Highlights

Monte Carlo simulation of Pickering particle dissolution and API release in Pickering Emulsions

Yi Feng,Antonio Buffo,Elena Simone

- Random sequential adsorption gives coverages of Pickering emulsions

- API release from a population of Pickering emulsions is studied

- Pickering particle dissolution induced coverage changes are included

Monte Carlo simulation of Pickering particle dissolution and API release in Pickering Emulsions

Yi Feng, Antonio Buffo and Elena Simone

Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi, 24, Torino, 10129, Italy

ABSTRACT

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1. Introduction

2. Methodology

2.1. Geometric modeling of Pickering emulsion

The coverage of Pickering emulsion droplets plays an important role in API release, because it affects the available surface area for API release. The coverage is determined by the adsorption of Pickering particles on the droplet surfaces. Unfortunately, measurement of coverage is challenging due to its multiscale multiphase physics. Therefore, numerical simulation is adopted in this work to obtain the coverage of Pickering emulsion droplets. Depending on the packing pattern of Pickering particles, different numerical methods can be used to model the adsorption process of Pickering particles.

Based on our experiments, this study focuses on the micron-sized elongated curcumin particles, which can be approximated as capsule-shaped particles consisting of two semi-spherical ends and a cylindrical section. A loose random packing pattern of these particles is observed on the emulsion droplet surfaces, which can be modeled using random sequential adsorption (RSA) method. In RSA, particles sequentially attempt to adsorb at random locations on the droplet surfaces. They are adsorbed only if they do not overlap with any previously adsorbed particles, and once adsorbed, they remain fixed in place. The RSA simulation can provide a detailed records of the adsorbed Pickering particles, including their size distribution and the coverage they provide, which are valuable for modeling the API release from Pickering emulsions.

The RSA approach is implemented using Monte Carlo method. Meanwhile, the probability of a successful adsorption reduces significantly as coverage increases, which makes the RSA simulations computationally expensive. The jamming state, which is the maximum coverage that can be achieved by RSA, is rarely reached in the simulations,

*Corresponding author
ORCID(s):

⁴¹ especially for anisotropic particles. Therefore, this study adopts a extrapolation method to obtain the jamming coverage,

⁴² ϕ_j. The RSA simulation is performed to reach a near-jamming state. The obtained coverage evolution curve is fitted

⁴³ to extrapolate the jamming coverage. Moreover, the size distribution of the adsorbed particles at the end of simulation

⁴⁴ is used to represent the size distribution of the adsorbed particles at the jamming state. These jamming coverage and

⁴⁵ particle size distribution are used to model the API release from Pickering emulsions.

⁴⁶   Details about the RSA simulation and extrapolation method for ϕ_j can be found in [?].

2.2. Dissolution of Pickering particles

⁴⁸   The dissolution of a particle can be described by the following mass transfer equation [?]:

$$\frac{dm_p}{dt} = -k_p A_p \left(C_{sat} - C_{p,c} \right), \tag{1}$$

⁴⁹ where m_p is the particle mass, k_p is the particle mass transfer coefficient, A_p is the particle surface area, C_{sat} is the

⁵⁰ saturation concentration, and $C_{p,c}$ is the concentration in the continuous (bulk) phase.

⁵¹   For a capsule-shaped particle consisting of two semi-spherical ends and a cylindrical section, it is natural to assume

⁵² that the particle surface shrinks along its normal direction during dissolution. Therefore, the height of the cylindrical

⁵³ section, l_c, remains constant during dissolution because the top and bottom faces of the cylindrical section are covered

⁵⁴ by the semi-spherical ends. It can be proved that the particle surface, of both the semi-spherical and cylindrical parts,

⁵⁵ shrinks at the same rate as (see Appendix ??):

$$\frac{dd_p}{dt} = -\frac{2k_p \left(C_{sat} - C_{p,c} \right)}{\rho_p}, \tag{2}$$

⁵⁶ where ρ_p is the particle density. The dissolution process can be governed by the reaction mechanism or the diffusion

⁵⁷ mechanism [?]. For reaction-controlled dissolution, it is assumed to be a first-order process, and a constant particle

⁵⁸ mass transfer coefficient k_p will be used. For a diffusion-controlled dissolution, the particle mass transfer coefficient

⁵⁹ can be written as:

$$k_p = \frac{Sh D_{p,c}}{d_{32,p}}, \tag{3}$$

⁶⁰ where $Sh = 2$ is the Sherwood number, $D_{p,c}$ is the particle diffusivity in the continuous phase, and $d_{32,p} = 6V_p/A_p$ is

⁶¹ the Sauter mean diameter of the particle with $V_p = \pi d_p^3/6 + \pi d_p^2 l_c/4$ be the particle volume and $A_p = \pi d_p^2 + \pi d_p l_c$ be

⁶² the particle surface area. The reaction-controlled dissolution process is size-independent, while the diffusion-controlled

⁶³ dissolution process is size-dependent. In experiments, the reacting k_p is generally easier to measure by monitoring the

particle concentration in the continuous phase. The diffusing k_p is relatively difficult to measure because it requires accurate measurement of particle diffusivity and size distribution in addition to particle concentration. Based on this consideration, the reaction mechanism will be adopted in most cases, whereas the diffusion mechanism will be used only for comparison with the reaction mechanism.

