Emulsion Droplets: Characteristics and Importance

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Influence of Droplet Characteristics on Emulsion Properties

Droplet Characteristics
- Concentration
- Particle size distribution
- Electrical charge
- Interfacial properties
- Physical state

Food Structure
- Organization
- Interactions

Quality Attributes
- Shelf-life
- Texture
- Appearance
- Flavor
- Nutrition

Need to know how to control, measure and report droplet characteristics!
Droplet Concentration: Influence on Emulsion Properties

FLUID-LIKE

Dilute

Concentrated

SOLID-LIKE

Skim Milk

Heavy Cream

Mayonnaise

Beverage

Infant Formula

Light Cream

Dressing (Regular)

Dressing (Light)

f

f_C

0% 20% 40% 60% 80% 100%

20% 40% 60% 80% 100%

Infant Formula

Light Cream

Dressing (Regular)

Dressing (Light)

Mayonnaise

Beverage

Infant Formula

Light Cream

Dressing (Regular)

Dressing (Light)

Mayonnaise

Beverage
Droplet Concentration: Influence on Emulsion Properties

Texture
Appearance
Stability

Rel. Viscosity vs. Droplet Concentration [%]

Lightness vs. Droplet Concentration [%]

Relative Creaming Vel. vs. Droplet Concentration [%]

Oil concentration effect
Droplet Concentration: Specification

- Disperse phase volume fraction:

\[
\phi = \frac{V_{\text{Droplets}}}{V_{\text{Emulsion}}}
\]

Volume\% = 100 \times \phi

- Disperse phase mass fraction:

\[
\phi_m = \frac{M_{\text{Droplets}}}{M_{\text{Emulsion}}}
\]

Mass\% = 100 \times \phi_m
Droplet Concentration: Number of Droplets per Unit Volume

Of major importance to:
- Fat crystallization in O/W emulsions (impurities/droplet)
- Distribution of reactants in emulsions (pro-oxidants/droplet)

\[ N = \frac{3 \phi}{4 \pi r^3} \]

\[ \sim 10^{12} - 10^{20} \text{ m}^{-3} \]
Of major importance to:

- Amount of emulsifier needed to cover surface
- Rate of surface mediated reactions e.g., lipid oxidation, lipid digestion

\[ S = \frac{3 \phi}{r} \]

\[ \sim 10^2 - 10^7 \text{ m}^2 \text{ m}^{-3} \]
Droplet Size: 
Influence on Emulsion Properties

- **Shelf-life:** Creaming, Droplet Aggregation
- **Quality:** Appearance, Flavor, Texture

Small Particles

Large Particles

![Small Particle Image](image1)

![Large Particle Image](image2)

![Graph Image](image3)
A manufacturer should establish a particle size distribution specification based on known product performance (e.g., stability, optics, texture, flavor, mouthfeel):

- Mean particle diameter < a critical diameter
- Median particle diameter < a critical diameter
- Percentage of droplets < a critical diameter
Representing Droplet Size Data

Prepare
 Measure
 Tabulate

Particle Size Distribution

<table>
<thead>
<tr>
<th>Size Range (µm)</th>
<th>(d_i) (µm)</th>
<th>(N_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 1</td>
<td>0.5</td>
<td>6</td>
</tr>
<tr>
<td>1 – 2</td>
<td>1.5</td>
<td>12</td>
</tr>
<tr>
<td>2 – 3</td>
<td>2.5</td>
<td>20</td>
</tr>
<tr>
<td>3 – 4</td>
<td>3.5</td>
<td>25</td>
</tr>
<tr>
<td>4 – 5</td>
<td>4.5</td>
<td>19</td>
</tr>
<tr>
<td>5 – 6</td>
<td>5.5</td>
<td>6</td>
</tr>
<tr>
<td>6 – 7</td>
<td>6.5</td>
<td>3</td>
</tr>
<tr>
<td>7 – 8</td>
<td>7.5</td>
<td>2</td>
</tr>
<tr>
<td>8 – 9</td>
<td>8.5</td>
<td>1</td>
</tr>
<tr>
<td>9 – 10</td>
<td>9.5</td>
<td>0</td>
</tr>
</tbody>
</table>

\(d_N = 3.4 \text{ µm}\)

Graph
Representing Droplet Size Data: What to Present?

