Supporting Information

Viscosity scaling in concentrated dispersions and its impact on colloidal aggregation

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In the following, we show how to discretize the population balance equations by approximating the cluster mass distribution by a sum of Gaussian functions.

The population balance equation in its continuous form reads:

$$\frac{dN(x,t)}{dt} = \frac{1}{2}\int_0^x k(x-y,y,t)N(x-y,t)N(y,t)dy - N(x,t)\int_0^\infty k(x,y,t)N(y,t)dy \quad \backslash* \text{ MERGEFORMAT } ($$

where $N(x,t)$ is defined such that $N(x,t)dx$ represents the concentration of aggregates of mass x to $x+dx$ at time t, and $k(x,y,t)$ is the aggregation rate constant between two clusters of mass x and y at time t.

We present here the discretization technique for the case of reaction limited aggregation, where the aggregation kernel is given by:

$$k(x,y,t) = \frac{2}{3}\frac{k_B T}{W}\left(x^\varepsilon + y^\varepsilon\right)\left(\frac{x^{-\varepsilon}}{\eta_{eff}(x,t)} + \frac{y^{-\varepsilon}}{\eta_{eff}(y,t)}\right)(xy)^\lambda \qquad \text{where} \quad \varepsilon = 1/d_f \quad \backslash* \text{ MERGEFORMAT (2}$$

where $\eta_{eff}(x,t)$ represents the effective viscosity experienced by an aggregate of mass x at time t. Note that since sr_i and ϕ are monotonic functions of time, defining $\eta_{eff}(x,t)$ is mathematically equivalent to defining $\eta_{eff}(sr_i,\phi)$, as done in the main text.

The discretized PBE in the case of diffusion limited aggregation case can be simply obtained by setting the Fuchs stability ratio and the power law exponent to $W = 1$ and $\lambda = 0$, respectively.

In the frame of the discretization technique employed, the cluster mass distribution is approximated by a sum of N_G Gaussian functions:

$$N(x,t) \approx \sum_{i=1}^{N_G} \alpha_i(t) \exp\left(-s_i(x-x_i)^2\right) \qquad \text{\\* MERGEFORMAT (3)}$$

where α_i are the time-dependent coefficients of the Gaussians, which are placed in the fixed grid positions x_i. The parameters s_i instead characterize the width of the Gaussian functions, and have been defined as follows in order to ensure proper overlapping between adjacent Gaussian functions, which is necessary for numerical stability:

$$s_i = \frac{1}{(x_{i+1} - x_i)^2} \qquad \text{\\* MERGEFORMAT (4)}$$

The grid points were spaced linearly up to $i = 20$, and then logarithmically up to $i = 5 \times 10^4$ with a total of 90 Gaussian functions.

For the sake of clarity, we define the function φ_i such as:

$$\varphi_i(x) = \exp\left(-s_i(x-x_i)^2\right) \qquad \text{\\* MERGEFORMAT (5)}$$

In order to reduce the size of the problem, the concentrations are evaluated only at the N_G grid points by using approximation * MERGEFORMAT (3):

$$\begin{bmatrix} N(x_1,t) \\ N(x_2,t) \\ \text{M} \\ N(x_{N_G},t) \end{bmatrix} \approx \begin{bmatrix} \sum_{i=1}^{N_G} \alpha_i(t)\varphi_i(x_1) \\ \sum_{i=1}^{N_G} \alpha_i(t)\varphi_i(x_2) \\ \text{M} \\ \sum_{i=1}^{N_G} \alpha_i(t)\varphi_i(x_{N_G}) \end{bmatrix} \qquad \text{* MERGEFORMAT (6)}$$

Equation * MERGEFORMAT (6) can be re-written in a more compact form as follows:

$$\underline{N}(t) = \underline{\underline{C}} \times \underline{\alpha}(t) \qquad \text{* MERGEFORMAT (7)}$$

where $\underline{N}(t)$ and $\underline{\alpha}(t)$ are vectors of length N_G, which contain the aggregate concentrations and the heights of the Gaussians at a given time t, respectively.