Furthermore, Pickering particles are adsorbed at the Pickering emulsion droplet surfaces. Only a porportion of the particle surface is exposed into the continuous phase, while the rest is inside the disperse droplet. In this work, particles are assumed to be only dissoluble in the continuous phase. The proportion exposed to the continuous phase affects the dissolution rate. This proportion depends on the particle contact angle. In this work, the proportion of the available surface area for dissolution is calculated using the following equation

$$k_a = \frac{\pi d_p^2 \frac{1-\cos\theta}{2} + \theta d_p l_c}{\pi d_p^2 + \pi d_p l_c} \tag{4}$$

where θ is the contact angle of particle. Eq. (**??**) depends only on particle sizes and contact angle, which implies a planar interface.

Finally, the diameter and mass change rate of the j-th Pickering particle adsorbed on the i-th Pickering emulsion droplet surface are written as:

$$\frac{dd_{p,i,j}}{dt} = -\frac{2k_{p,i,j}k_{a,i,j}\left(C_{sat} - C_{p,c}\right)}{\rho_p}, \tag{5}$$

$$\frac{dm_{p,i,j}}{dt} = \frac{\pi}{2}\rho_p\left(d_{p,i,j}^2 + d_{p,i,j}l_{c,i,j}\right)\frac{dd_{p,i,j}}{dt}. \tag{6}$$

The particle concentration in the continuous phase can be evaluated using the particle mass conservation as:

$$\frac{dC_{p,c}}{dt} = -\frac{1}{V_c}\sum_{i=1}^{N_d}\sum_{j=1}^{N_{p,i}}\frac{dm_{p,i,j}}{dt}, \tag{7}$$

where $C_{p,c}$ is the particle concentration in the continuous phase and V_c is the volume of the continuous phase, N_d is the droplet number and $N_{p,i}$ is the number of particles adsorbed on the i-th droplet.

Particle dissolution affects API release from the Pickering emulsion droplets through coverage. The coverage of the i-th droplet can be calculated as:

$$\phi_i = \sum_{j=1}^{N_{p,i}} \varphi(r_{p,i,j}, l_{c,i,j}, \theta, r_{d,i}), \tag{8}$$

where $\varphi(r_{p,i,j}, l_{c,i,j}, \theta, r_{d,i})$ is the coverage of the j-th particle adsorbed on the i-th droplet, depengind on particle sizes, contact angle, and droplet size. It is calculated using numerical ingeraval, whose details are provided in [?].

2.3. Release of API from Pickering emulsions

The release of API from the i-th dispersed droplet to the continuous phase can be described using the interface transport concentration equation [?] as:

$$\frac{dC_{API,d,i}}{dt} = -\frac{1}{\frac{P}{k_{d,i}} + \frac{1}{k_{c,i}}} \frac{A_{d,i}(1-\phi_i)}{V_{d,i}} \left(P C_{API,d,i} - C_{API,c} \right), \tag{9}$$

where $C_{API,d,i}$ is the API concentration in the i-th droplet, $C_{API,c}$ is the API concentration in the continuous phase, $P = C^*_{API,c}/C^*_{API,d}$ is the partition coefficient with $C^*_{API,d}$ and $C^*_{API,c}$ are the API concentration at the interface of the disperse and continuous phases, respectively, $k_{d,i} = Sh\mathcal{D}_{API,d}/d_{d,i}$ is the mass transfer coefficient in the disperse phase, $k_{c,i} = Sh\mathcal{D}_{API,c}/d_{d,i}$ is the mass transfer coefficient in the continuous phase, $\mathcal{D}_{API,d}$ and $\mathcal{D}_{API,c}$ are the API diffusivities in the disperse and continuous phases, respectively, $A_{d,i}, V_{d,i}, \phi_i$ are the surface area, volume, and coverage of the i-th droplet, respectively.

Accordingly, the governing equation for API concentration in the continuous phase can be written as:

$$\frac{dC_{API,c}}{dt} = -\frac{1}{V_c} \sum_{i=1}^{N_d} \left(V_{d,i} \frac{dC_{API,d,i}}{dt} \right) = \sum_{i=1}^{N_d} \left(\frac{1}{\frac{P}{k_{d,i}} + \frac{1}{k_{c,i}}} \frac{A_{d,i}(1-\phi_i)}{V_c} \left(P C_{API,d,i} - C_{API,c} \right) \right), \tag{10}$$

where V_c is the volume of the continuous phase.

