

¹ Highlights

² **Monte Carlo simulation of Pickering particle dissolution and API release in Pickering**
³ **Emulsions**

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- ⁵ • Random sequential adsorption gives coverages of Pickering emulsions
⁶ • API release from a population of Pickering emulsions is studied
⁷ • Pickering particle dissolution induced coverage changes are included

⁸ Monte Carlo simulation of Pickering particle dissolution and API ⁹ release in Pickering Emulsions

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ABSTRACT

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\begin{abstract} ... \end{abstract} and \begin{keyword} ... \end{keyword} which contain the abstract and keywords respectively.

Each keyword shall be separated by a \sep command.

²¹ 1. Introduction

²² 2. Methodology

²³ 2.1. Geometric modeling of Pickering emulsion

²⁴ The coverage of Pickering emulsion droplets plays an important role in API release, because it affects the available
²⁵ surface area for API release. The coverage is determined by the adsorption of Pickering particles on the droplet surfaces.
²⁶ Unfortunately, measurement of coverage is challenging due to its multiscale multiphase physics. Therefore, numerical
²⁷ simulation is adopted in this work to obtain the coverage of Pickering emulsion droplets. Depending on the packing
²⁸ pattern of Pickering particles, different numerical methods can be used to model the adsorption process of Pickering
²⁹ particles.

³⁰ Based on our experiments, this study focuses on the micron-sized elongated curcumin particles, which can be
³¹ approximated as capsule-shaped particles consisting of two semi-spherical ends and a cylindrical section. A loose
³² random packing pattern of these particles is observed on the emulsion droplet surfaces, which can be modeled using
³³ random sequential adsorption (RSA) method. In RSA, particles sequentially attempt to adsorb at random locations on
³⁴ the droplet surfaces. They are adsorbed only if they do not overlap with any previously adsorbed particles, and once
³⁵ adsorbed, they remain fixed in place. The RSA simulation can provide a detailed records of the adsorbed Pickering
³⁶ particles, including their size distribution and the coverage they provide, which are valuable for modeling the API
³⁷ release from Pickering emulsions.

³⁸ The RSA approach is implemented using Monte Carlo method. Meanwhile, the probability of a successful
³⁹ adsorption reduces significantly as coverage increases, which makes the RSA simulations computationally expensive.

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40 The jamming state, which is the maximum coverage that can be achieved by RSA, is rarely reached in the simulations,
 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 [1].

47 2.2. Dissolution of Pickering particles

48 2.2.1. Particle-resolved dissolution model

49 The dissolution of a particle can be described by the following mass transfer equation [2]:

$$\frac{dm_p}{dt} = -k_p A_p (C_{\text{sat}} - C_{p,c}), \quad (1)$$

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

52 For a capsule-shaped particle consisting of two semi-spherical ends and a cylindrical section, it is natural to assume
 53 that the particle surface shrinks along its normal direction during dissolution. Therefore, the height of the cylindrical
 54 section, l_c , remains constant during dissolution because the top and bottom faces of the cylindrical section are covered
 55 by the semi-spherical ends. It can be proved that the particle surface, of both the semi-spherical and cylindrical parts,
 56 shrinks at the same rate as (see Appendix A):

$$\frac{dd_p}{dt} = -\frac{2k_p (C_{\text{sat}} - C_{p,c})}{\rho_p}, \quad (2)$$

57 where ρ_p is the particle density. The dissolution process can be governed by the reaction mechanism or the diffusion
 58 mechanism [3]. For reaction-controlled dissolution, it is assumed to be a first-order process, and a constant particle
 59 mass transfer coefficient k_p will be used. For a diffusion-controlled dissolution, the particle mass transfer coefficient
 60 can be written as:

$$k_p = \frac{\text{Sh} \mathcal{D}_{p,c}}{d_{32,p}}, \quad (3)$$

61 where $\text{Sh} = 2$ is the Sherwood number, $\mathcal{D}_{p,c}$ is the particle diffusivity in the continuous phase, and $d_{32,p} = 6V_p/A_p$ is
 62 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

the particle surface area. The reaction-controlled dissolution process is size-independent, while the diffusion-controlled 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 portion of the particle surface is exposed into the continuous phase, while the rest is inside the dispersed droplet. In this work, particles are assumed to be only dissolvable 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

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

where θ is the contact angle of particle. Eq. (4) depends only on particle sizes and contact angle, which implies a planar interface.

