Multi-body coalescence in Pickering emulsions

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Particle-stabilized Pickering emulsions have shown unusual behaviours such as the formation of non-spherical droplets and the sudden halt of coalescence between individual droplets. Here we report another unusual behaviour of Pickering emulsions—the simultaneous coalescence of multiple droplets in a single event. Using latex particles, silica particles and carbon nanotubes as model stabilizers, we show that multi-body coalescence can occur in both water-in-oil and oil-in-water emulsions. The number of droplets involved in the nth coalescence event equals four times the corresponding number of the tetrahedral sequence in close packing. Furthermore, coalescence is promoted by repulsive latex and silica particles but inhibited by attractive carbon nanotubes. The revelation of multi-body coalescence is expected to help better understand Pickering emulsions in natural systems and improve their designs in engineering applications.

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Pickering emulsions are made of particle-stabilized droplets suspended in an immiscible continuous liquid phase. They are important soft matter systems that form naturally in crude oils and food products and have been engineered for drug delivery, water purification and material processing. Compared with ordinary emulsions, Pickering emulsions are distinctly stable because the removal of interfacial particles requires a large amount of energy. When individual Pickering droplets are forced to coalesce, the extraordinary stability brought about by interfacial particles can lead to the formation of nonspherical droplets and the arrest of droplet coalescence. Little is known, however, about the coalescence of a collection of hundreds and thousands of Pickering droplets as in real emulsions. This is particularly important when particle stabilizers are used to produce near-monodispersed droplets, during which the distribution of droplet size can be significantly broadened by coalescence under gravity, floatation and shear.

Here we report for the first time that the presence of stabilizers at the oil–water interface can lead to multi-body coalescence in an ensemble of Pickering droplets—a phenomenon that has not been reported for either Pickering or ordinary emulsions. More interestingly, the number of droplets involved in coalescence equals four times the corresponding number of the tetrahedral sequence, indicating the inclusion of all closely packed nearest neighbours in a single coalescence event. As a result, a magic size distribution is produced with distinctive maxima related to each other through the cubic root of four times the tetrahedral numbers.

**Figure 1 | Pickering emulsions made of three types of stabilizers.** Results obtained with different analytical techniques are organized in columns: (a-c) transmission electron micrographs of stabilizers, (d-f) digital photographs of emulsions during mixing, (g-i) photographs taken at the end of standing and (j-l) optical micrographs of emulsions after standing. Results obtained with different stabilizers are organized in rows: (a,b,g,j) latex particle-stabilized water droplets in dodecane, (b,e,h,k) silica particle-stabilized 1,2-dichlorobenzene (DCB) droplets in water and (c,f,i,l) carbon nanotube-stabilized water droplets in dodecane. Mass ratio between droplets and the continuous phase: (d,g,j), 0.0667; (e,h,k), 0.0650; (f,i,l), 0.0667. Stabilizer-to-droplet mass ratio: (d,g,j), 0.02; (e,h,k), 0.03; (f,i,l), 0.02. Scale bars: a-c, 500 nm; inset in e, 5 nm and j-l, 250 μm.
with surface tension-tuning magnetite (Fe₃O₄) nanoparticles (Fig. 1c) are several micrometers long and have a diameter of ca. 15 nm (ref. 6). Pickering emulsions stabilized by latex particles, silica particles and CNTs are prepared following a conventional protocol²⁰, involving two consecutive steps. First, water, oil and stabilizers are mixed and then shaken vigorously by hand for 10 min (Fig. 1d–f), forming Pickering emulsions containing stabilizer-wrapped droplets. Then, emulsions are left standing undisturbed on top of a bench for 10 min, allowing droplets to precipitate (Fig. 1g–i), forming a closely packed ensemble of several normally distributed populations of droplets. Of these distributions, the mean diameter of the corresponding droplet population. We find that $d_n$ decreases with increasing stabilizer-to-droplet mass ratio $\alpha$, as shown in Fig. 2d–f. The inverse dependence of $d_n$ on $\alpha$ can be readily explained by matching the total surface area of droplets and the total cross-section area of interfacial stabilizers:

$$d_n = \frac{6\rho(1-\eta)\tau_n}{\alpha^{-1}},$$

where $\rho$ is the specific gravity of stabilizers with respect to the droplet phase, $\eta$ is the porosity of interfacial packing and $\tau_n$ is packing thickness. Conformation of experimental data to equation (1) indicates that fulfilling the interfacial area requirement for accommodating all stabilizer particles is an important determinant of droplet size.

