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Static Multiple Light Scattering (SMLS)

Issue:
- What is Static Multiple Light Scattering (SMLS)?
- How to use SMLS to study instability phenomena of dispersions?

Contents:
- SMLS principle
- Study of migration phenomena: creaming and sedimentation
- Study of size increase: flocculation, coalescence, and ripening
- Measurement limits

Introduction

Static Multiple Light Scattering (SMLS) is an optical method to directly characterize concentrated liquid dispersions in their native state.

Many emulsions or suspensions are used in concentrated form. Optical methods such as laser diffraction (SLS) or dynamic light scattering (DLS) offer limited possibilities in terms of analysis of such formulations. In addition, concentrated products have to be diluted and therefore mixed (mechanical stress) which changes the dispersion state. SMLS can be used to characterized the dispersions without dilution or change of the initial state.

1. Principle

SMLS consists in sending photons (near infrared light source) into the sample. These photons, after being scattered many times by the particles (or droplets) of the dispersion, leave the sample and are detected by two synchronous detectors: Backscattering (BS) for opaque samples and Transmission (T) for transparent samples (**Figure 1**).

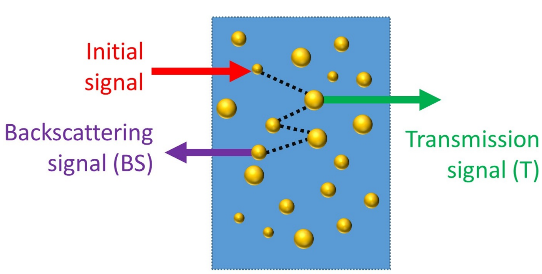

Figure 1. Difference between Backscattering (BS) and Transmission (T) signal for a dispersion.

1.1 Transmission flux

In diffusive optics, the photon mean free path (l) represents the mean distance traveled by photons before undergoing a scattering phenomenon (**Figure 2**). The measurement is performed by sending a light beam through the cell and detecting the photons that pass through the dispersion, without being scattered. Thus, the higher the number of photons passing through the cell, the higher the l value.

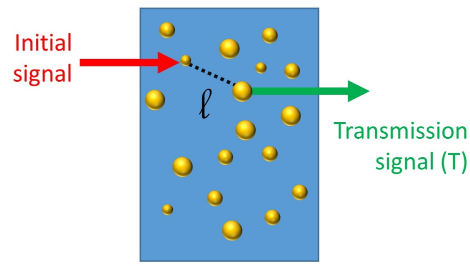

Figure 2. Representation of mean free path l for transmission flux.

The Lambert-Beer law gives an analytical expression of the transmitted flux T as a function of l:

$$T = T_0 \cdot exp(-\frac{2r_i}{l})$$

with r_i the internal radius of the measurement cell and T_0 the transmittance of the continuous phase. The expression of l is obtained from Mie Theory:

$$l = \frac{2d}{3\Phi Q_s}$$

with d the particle (or droplet) mean diameter, Φ the volume fraction, and Q_s a parameter given by the Mie theory.

Therefore, the transmission flux depends directly on the dispersion parameters: particle mean diameter d and their volume fraction Φ.

1.2 Backscattering flux

For BS phenomenon, the photon transport mean free path is called l^* and corresponds to the distance above which the photon loses the initial direction of the incident beam, or from another point of view, it corresponds to the distance of penetration of the photon in the dispersion (**Figure 3**).

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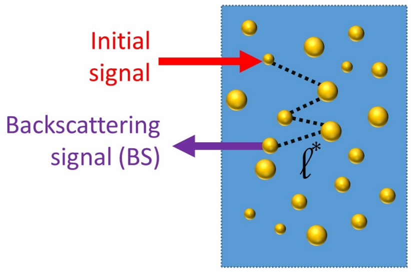

Figure 3. Representation of mean free path l^* for backscattering phenomenon.

The central part of the backscattered light spot has a radius of $4l^*$. Therefore, the measured BS flux can be linked to l^*:

$$BS = \frac{1}{\sqrt{l^*}}$$

According to Mie theory, l^* is inversely proportional to the volume fraction of the particles Φ and proportional to their mean diameter d:

$$l^* = \frac{2d}{3\Phi(1-g)Q_s}$$

g and Q_s are parameters given by the Mie theory.

As for the transmission phenomenon, the backscattering measurement also depends directly on the particle mean diameter d and their volume fraction Φ.

2. Instability phenomena of dispersions

To evaluate the temporal evolution of the dispersion, the measurement operates in scanning mode: the optical read head scans the length of the sample, acquiring T and BS data along the sample. Transmission is used to analyse clear to turbid dispersions and backscattering is used to analyse opaque and concentrated dispersions (**Figure 4**). Two curves providing the transmitted and backscattered light flux in % relative to the standards as a function of the sample height can be plotted.

In order to better analyze the variations of the profiles, the first profile at t_0 is selected as a reference and subtracted from all other profiles to obtain ΔBS and ΔT. At a given time t the expressions are

$$\Delta BS(t) = BS(t) - BS(t_0)$$

$$\Delta T(t) = T(t) - T(t_0)$$

The calculation of ΔBS (or ΔT in the case of diluted products) is used when the system undergoes several instabilities simultaneously (migration and increase in size) and it becomes difficult to set the threshold for phase thickness calculations.