For the i -th droplet, the diameter and mass change rate of its j -th adsorbed particle are written as:

$$\frac{dd_{p,j}^{(i)}}{dt} = -\frac{2k_{p,j}^{(i)} k_{a,j}^{(i)} (C_{\text{sat}} - C_{p,c})}{\rho_p}, \quad (5)$$

77

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

78 Particle dissolution affects API release through coverage. For the i -th droplet, the coverage is

$$\phi^{(i)} = \sum_{j=1}^{N_p^{(i)}} \varphi \left(r_{p,j}^{(i)}, l_{c,j}^{(i)}, \theta, r_d^{(i)} \right), \quad (7)$$

79 where φ is the coverage contribution of one adsorbed particle as a function of particle size, contact angle, and droplet
80 size, and $N_p^{(i)}$ is the number of particles on droplet i . The detailed numerical evaluation of φ is provided in [1].

81 **2.3. Particle dissolution solved using population balance equation**

82 The dissolution process of Pickering particles can be described by population balance equation. Anisotropic
 83 Capsule-shaped particles require two internal coordinates to describe their length and diameter. Therefore, a bivariate
 84 particle size distribution (PSD) is adopted, $n(t, r_p, l_c)$. The population balance equation for particle dissolution can be
 85 written as [4]:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial r_p} \left(\frac{dr_p}{dt} n \right) + \frac{\partial}{\partial l_c} \left(\frac{dl_c}{dt} n \right) = 0 \quad (8)$$

86 As mentioned previously, l_c remains constant during particle dissolution, which gives $dl_c/dt = 0$. Therefore,
 87 Eq. (15) can be simplified as:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial r_p} \left(\frac{dr_p}{dt} n \right) = 0 \quad (9)$$

88 where dr_p/dt can be calculated using Eq. (5).

89 **2.3.1. Sectional method for PBE**

90 The bivariate PBE (Eq. (16)) can be solved using sectional method (SM). The two internal coordinate spaces are
 91 discretized into two-dimensional grid.

$$N_{i,j} = \int_{r_{p,i-1/2}}^{r_{p,i+1/2}} \int_{l_{c,j-1/2}}^{l_{c,j+1/2}} n dr_p dl_c \quad (10)$$

92 Then, the PSD can be written as:

$$n(t, r_p, l_c) = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} N_{i,j}(t) \delta(r_p - \mathcal{R}_{p,i}) \delta(l_c - \mathcal{L}_{c,j}) \quad (11)$$

93 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.

94 **2.3.2. Conditioned quadrature-based moment method for PBE**

95 The bivariate PBE (Eq. (16)) can be also solved using conditioned quadrature-based moment method (CQMOM).
 96 The moment equations can be obtained by integrating Eq. (16) over the two internal coordinates:

$$\frac{\partial \mathcal{M}_{i,j}}{\partial t} + \int_0^{+\infty} \int_0^{+\infty} \frac{\partial}{\partial r_p} \left(\frac{dr_p}{dt} n \right) dr_p dl_c = 0 \quad (12)$$

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

98 **2.3.3. Extension to a population of droplets**

99 For a population of N_d droplets, the continuous-phase particle concentration follows mass conservation:

$$\frac{dC_{p,c}}{dt} = -\frac{1}{V_c} \sum_{i=1}^{N_d} \sum_{j=1}^{N_p^{(i)}} \frac{dm_{p,j}^{(i)}}{dt}, \quad (13)$$

100 where V_c is the continuous-phase volume.

101 **2.4. API release from Pickering emulsion droplets**

102 The release of API from the i -th dispersed droplet to the continuous phase can be described by

$$\frac{dC_{API,d}^{(i)}}{dt} = -\frac{1}{\frac{P}{k_d^{(i)}} + \frac{1}{k_c^{(i)}}} \frac{A_d^{(i)} (1 - \phi^{(i)})}{V_d^{(i)}} (PC_{API,d}^{(i)} - C_{API,c}), \quad (14)$$

103 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,

104 $P = C_{API,c}^*/C_{API,d}^*$ is the partition coefficient, and $A_d^{(i)}$, $V_d^{(i)}$, and $\phi^{(i)}$ are the surface area, volume, and coverage of the
105 i -th droplet, respectively.

