\overline{n}_A(j)\overline{n}_A(k)E(i, j+k) \tag{B1}$$

$$\frac{d\overline{n}_B(i)}{dt} = -k_c\overline{n}_A(i)\overline{n}_B(i) - k_c\overline{n}_B(i)\sum_{j=0}^{\infty}\overline{n}_B(j) + \frac{k_c}{2}\sum_{j=0}^{\infty}\sum_{k=0}^{\infty}\overline{n}_B(j)\overline{n}_B(k)E(i, j+k) \tag{B2}$$

$$\frac{d\overline{n}_C(i)}{dt} = k_c\overline{n}_A(i)\overline{n}_B(i) - k_n(i)\overline{n}_C(i) - k_c\overline{n}_C(i)\left[\sum_{j=0}^{\infty}\overline{n}_C(j) + \sum_{j=n^*}^{\infty}\overline{n}_S(j)\right] + \frac{k_c}{2}\sum_{j=0}^{\infty}\sum_{k=0}^{\infty}\overline{n}_C(j)\overline{n}_C(k)E(i, j+k) \tag{B3}$$

$$\frac{d\overline{n}_S(i)}{dt} = k_n(i)\overline{n}_C(i) - k_c\overline{n}_S(i)\sum_{j=0}^{\infty}\overline{n}_C(j) + k_c\sum_{j=1}^{i-n^*}\overline{n}_S(i-j)\overline{n}_C(j) \tag{B4}$$

$$\frac{dM_S^{(0)}(t)}{dt} = \sum_{i=n^*}^{\infty}k_n(i)\overline{n}_C(i,t) \tag{B5}$$

$$\frac{dM_S^{(1)}(t)}{dt} = \sum_{i=n^*}^{\infty}ik_n(i)\overline{n}_C(i,t) + k_cM_S^{(0)}(t)\sum_{i=n^*}^{\infty}i\,\overline{n}_C(i,t) \tag{B6}$$

Equation B1 is the rate of change of number density $\overline{n}_A$. The first term in the right hand side (RHS) is death term due to collision with $\overline{n}_B$, leading to reaction. The second and third terms are death and birth terms of $\overline{n}_A$, respectively, due to coalescence-exchange of $\overline{n}_A$ themselves. It should be noted that only coalescence-exchange of $\overline{n}_A$ themselves and $\overline{n}_A(i)$ with $\overline{n}_B(i)$ are considered to avoid the formation of bivariate populations. Equation B2 is analogous to B1, the former being for $\overline{n}_B$.

Equation B3 is the rate of change of number density $\overline{n}_C$. The first term in RHS is the birth term due to collision of $\overline{n}_A$ and $\overline{n}_B$. The second and fourth terms are death of $\overline{n}_C$ due to nucleation and growth via coalescence-exchange of $\overline{n}_C$ and $\overline{n}_S$, respectively. The third and fifth terms are death and birth terms, respectively, due to coalescence-exchange of n_C themselves.

Equation B4 is the rate of change of number density of $\overline{n}_S$. The first term in RHS is birth due to nucleation. Second and third terms are death and birth of $\overline{n}_S$, respectively, due to collision with $\overline{n}_C$. Equations B5 and B6 are zeroth and first moment of $\overline{n}_S$, respectively.

Equations B1-B3 are integrated for i =1 to Z_{max}, together with equations B5 and B6, thus the number of equations to be solved in the univariate PBE model is: $3Z_{max}+2$ only.

Appendix C: Nomenclature for the symbols used in the models.

B_k	Birth rate of k^{th} class drops, s^{-1}
C(l)	Product C in dissolved form in water
C(s)	Product C as a solid particle
d_{av}	Average nanoparticle diameter, m
d_{drop}	Diameter of a microemulsion drop, m
D_k	Death rate of k^{th} class drops, s^{-1}
$E(i, j)$	Expectation of obtaining i molecules in a drop from j molecules in a dimer
$E(i,k;j,l)$	Expectation of obtaining i out of k molecules of first kind and j out of l molecules of second kind in a drop after redispersion, when drops are indistinguishable
$\tilde{E}(i,k;j,l)$	Expectation of obtaining i out of k molecules of first kind and j out of l molecules of second kind in a drop after redispersion, when drops are distinguishable
i_{av}	Average number of product molecules per nanoparticle, also referred as MAN
k_0	Preexponential term in the expression of nucleation rate, s^{-1}
k_B	Boltzmann constant, 1.0386×10^{-23}, J mol^{-1} K^{-1}
k_c	Rate constant of coalescence-exchange of drops, s^{-1}
k_n	Rate constant of nucleation rate, s^{-1}
K_s	Solubility product of CdS, mol^2 L^{-2}
$M_s^{(n)}$	n^{th} moment of number density function of n_s

MAN	Mean aggregate number
M_w	Molecular weight of CdS, kg kmol^{-1}
n	Number density of any given class of drops, m^{-3}
$\overline{n}$	Nondimensional number density of a class of drops
n^*	Critical number of molecules required for nucleation
n_A^0	Number density of drops having reactant A before mixing, m^{-3}
n_B^0	Number density of drops having reactant B before mixing, m^{-3}
N	Total number of drops used in MC simulation
N_A	Avogadro number, 6.023×10^{23} molecules mol^{-1}
N_{drop}	Total number density of drops, m^{-3}
N_p	Total number density of nanoparticles, m^{-3}
$p_{i,j}$	Binomial probability of obtaining i molecules in a drop from j molecules in a dimer
q_d	Collision frequency of drops, m^3 s^{-1}
R	Molar ratio of water to surfactant
T	Temperature, K
v_m	Volume of one C(s) molecule, m^3
x	Molar ratio of reactants
Z_{max}	Maximum number of molecules of all kinds [A, B, C(l), C(s)] that can be present together in a drop

Greek letters

β_d	Coalescence efficiency of drop-drop collisions
η	Viscosity of the oil, kg m^{-1} s^{-1}

λ Supersaturation ratio of C(l)

μ_A Mean number of reactant A molecules in drops

μ_B Mean number of reactant B molecules in drops

ρ Density of CdS, kg m^{-3}

σ Interfacial tension between solid nuclei and surrounding drop liquid, N m^{-1}

τ Time scale of a rate process, s

Subscripts

A Drops containing only reactant A

B Drops containing only reactant B

c Coalescence-exchange between nonnucleated drops

C Drops containing only C in dissolved form [C(l)]

CA Drops containing C in dissolved form [C(l)] and reactant A

CB Drops containing C in dissolved form [C(l)] and reactant B

d Life time of a dimer

g Growth of C(s)

n Nucleation of C(s)

S Drops containing only C in solid form [C(s)]

SA Drops containing C in solid form [C(s)] and reactant A

SB Drops containing C in solid form [C(s)] and reactant B

Complete list of authors of reference 3.

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