We further compare $d_n (n>0)$ with $d_0$, revealing a linear relationship between them:

$$d_n = k_d d_0; \quad n = 1, 2, 3,$$

as shown in Fig. 2g–i. The scaling factor $k_d$ is estimated from the slope of linear regression. For $n = 1, 2$ and $3, k_1 \approx 1.6, k_2 \approx 2.5$ and $k_3 \approx 6$.

**Figure 2** | Size distributions of three types of Pickering droplets. Results of different analyses are organized in columns: (a–c) diameter histograms showing distinctive maxima: $d_n (n = 0, 1, 2, 3)$, (d–f) inverse correlations of $d_n$ with stabilizer-to-droplet mass ratio $\alpha$ and (g–i) linear correlations of $d_n$ with $d_n$ (n > 0) with $d_0$. Results for different stabilizers are organized in rows: (a,d,g) latex particle-stabilized water droplets in dodecane, (b,e,h) silica particle-stabilized 1,2-dichlorobenzene (DCB) droplets in water and (c,f,i) carbon nanotube-stabilized water droplets in dodecane. Curves in d–f are least-square regressions to equation (1). Lines in g–i are regressions to equation (2). Mass ratio between droplets and the continuous phase: (a,d,g), 0.0667; (b,e,h), 0.0650; (c,f,i), 0.0667. Stabilizer-to-droplet mass ratio: a, 0.02; b, 0.03 and c, 0.02. Error bars represent s.e.
$k_n \approx 3.4$ for all three emulsion systems. The conservation of $k_n$’s among different emulsion systems suggests the presence of a universal mechanism that controls the evolution of droplet size.

**Evolution of droplet size through multi-body coalescence.** To elucidate the mechanism of size evolution for Pickering droplets, we first focus on the mean diameter of deconvoluted droplet.
population without considering dispersion of the population. As shown in Fig. 3a (see Supplementary Table 1 for data), $k_n$ equals the cubic root of four times the corresponding tetrahedral number, $T_n$:

$$k_n = \sqrt[3]{T_n}; T_n = \sum_{j=1}^{n} 2j(j+1),$$ (3)

suggesting that a $d_n$ droplet has the same volume as $T_n$ droplets and thus is formed by their coalescence. For $n = 1, 2$ and $3$, $T_n = 4, 16$ and 40; therefore, the coalescence of these Pickering droplets is multi-body in nature.

Multi-body coalescence requires droplets to be closely packed, which is facilitated by the density difference between water and oil in our experimental systems (cf. Fig. 1g–i)\textsuperscript{28}. As illustrated in Fig. 3b and Table 1, four nearest-neighbouring $d_0$ droplets form a tetrahedron in a face-centred close (FCC) packed ensemble. When all four droplets coalesce simultaneously, the new droplet has a diameter of $d_1 = \sqrt{T_1}d_0$, where $T_1 = 4$. The $d_1$ droplet has 12 nearest $d_0$ neighbours in FCC, yielding a $d_2$ droplet after coalescing with the $d_1$ droplet: $d_2 = \sqrt{T_2}d_0$, where $T_2 = 4 + 12 = 16$. Similarly, a $d_3$ droplet is formed by the coalescence of the $d_2$ droplet with its 24 nearest neighbours: $d_3 = \sqrt{T_3}d_0$, where $T_3 = 16 + 24 = 40$.

We further examine multi-body coalescence by considering the material conservation of interfacial stabilizers before and after coalescence, which requires:

$$T_n \rho (1 - \eta) t_0 \pi d_n^2 = \rho (1 - \eta) t_n \pi d_n^2.$$ (4)

By combining this equation with equation (2), we obtain:

$$t_n/t_0 = \sqrt{T_n}/k_n = k_n.$$ (5)

for constants $\rho$ and $\eta$. Indeed, equation (5) holds for all three emulsion systems as illustrated in Fig. 3c (see Supplementary Table 2 for data).