The matrix $\underline{\underline{C}}$, of size $[N_G \times N_G]$, is the so-called change of base matrix, allowing to "move" from the concentration space to the Gaussian one.

$$\underline{\underline{C}} = \begin{bmatrix} \varphi_1(x_1) & \varphi_2(x_1) & \text{K} & \varphi_{N_G}(x_1) \\ \varphi_1(x_2) & \varphi_2(x_2) & \text{K} & \varphi_{N_G}(x_2) \\ \text{M} & \text{M} & \text{O} & \text{M} \\ \varphi_1(x_{N_G}) & \varphi_2(x_{N_G}) & \text{K} & \varphi_{N_G}(x_{N_G}) \end{bmatrix} \qquad \text{* MERGEFORMAT (8)}$$

Introducing the approximation * MERGEFORMAT (3) in the left hand side of equation * MERGEFORMAT (1) and recalling that the coefficients x_i and s_i are constant in time, one gets:

$$\frac{d\underline{N}(t)}{dt} = \underline{\underline{C}} \frac{d\underline{\alpha}(t)}{dt} \qquad \text{* MERGEFORMAT (9)}$$

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In order to treat the right hand side, let us first re-write the aggregation kernel shown in equation * MERGEFORMAT (2) as follows:

$$k\left(x,y,t\right)=\frac{2}{3}\frac{k_B T}{W}\left(\frac{x^\lambda}{\eta_{e\!f\!f}(x,t)}y^\lambda+x^{\lambda+\varepsilon}\frac{y^{\lambda-\varepsilon}}{\eta_{e\!f\!f}(y,t)}+\frac{x^{\lambda-\varepsilon}}{\eta_{e\!f\!f}(x,t)}y^{\lambda+\varepsilon}+x^\lambda\frac{y^\lambda}{\eta_{e\!f\!f}(y,t)}\right)\quad\text{* MERGEFORMAT (10}$$

The loss term in equation * MERGEFORMAT (1) is given by:

$$\underline{\underline{C}}\left(\frac{d\underline{\alpha}(t)}{dt}\right)_{-}=-\frac{2}{3}\frac{k_B T}{W}\left(\underline{\underline{C}}\underline{\alpha}^{w_E}(t)\sum_{j=1}^{N_G}\alpha_j^{w_F}(t)\int_0^\infty\varphi_j(y)dy\right.$$
$$+\underline{\underline{C}}\underline{\alpha}^{w_G}(t)\sum_{j=1}^{N_G}\alpha_j^{w_H}(t)\int_0^\infty\varphi_j(y)dy$$
$$+\underline{\underline{C}}\underline{\alpha}^{w_H}(t)\sum_{j=1}^{N_G}\alpha_j^{w_G}(t)\int_0^\infty\varphi_j(y)dy$$
$$\left.+\underline{\underline{C}}\underline{\alpha}^{w_F}(t)\sum_{j=1}^{N_G}\alpha_j^{w_E}(t)\int_0^\infty\varphi_j(y)dy\right)$$

* MERGEFORMAT (11)

where the weighted coefficients are defined as:

$$\underline{\alpha}^{w_E}(t)=\underline{\underline{C}}^{-1}\underline{\underline{W}}_E(t)\underline{\underline{C}}\underline{\alpha}(t)\qquad\text{* MERGEFORMAT (12)}$$

$$\underline{\alpha}^{w_F}(t)=\underline{\underline{C}}^{-1}\underline{\underline{W}}_F\underline{\underline{C}}\underline{\alpha}(t)\qquad\text{* MERGEFORMAT (13)}$$

$$\underline{\alpha}^{w_G}(t)=\underline{\underline{C}}^{-1}\underline{\underline{W}}_G\underline{\underline{C}}\underline{\alpha}(t)\qquad\text{* MERGEFORMAT (14)}$$

$$\underline{\alpha}^{w_H}(t)=\underline{\underline{C}}^{-1}\underline{\underline{W}}_H(t)\underline{\underline{C}}\underline{\alpha}(t)\qquad\text{* MERGEFORMAT (15)}$$

with the following matrixes:

$$\underline{\underline{W_E}}(t) = \begin{bmatrix} x_1^\lambda / \eta_{eff}(x_1,t) & 0 & 0 & 0 \\ 0 & x_2^\lambda / \eta_{eff}(x_2,t) & 0 & 0 \\ M & M & O & M \\ 0 & 0 & L & x_N^\lambda / \eta_{eff}(x_N,t) \end{bmatrix} \qquad \text{* MERGEFORMAT (16)}$$