Monodisperse
- Droplets all same size
- Report $d$ or $r$

Polydisperse
- Droplets different sizes
- Report PSD
- Report mean $d$ or $r$
- Report width
Particle Size Distributions
Graphical Representation

Histogram:
Amount in specific size categories is reported

Frequency:
Amount is equal to the area under the curve

Cumulative:
Amount below a specific size is reported

\[ V_{i} = F_{i} \times \Delta d_{i} \]

\[ C_{i} = \% < d_{i} \]
Representing Droplet Size Data: Specifying Size and Frequency

1. **Size Parameter.** A measurement of the size of the particles in the size-class: radius \((r)\) or diameter \((d)\)

2. **Frequency Parameter.** A measurement of the amount of particles present in the size-class: number \((N)\), surface \((S)\) or volume \((V)\)

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Amount can be absolute, fraction or percentage.
Particle Size Distributions: Use Appropriate Frequency Parameter!

![Graphs showing particle size distributions with number and volume percentages for 0 mM and 150 mM NaCl. Equations for volume calculation: $V_i = (\pi/6) N_i d_i^3$.](image)

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Representing Droplet Size Data: Using Mean Particle Sizes

Average values simplify presentation, but information is lost!

Which mean is the best to use?
Representing Droplet Size Data: Defining Mean and Width

**Mean:**
\[ \bar{x} = \sum_{i} \phi_i x_i \]

**Width:**
\[ \sigma = \sqrt{\sum_{i} \phi_i (x_i - \bar{x})^2} \]

Here:
- \( x_i \) = size parameter
- \( \phi_i \) = frequency weighting parameter

**Mean** = Measure of Central Tendency

**Width** = Measure of Spread of Data Around Mean (\( x/s \))
## Representing Droplet Size Data: Defining Mean and Width

### Mean

<table>
<thead>
<tr>
<th>Name of Mean</th>
<th>Frequency Weighting Parameter</th>
<th>Size Parameter</th>
<th>Definition of Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_N$</td>
<td>$\phi_{N,i} = N_i/\Sigma N_i$</td>
<td>$d_i$</td>
<td>$\Sigma \phi_{N,i} \times d_i$</td>
</tr>
<tr>
<td>$d_S$</td>
<td>$\phi_{S,i} = S_i/\Sigma S_i$</td>
<td>$d_i$</td>
<td>$\Sigma \phi_{S,i} \times d_i$</td>
</tr>
<tr>
<td>$d_V$</td>
<td>$\phi_{V,i} = V_i/\Sigma V_i$</td>
<td>$d_i$</td>
<td>$\Sigma \phi_{V,i} \times d_i$</td>
</tr>
</tbody>
</table>

### Width

<table>
<thead>
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<th>Name of Width</th>
<th>Definition of SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_N$</td>
<td>$\sqrt{[\Sigma \phi_{N,i} \times (d_i - d_N)^2]}$</td>
</tr>
<tr>
<td>$\sigma_S$</td>
<td>$\sqrt{[\Sigma \phi_{S,i} \times (d_i - d_S)^2]}$</td>
</tr>
<tr>
<td>$\sigma_V$</td>
<td>$\sqrt{[\Sigma \phi_{V,i} \times (d_i - d_V)^2]}$</td>
</tr>
</tbody>
</table>

\[ \bar{x} = \sum_{i} \phi_{i} x_{i} \]

\[ \sigma = \sqrt{\sum_{i} \phi_{i} (x_{i} - \bar{x})^2} \]
### Defining Mean Particle Sizes: Equivalent Ways of Expressing Means

<table>
<thead>
<tr>
<th>Name of Mean</th>
<th>Definition ( \tfrac{\sum N_i/\sum N_i \times d_i}{\sum S_i/\sum S_i \times d_i} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_N )</td>
<td>( \sum (N_i/\Sigma N_i \times d_i) )</td>
</tr>
<tr>
<td>( d_S )</td>
<td>( \sum (S_i/\Sigma S_i \times d_i) )</td>
</tr>
<tr>
<td>( d_V )</td>
<td>( \sum (V_i/\Sigma V_i \times d_i) )</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>Name of Mean</th>
<th>Definition ( \tfrac{\sum N_i d_i}{\sum N_i} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_{10} )</td>
<td>( \sum N_i d_i/\Sigma N_i )</td>
</tr>
<tr>
<td>( d_{32} )</td>
<td>( \sum N_i d_i^3/\Sigma N_i d_i^2 )</td>
</tr>
<tr>
<td>( d_{43} )</td>
<td>( \sum N_i d_i^4/\Sigma N_i d_i^3 )</td>
</tr>
</tbody>
</table>

\[ S_i \propto N_i d_i^2 \]
\[ V_i \propto N_i d_i^3 \]
Representing Droplet Size Data:
Use Appropriate Mean Size!