2.4. Particle dissolution solved using population balance equation

The dissolution process of Pickering particles can be described by population balance equation. Anisotropic Capsule-shaped particles require two internal coordinates to describe their length and diameter. Therefore, a bivariate particle size distribution (PSD) is adopted, $n(t, r_p, l_c)$. The population balance equation for particle dissolution can be written as [?]:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial r_p} \left(\frac{dr_p}{dt} n \right) + \frac{\partial}{\partial l_c} \left(\frac{dl_c}{dt} n \right) = 0 \tag{11}$$

101   As mentioned previously, l_c remains constant during particle dissolution, which gives $dl_c/dt = 0$. Therefore,

102 Eq. (??) can be simplified as:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial r_p}\left(\frac{dr_p}{dt}n\right) = 0 \tag{12}$$

103 where dr_p/dt can be calculated using Eq. (??)

2.4.1. Sectional method for PBE

105   The bivariate PBE (Eq. (??)) can be solved using sectional method (SM). The two internal coordinate spaces are

106 discretized into two-dimensional grid.

$$N_{i,j} = \int_{r_{p,i-1/2}}^{r_{p,i+1/2}} \int_{l_{c,j-1/2}}^{l_{c,j+1/2}} n \, dr_p \, dl_c \tag{13}$$

107   Then, the PSD can be written as:

$$n\left(t, r_p, l_c\right) = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} N_{i,j}(t)\delta(r_p - \mathcal{R}_{p,i})\delta(l_c - \mathcal{L}_{c,j}) \tag{14}$$

108 where $\mathcal{R}_{p,i}$ and $\mathcal{L}_{c,j}$ are the pivotal points in the intervals $[r_{p,i-1/2}, r_{p,i+1/2})$ and $[l_{c,j-1/2}, l_{c,j+1/2})$, respectively.

2.4.2. Conditioned quadruture-based moment method for PBE

110   The bivariate PBE (Eq. (??)) can be also solved using conditioned quadruture-based moment method (CQMOM).

111 The moment equations can be obtained by integrating Eq. (??) over the two internal coordinates:

$$\frac{\partial \mathcal{M}_{i,j}}{\partial t} + \int_0^{+\infty} \int_0^{+\infty} \frac{\partial}{\partial r_p}\left(\frac{dr_p}{dt}n\right) dr_p \, dl_c = 0 \tag{15}$$

112 where $\mathcal{M}_{i,j} = \int_0^{+\infty} \int_0^{+\infty} n \, dr_p \, dl_c$.

3. Results and discussion

4. Conclusions

A. Dissolution rate of capsule-shaped particles

A.1. Diameter change rate of capsule-shaped particles

For one of the semi-spherical ends of a capsule-shaped particle, we have:

$$\frac{\mathrm{d}m_{\text{semi}-\text{sph}}}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{2}\left(\frac{1}{6}\pi d_{\text{p}}^3 \rho_{\text{p}}\right)\right) = \frac{1}{4}\pi\rho_{\text{p}}d_{\text{p}}^2\frac{\mathrm{d}d_{\text{p}}}{\mathrm{d}t}. \tag{A.1}$$

Substitute the above equation and $A_{\text{semi}-\text{sph}} = \left(\pi d_{\text{p}}^2\right)/2$ into Eq. (??), we have:

$$\frac{1}{4}\pi\rho_{\text{p}}d_{\text{p}}^2\frac{\mathrm{d}d_{\text{p}}}{\mathrm{d}t} = -\frac{1}{2}\pi d_{\text{p}}^2 k\left(C_{\text{sat}} - C_{\text{p,c}}\right), \tag{A.2}$$

which gives

$$\frac{\mathrm{d}d_{\text{p}}}{\mathrm{d}t} = -\frac{2k\left(C_{\text{sat}} - C_{\text{p,c}}\right)}{\rho_{\text{p}}}. \tag{A.3}$$

Similarly, for the cylindrical section of the particle,

$$\frac{\mathrm{d}m_{\text{cyl}}}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{4}\pi d_{\text{p}}^2 l_c \rho_{\text{p}}\right) = \frac{1}{2}\pi\rho_{\text{p}}d_{\text{p}}l_c\frac{\mathrm{d}d_{\text{p}}}{\mathrm{d}t}, \tag{A.4}$$

where l_c is the height of the cylindrical section, which is a constant because its top and bottom faces are covered by the semi-spherical ends. Since dissolution happens only at the lateral face of the cylindrical section, the dissolution surface area is $A_{\text{cyl}} = \pi d_{\text{p}}l_c$. Substitute them into Eq. (??), we have:

$$\frac{1}{2}\pi\rho_{\text{p}}d_{\text{p}}l_c\frac{\mathrm{d}d_{\text{p}}}{\mathrm{d}t} = -k\pi d_{\text{p}}l_c\left(C_{\text{sat}} - C_{\text{p,c}}\right), \tag{A.5}$$

which gives

$$\frac{\mathrm{d}d_{\text{p}}}{\mathrm{d}t} = -\frac{2k\left(C_{\text{sat}} - C_{\text{p,c}}\right)}{\rho_{\text{p}}}. \tag{A.6}$$

Eq. (??) and Eq. (??) are identical, indicating that the diameters of the semi-spherical ends and the cylindrical section of a capsule-shaped particle decrease at the same rate.