**Polydispersity and size evolution.** In the analyses described above, we have assumed that each deconvoluted droplet population has a single diameter, $d_n (n = 0, 1, 2, 3)$, equal to the mean
of the Gaussian fit of experimental data. For the 0th droplet population, this assumption can be validated by considering that \( d_0 \) droplets are formed under vigorous shaking—an independent and identical process with a finite variance. However, will the coalescence of normally distributed \( d_0 \) droplets produce normally distributed \( d_n \) \((n > 0)\) droplets?

Coalescence progresses through the conservation of volume:

\[
d_n = \sum_{i=1}^{T_n} d_{n-i}.
\]

According to equation (6), we can prove that the probability density function of \( d_n \) is the \( T_n \)-fold convolution power of the probability density function of \( d_0 \) (see Supplementary Note 1 for derivation), which cannot be evaluated analytically. To obtain the distribution of the \( n \)th droplet population, we resort to the Monte Carlo method, which computes one million \( d_n \) values from randomly selected \( d_0 \)'s using equation (6).

The histograms of simulated \( d_n \)'s \((n > 0)\) are shown in Fig. 4a, along with the normally distributed 0th population. The histograms can be well-approximated by normal distributions (similarity to normality \( > 99.8\% \), as measured by Kolmogorov–Smirnov statistic)\(^{28, 29}\), confirming that the normal distribution is conserved through coalescence. The means of simulated \( d_n \)'s are compared with those estimated from experimental data in Fig. 4b. The two data sets exhibit an excellent linear correlation with a near-unity slope of 1.01 \((\pm 0.01)\) \((R^2 = 0.96)\), validating the use of Gaussian fits to estimate \( d_n \)'s.

Coalescence probability and interparticle force. Although Pickering droplets prepared with different stabilizers coalesce following the same tetrahedral sequence, the selection of stabilizer can, however, affect coalescence probability. This is revealed by examining the variation of relative abundance \( N_i/N_0 \) \((i = 0, 1, 2, 3)\) of each droplet population with \( z \), as shown in Fig. 5. Here \( N_i \) is the number of \( d_i \) droplets estimated by integrating the \( i \)th Gaussian fit and \( N_0 = \sum_{i=0}^{3} N_i \). As \( z \) increases, \( N_i/N_0 \) \((i > 0)\) increases at the expense of \( N_0/N_0 \) for latex and silica-stabilized droplets (Fig. 5a,b), indicating that the addition of stabilizers promotes coalescence. For CNT-stabilized droplets (Fig. 5c), the opposite is observed, revealing improved stability of \( d_0 \) droplets and suppressed coalescence with the addition of CNTs.

To understand why coalescence is promoted by latex and silica particles but suppressed by CNTs, we divide coalescence into two consecutive processes: packing and fusion, as illustrated in Fig. 6. Packing presses \( d_0 \) droplets together and transforms them from spheres to rounded polyhedrons. To pack droplets sufficiently close for coalescence, Laplace pressure \( p_0 \) must be overcome by the external pressure provided by the droplets’ weight, \( p \):

\[
P > p_0; p_0 = \frac{4\gamma}{d},
\]

where \( \gamma \) is interfacial tension. Fusion between droplets then happens with the rupture of the separating liquid film, which requires the internal pressure of polyhedral droplets, \( p_0 \), to exceed the disjoining pressure of the film, \( \Pi \) (a property of the continuous phase)\(^{31, 32}\):

\[
p_0 > \Pi; p_0 = \frac{4\gamma}{d_0} C,
\]

where \( C \) is a constant related to droplet packing fraction.
The interfacial tension includes contributions from both stabilizer-wrapped droplets, $\gamma_d$, and interactions between interfacial stabilizers, $\gamma_s$:

$$\gamma = \gamma_d + \gamma_s.$$  

Equation (9)

For stabilized droplets$^2$,

$$\gamma_d = \gamma_{ow} \left[1 - (1 - \eta)\cos^2 \theta\right],$$  

where $\gamma_{ow}$ is the oil–water interfacial tension and $\theta$ is the contact angle formed by the continuous phase, the stabilizer surface and the droplet phase. According to equation (10), $\gamma_d$ is constant for a given emulsion system; therefore, $\gamma$ varies with $\gamma_s$.