$$\underline{\underline{W_F}} = \begin{bmatrix} x_1^\lambda & 0 & 0 & 0 \\ 0 & x_2^\lambda & 0 & 0 \\ M & M & O & M \\ 0 & 0 & L & x_N^\lambda \end{bmatrix} \qquad \text{* MERGEFORMAT (17)}$$

$$\underline{\underline{W_G}} = \begin{bmatrix} x_1^{\lambda+\varepsilon} & 0 & 0 & 0 \\ 0 & x_2^{\lambda+\varepsilon} & 0 & 0 \\ M & M & O & M \\ 0 & 0 & L & x_N^{\lambda+\varepsilon} \end{bmatrix} \qquad \text{* MERGEFORMAT (18)}$$

$$\underline{\underline{W_H}}(t) = \begin{bmatrix} x_1^{\lambda-\varepsilon} / \eta_{eff}(x_1,t) & 0 & 0 & 0 \\ 0 & x_2^{\lambda-\varepsilon} / \eta_{eff}(x_2,t) & 0 & 0 \\ M & M & O & M \\ 0 & 0 & L & x_N^{\lambda-\varepsilon} / \eta_{eff}(x_N,t) \end{bmatrix} \qquad \text{* MERGEFORMAT (19)}$$

Let us recall that:

$$\int_0^\infty e^{-s_j(y-x_j)^2} dy = \frac{1}{2}\sqrt{\frac{\pi}{s_j}}\left(1 + \mathrm{erf}\left(x_j\sqrt{s_j}\right)\right) \qquad \text{* MERGEFORMAT (20)}$$

As in the present case, the selected grid ensures that $x_j\sqrt{s_j} > 2$ for every $j > 2$, we apply the following approximation:

$$\int_0^\infty e^{-s_j(y-x_j)^2} dy \approx \sqrt{\frac{\pi}{s_j}} \qquad \text{* MERGEFORMAT (21)}$$

The loss term then becomes:

$$\underline{\underline{C}}\left(\frac{d\underline{\alpha}(t)}{dt}\right)_{-} = -\frac{2}{3}\frac{k_B T}{W}\left(\underline{\underline{C}}\underline{\alpha}^{w_E}(t)\sum_{j=1}^{N_G}\alpha_j^{w_F}(t)\sqrt{\frac{\pi}{s_j}}\right.$$

$$+\underline{\underline{C}}\underline{\alpha}^{w_G}(t)\sum_{j=1}^{N_G}\alpha_j^{w_H}(t)\sqrt{\frac{\pi}{s_j}}$$

$$+\underline{\underline{C}}\underline{\alpha}^{w_H}(t)\sum_{j=1}^{N_G}\alpha_j^{w_G}(t)\sqrt{\frac{\pi}{s_j}}$$

$$\left.+\underline{\underline{C}}\underline{\alpha}^{w_F}(t)\sum_{j=1}^{N_G}\alpha_j^{w_E}(t)\sqrt{\frac{\pi}{s_j}}\right)$$

* MERGEFORMAT (22)

By using the weighting coefficient previously introduced, the production term of equation * MERGEFORMAT (1) can be treated as follows:

$$\left(\frac{dN(x,t)}{dt}\right)_{+} = \frac{1}{3}\frac{k_B T}{W}\left(\int_0^x\left(\sum_{i=1}^{N_G}\alpha_i^{w_E}(t)\varphi_i(x-y)\sum_{j=1}^{N_G}\alpha_j^{w_F}(t)\varphi_j(y)\right)dy\right.$$

$$+\int_0^x\left(\sum_{i=1}^{N_G}\alpha_i^{w_G}(t)\varphi_i(x-y)\sum_{j=1}^{N_G}\alpha_j^{w_H}(t)\varphi_j(y)\right)dy$$

$$+\int_0^x\left(\sum_{i=1}^{N_G}\alpha_i^{w_H}(t)\varphi_i(x-y)\sum_{j=1}^{N_G}\alpha_j^{w_G}(t)\varphi_j(y)\right)dy$$

$$\left.+\int_0^x\left(\sum_{i=1}^{N_G}\alpha_i^{w_F}(t)\varphi_i(x-y)\sum_{j=1}^{N_G}\alpha_j^{w_E}(t)\varphi_j(y)\right)dy\right)$$