106 The API mass transfer coefficient in the dispersed phase and continuous phase are $k_d^{(i)}$ and $k_c^{(i)}$, respectively, which
107 can be calculated as:

$$k_d^{(i)} = \frac{Sh D_{API,d}}{d_d^{(i)}}, \quad k_c^{(i)} = \frac{Sh D_{API,c}}{d_d^{(i)}}, \quad (15)$$

108 where $D_{API,d}$ and $D_{API,c}$ are the API diffusivity in the dispersed phase and continuous phase, respectively, and $d_d^{(i)}$
109 is the diameter of the i -th droplet. The Sherwood number is assumed to be 2 for all droplets, which corresponds to a
110 diffusion-controlled mass transfer process with a stagnant layer around the droplet.

111 According to API mass conservation, the governing equation for API concentration in the continuous phase can
112 be written as:

$$\frac{dC_{API,c}}{dt} = -\frac{1}{V_c} \sum_{i=1}^{N_d} V_d^{(i)} \frac{dC_{API,d}^{(i)}}{dt} = \sum_{i=1}^{N_d} \frac{1}{\frac{P}{k_d^{(i)}} + \frac{1}{k_c^{(i)}}} \frac{A_d^{(i)} (1 - \phi^{(i)})}{V_c} (PC_{API,d}^{(i)} - C_{API,c}), \quad (16)$$

113 where V_c is the volume of the continuous phase.

¹¹⁴ **3. Results and discussion**

¹¹⁵ **4. Conclusions**

¹¹⁶ **A. Dissolution rate of capsule-shaped particles**

¹¹⁷ **A.1. Diameter change rate of capsule-shaped particles**

¹¹⁸ For one of the semi-spherical ends of a capsule-shaped particle, we have:

$$\frac{dm_{\text{semi-sph}}}{dt} = \frac{d}{dt} \left(\frac{1}{2} \left(\frac{1}{6} \pi d_p^3 \rho_p \right) \right) = \frac{1}{4} \pi \rho_p d_p^2 \frac{dd_p}{dt}. \quad (\text{A.1})$$

¹¹⁹ Substitute the above equation and $A_{\text{semi-sph}} = \left(\pi d_p^2 \right) / 2$ into Eq. (1), we have:

$$\frac{1}{4} \pi \rho_p d_p^2 \frac{dd_p}{dt} = -\frac{1}{2} \pi d_p^2 k (C_{\text{sat}} - C_{p,c}), \quad (\text{A.2})$$

¹²⁰ which gives

$$\frac{dd_p}{dt} = -\frac{2k (C_{\text{sat}} - C_{p,c})}{\rho_p}. \quad (\text{A.3})$$

¹²¹ Similarly, for the cylindrical section of the particle,

$$\frac{dm_{\text{cyl}}}{dt} = \frac{d}{dt} \left(\frac{1}{4} \pi d_p^2 l_c \rho_p \right) = \frac{1}{2} \pi \rho_p d_p l_c \frac{dd_p}{dt}, \quad (\text{A.4})$$

¹²² where l_c is the height of the cylindrical section, which is a constant because its top and bottom faces are covered by
¹²³ the semi-spherical ends. Since dissolution happens only at the lateral face of the cylindrical section, the dissolution
¹²⁴ surface area is $A_{\text{cyl}} = \pi d_p l_c$. Substitute them into Eq. (1), we have:

$$\frac{1}{2} \pi \rho_p d_p l_c \frac{dd_p}{dt} = -k \pi d_p l_c (C_{\text{sat}} - C_{p,c}), \quad (\text{A.5})$$

¹²⁵ which gives

$$\frac{dd_p}{dt} = -\frac{2k (C_{\text{sat}} - C_{p,c})}{\rho_p}. \quad (\text{A.6})$$

¹²⁶ Eq. (A.3) and Eq. (A.6) are identical, indicating that the diameters of the semi-spherical ends and the cylindrical
¹²⁷ section of a capsule-shaped particle decrease at the same rate.

CRediT authorship contribution statement

128 **Yi Feng:** Conceptualization of this study, Methodology, Software. **Antonio Buffo:** Data curation, Writing -
129
130 Original draft preparation. **Elena Simone:** Data curation, Writing - Original draft preparation.

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