$\gamma_s$ can arise from the electrostatic repulsion between interfacial stabilizers. Latex particles, silica particles and CNTs are all negatively charged, as confirmed by their negative zeta potentials in water (latex, $-18 (\pm 7) \text{ mV}$; silica, $-21 (\pm 7) \text{ mV}$; CNTs, $-13 (\pm 1) \text{ mV}$). Charge-induced repulsion, $\gamma_{cp}$, pushes stabilizer particles away from one another, reducing interfacial tension that pulls stabilizers together (that is, $\gamma_s = -\gamma_{cp} < 0$):

$$\gamma = \gamma_d - \gamma_{cp}.$$  

Equation (11)

An indication of interparticle repulsion is the random close packing$^3$ patterns formed by latex and silica particles at the oil–water interface and revealed by confocal laser scanning microscopy, as shown in Fig. 7a–c and d–f, respectively. With low $\gamma$, equation (7) is readily fulfilled. The probability of coalescence is thus controlled by the difference between $p_p$ and $\Pi$ according to equation (8). As $\alpha$ increases, $d_0$ decreases according to equation (1). This leads to an increase of $p_p$, improving the chances of overcoming $\Pi$ to coalesce and produce more $d_n$ ($n > 0$) droplets at greater $\alpha$ (cf. Fig. 5a,b).

Different from latex and silica particles, CNTs form an extended network at the oil–water interface, as revealed by the confocal micrographs shown in Fig. 7g–i. Formation of the network can be attributed to strong $\pi$–$\pi$ attractions between individual nanotubes, which overtake electrostatic repulsions between them (that is, $\gamma_s = \gamma_{\pi-\pi} - \gamma_{cp} > 0$)$^6$,:

$$\gamma = \gamma_d + \gamma_{\pi-\pi} - \gamma_{cp}$$

Equation (12)

With high $\gamma$, equation (8) is readily fulfilled, leaving the control of coalescence probability to equation (7). As $\alpha$ increases, $d_0$ decreases and $p_0$ increases, resulting in a decrease of coalescence and minimal amounts of $d_n$ ($n > 0$) droplets with large $\alpha$ (cf. Fig. 5c).

**Discussion**

We have shown that closely packed Pickering droplets can coalesce through a multi-body mechanism. We hypothesize that the determining factor of multi-body coalescence is the presence of stabilizers at the oil–water interface, which slows down coalescence. In ordinary emulsions where droplets are stabilized by surfactant molecules or ions, coalescence happens rapidly between two droplets$^3$,$. Recent measurements have, however, shown that coalescence between

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**Table 2 | Progression of coalescence in HCP*.**

<table>
<thead>
<tr>
<th>$n$</th>
<th>Nearest Neighbors†</th>
<th>Droplets Involved in the $n^{th}$ Coalescence</th>
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<tbody>
<tr>
<td></td>
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<td>All Droplets Involved</td>
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<tr>
<td>1</td>
<td></td>
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<tr>
<td>2</td>
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<td>3</td>
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CNT, carbon nanotube; HCP, hexagonal close packing.

†Thickness of the CNT layer is exaggerated for visual effects. Grey droplets are not nearest neighbours and do not participate in coalescence.

‡The close-packed [111] plane is marked in orange. The HCP unit cell is marked by yellow lines. The tetradecahedron formed by 12 coordinating neighbours around a central $d_0$ droplet is marked by cyan lines. The octahedron (tetrahedron for $n=1$) formed by coalescing droplets is marked by black lines.

‡To illustrate that only certain enclosing neighbours can coalesce with the droplet (an interstitial void for $n=1$) in the centre.
two particle-stabilized droplets is orders of magnitude slower. The extended transition time provides an opportunity for all of the nearest neighbours to be involved in a single coalescence event once coalescence is initiated between two droplets.

We formulate the multi-body coalescence theory in the FCC configuration. If Pickering droplets are packed in the hexagonal close packing (HCP) configuration, the number of droplets involved in the first coalescence event is the same as in FCC but decreases gradually for the second and third events, as illustrated in Table 2. The \( k_n \) values for HCP are 1.6, 2.4 and 2.5 compared with 1.6, 2.5 and 3.4 for FCC. According to experimentally determined \( k_n \)s, the packing of Pickering droplets is better represented by FCC. Nonetheless, multi-body coalescence requires only short-range ordering because significant coalescence occurs in the first few coordination shells surrounding an interstitial void. In the longer range, the lack of organization, such as that in random close packing, should not affect the outcome of multi-body coalescence in Pickering emulsions.