MERGEFORMAT

(23)

Let us recall the definition of the convolution of two functions f and g on the domain of definition R :

$$(f*g)(x)=\int_R f(y)g(x-y)dy$$

* MERGEFORMAT (24)

Applying the above definition and using the matrix form, one obtains:

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$$\left(\underline{\underline{C}} \frac{d\underline{\alpha}(t)}{dt} \right)_{+} = \frac{2}{3} \frac{k_B T}{W} \left(\underline{\underline{C}}\alpha^{w_E}(t) * \underline{\underline{C}}\alpha^{w_F}(t) + \underline{\underline{C}}\alpha^{w_G}(t) * \underline{\underline{C}}\alpha^{w_H}(t) \right) \text{MERGEFORMAT}$$

(25)

The convolution of two Gaussians results in another Gaussian whose position and width can be computed from the parameters of the two convoluted Gaussians. Accordingly, we define $\underline{\underline{\psi}}$, $\underline{\gamma}^{w_{EF}}$ and $\underline{\gamma}^{w_{GH}}$ such as:

$$\underline{\underline{C}}\alpha^{w_E}(t) * \underline{\underline{C}}\alpha^{w_F}(t) = \underline{\underline{\psi}}\underline{\gamma}^{w_{EF}}(t) \qquad \text{\\* MERGEFORMAT (26)}$$

$$\underline{\underline{C}}\alpha^{w_G}(t) * \underline{\underline{C}}\alpha^{w_H}(t) = \underline{\underline{\psi}}\underline{\gamma}^{w_{GH}}(t) \qquad \text{\\* MERGEFORMAT (27)}$$

where:

$$\psi_{i,j}(x) = \exp\left(-s_{i,j}\left(x - x_{i,j}\right)^2\right) \text{ with } \begin{cases} x_{i,j} = x_i + x_j \\ s_{i,j} = \dfrac{s_i s_j}{s_i + s_j} \end{cases} \text{\\* MERGEFORMAT (28)}$$

$$\gamma_{i,j}^{w_{EF}}(t) = \alpha_i^{w_E}(t)\alpha_j^{w_F}(t)\sqrt{\frac{\pi}{s_j + s_i}} \qquad \text{\\* MERGEFORMAT (29)}$$

$$\gamma_{i,j}^{w_{GH}}(t) = \alpha_i^{w_G}(t)\alpha_j^{w_H}(t)\sqrt{\frac{\pi}{s_j + s_i}} \qquad \text{\\* MERGEFORMAT (30)}$$

Finally, the discretized balance to be solved reads:

$$\frac{d\underline{\alpha}(t)}{dt} = \underline{\underline{C}}^{-1} \times \frac{2}{3}\frac{k_B T}{W} \times \left(-\underline{\underline{C}}\underline{\alpha}^{w_E}(t)\sum_{j=1}^{N_G}\alpha_j^{w_F}(t)\sqrt{\frac{\pi}{s_j}} \right.$$

$$-\underline{\underline{C}}\underline{\alpha}^{w_G}(t)\sum_{j=1}^{N_G}\alpha_j^{w_H}(t)\sqrt{\frac{\pi}{s_j}}$$

$$-\underline{\underline{C}}\underline{\alpha}^{w_H}(t)\sum_{j=1}^{N_G}\alpha_j^{w_G}(t)\sqrt{\frac{\pi}{s_j}} \qquad \text{* MERGEFORMAT (31)}$$

$$\left. -\underline{\underline{C}}\underline{\alpha}^{w_F}(t)\sum_{j=1}^{N_G}\alpha_j^{w_E}(t)\sqrt{\frac{\pi}{s_j}} \right)$$

$$+\underline{\underline{\psi}}\underline{\gamma}^{w_{EF}}(t)+\underline{\underline{\psi}}\underline{\gamma}^{w_{GH}}(t) \Big)$$

Note that at each integration step, the weighted average aggregate size is computed from the ratio between the second and first order moment in order to compute the normalized viscosity that the aggregates of different sizes experience (equation (12) of the main text). The normalized viscosity is then re-scaled in an effective viscosity from the knowledge of the macroscopic viscosity computed with the modified Einstein equation (equations (7) and (9) of the main text).