Effect of pH on Emulsion Stability:
Protein stabilized emulsion containing cationic polysaccharide
Representing Droplet Size Data: Use Appropriate Mean Size!

Effect of pH on Emulsion Stability:
Protein stabilized emulsion containing cationic polysaccharide

Using appropriate means can help identify issues with particular particles size classes!
Representing Droplet Size Data: Choose Appropriate Mean Size!

\[
d_{10} = 0.09 \text{ mm} \\
d_{32} = 0.21 \text{ mm} \\
d_{43} = 1.20 \text{ mm}
\]

**Note:**
- \(d_{10}\) and \(d_{32}\) are sensitive to the majority of particles
- \(d_{43}\) is sensitive to the presence of a few large aggregates
Representing Droplet Size Data:
Always Examine Full PSD!

\[ d_{10} = 5 \text{ µm} \]
\[ \sigma_{10} = 2 \text{ µm} \]

These distributions have the same mean diameter and the same distribution width!!!
Representing Droplet Size Data: Some Factors to Consider

Using and Reporting Droplet Size Data:

• **Size Parameter**
  – *Diameter or Radius?*

• **Frequency Parameter**
  – *Number or Volume?*

• **Always Examine PSD**

• **Mean Size & Width**
  – \(d_{10}, d_{32}, d_{43}\)?
Factors Affecting Choice of Appropriate Mean Size:

- **Instrument**: The sensitivity of an instrument to the particles in a particular size category depends on its underlying physical principles.
- **Feature of PSD of Interest**: Majority of particles or presence of large aggregates?
- **Utilization of Information**: Sometimes a particular mean size is required in a calculation, e.g., $d_{32}$ is used to calculate the surface area of an emulsion.
Droplets interactions have a large impact on emulsion microstructure and overall properties.

Non-flocculated:
- Low Viscosity
- Stable to Creaming

Flocculated:
- High Viscosity
- Unstable to Creaming
Aggregation Depends on Balance of Colloidal Interactions

ATTRACTION
- van der Waals
- Hydrophobic
- Depletion

REPULSION
- Electrostatic
- Steric

Aggregation occurs when attractive interactions outweigh repulsive interactions
Predicting Colloidal Interactions

- Sign
- Magnitude
- Range
Knowledge of colloidal interactions used to:

- Predict stability to droplet aggregation
- Identify origin of emulsion instability
- Develop strategies to prevent instability
- Predict emulsion rheology

**Stable**

**Unstable**
Influences droplet stability to aggregation, and therefore physicochemical properties

Influences droplet interactions with other charged species - biopolymers, mineral ions, vitamins, antioxidants, etc
Adsorption of charged species to droplet surfaces

- Emulsifiers, biopolymers, small ions (e.g. OH⁻)

![Diagram showing charged species and droplet charge origin](image)
Droplet Charge: Measurement of $\zeta$-Potential

Measure Direction and Velocity gives **Sign** and **Magnitude**

- Charge measured by electro-kinetic techniques
- *Effective* electrical potential on droplet
- Depends on charge density and ionic strength
Knowledge of droplet charge can be used to:

- Predict emulsion stability to droplet aggregation
- Characterize interactions between droplets and other charged species
Influence emulsion stability to flocculation, coalescence, partial coalescence, Ostwald ripening & creaming

Influence partitioning of food ingredients
- antioxidants, flavors, colors, minerals etc

Influence release characteristics

Characteristics:
- Composition
- Thickness
- Rheology
- Charge
A better understanding of the role of droplet characteristics on emulsion properties would enable manufacturers to improve product shelf-life, appearance, flavor, texture and develop reduced fat products.