### Methods

#### Reagents

Reagent-grade chemicals were purchased from Sigma-Aldrich and Fisher Scientific except where otherwise stated. Deionized (DI) water (18.2 MΩ cm \(^{-1}\)) was used in solution making, washing and rinsing was generated using a Millipore system (Billerica, MA, USA) on site. We prepared Pickering emulsions by shaking and standing (see below).

#### Latex particle-stabilized water droplets in dodecane

Latex particles were obtained by drying an aqueous solution in vacuum overnight. The particles were then dispersed in dodecane (99%, TCI America) at various concentrations. To make Pickering emulsions, 50 mL DI water was added to 1 mL dodecane. The mixture was shaken by hand vigorously for 10 min. The mixture was shaken by hand vigorously for 10 min and then left standing on bench for 10 min.

#### Silica particle-stabilized DCB droplets in water

Silica particles were first coated with 3-aminopropyltrimethoxysilane (APTMS, 97%) to modify their surface wettability. To do so, 0.1 mL particle solution (10 \( \times 10^{-3}\) M) was dried in an oven at 120°C overnight and was then mixed with 10 mL toluene (\( 99.8\% \)) and 100 \( \mu\)L APTMS. The mixture was shaken for 2 h. The particles were washed with toluene five times and with ethanol three times. The particles were then dried in an oven overnight to remove residual ethanol and immerse in water before use. To make a Pickering emulsion, 50 \( \mu\)L DI water was added to 1 mL DCB water with different concentrations of silica particles. The mixture was shaken by hand vigorously and left standing undisturbed following the same procedure for making latex-stabilized emulsions.

#### CNT-stabilized water droplets in dodecane

The mixture was shaken and left standing quiescently following the same protocol for making latex and silica-stabilized emulsions.

#### Optical microscopy

Diameters of particle-stabilized droplets were measured using images taken by an optical microscope (Motic BA300POL). To do so, emulsions were poured on either glass (for silica-stabilized droplets) or plastic (for latex and CNT-stabilized droplets) Petri dishes. The emulsions were dispensed with the corresponding continuous phases to minimize droplet overlapping in the imaging field. For each sample, ~30 images were taken randomly with a \( \times 10\) objective lens (resolution: 1.25 μm per pixel). Diameters were measured using software ImageJ. Some droplets stabilized by silica particles (<5%) were found at the arrested coalescence state with non-spherical shapes (Supplementary Fig. 2). They were excluded in subsequent diameter analyses.

#### Confocal laser scanning microscopy

Interfacial stabilizers were visualized using a confocal laser scanning microscope (Nikon A1R) equipped with a \( \times 100\) Plan Apo total internal reflection fluorescence objective lens. The oil phases were illuminated using Alex Fluor 488. Concentrations of the fluorescent dyes were: latex particle-stabilized water droplets in dodecane, 0.001 mm Alex Fluor 488 in water and 0.1 mM Nile red in dodecane; silica particle-stabilized DCB droplets in water, 0.03 mM Nile red in DCB and 0.01 mM Alex Fluor 488 in water; and CNT-stabilized water droplets in dodecane, 0.01 mM Alex Fluor 488 in water and 0.03 mM Nile red in dodecane. The oil-in-water emulsion stabilized by silica particles was imaged using a custom-made hydrophilic glass-in-oil emulsions stabilized by latex particles and CNTs, the reservoir was treated with a 1:100 octadecyltrichlorosilane toluene solution to create a hydrophobic coating before use.

### References


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**Author contributions**

C.N., H.W. and T.W. designed the study and analyzed data. T.W. and H.W. performed the experiments. B.J. contributed to the design of confocal measurements. F.L. performed Monte Carlo simulation and contributed to the statistical analysis of experimental data. P.C.B. contributed to the interpretation of droplet packing. All authors contributed to the writing of the paper.

**Additional information**

**Supplementary Information** accompanies this paper at http://www.nature.com/naturecommunications

**Competing financial interests:** The authors declare no competing financial interests.