It is important to keep in mind that in the case of a transmission signal, there is also a backscattering signal in the same zone. This is due to secondary reflections of the light on the glass cell. Therefore, in this zone one should only work on the transmission signal, not on the backscattering one.

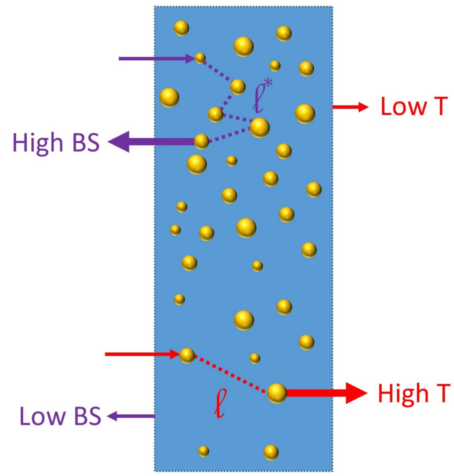

Figure 4. Influence of volume fraction (sample concentration) on the intensity of the signal exiting the sample.

2.1 Creaming

Creaming is the migration of the dispersed phase of an emulsion or a suspension, under the influence of buoyancy. Creaming is possible when the density of the dispersed phase is lower than the continuous phase (**Figure 5**).

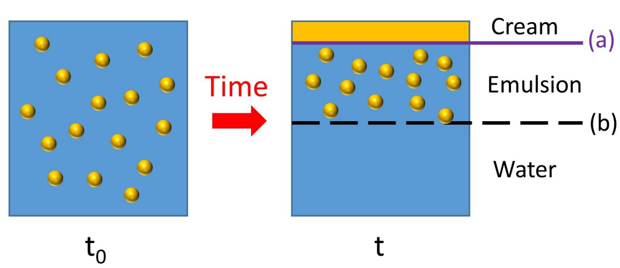

Figure 5. Creaming phenomenon from t_0 to t.

Creaming induces an increase of the dispersed phase concentration at the top of the dispersion and a decrease at the bottom. Two different fronts are formed:

a) cream layer limit: phase separation between the oil layer and the emulsion,

b) emulsion layer limit (clarification front): phase separation between the emulsion and the aqueous phase.

The evolution of ΔBS is shown in **Figure 6**. The backscattering flux decreases at the bottom of the sample due to a decrease of the concentration of the dispersed phase (clarification) and it increases at the top of the sample due to an increase of the concentration of the dispersed phase (creaming). Creaming can lead to a phase separation, with a clear phase at the top shown by a transmission peak.

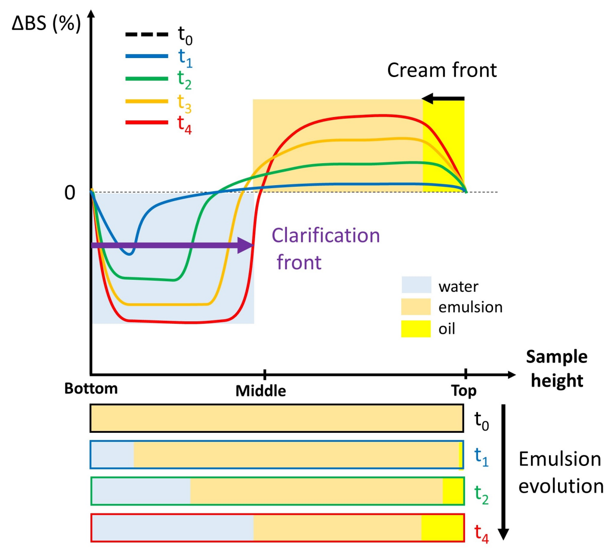

Figure 6. ΔBS profile for creaming phenomenon.

2.2 Sedimentation

Sedimentation is the opposite of creaming: segregation of the dispersed phase of an emulsion or a suspension, under the influence of buoyancy. Sedimentation is possible when the density of the dispersed phase is higher than the continuous phase (**Figure 7**).

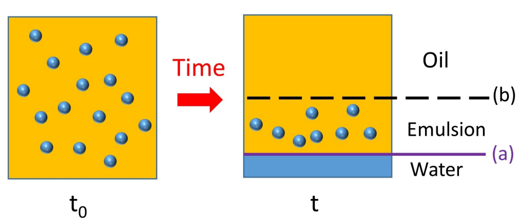

Figure 7. Sedimentation phenomenon from t_0 to t.

Two different fronts are formed:

a) sedimentation layer limit: phase separation between the water layer and the emulsion,

b) emulsion layer limit (clarification front): phase separation between the emulsion and the oil phase.

Sedimentation induces a decrease in the concentration of the dispersed phase at the top of the sample (clarification), leading to a decrease in the backscattering flux; and an increases at the bottom of the sample due to an increase of the concentration of the dispersed phase (**Figure 8**). Sedimentation can lead to a phase separation, with a clear phase at the bottom shown by a transmission peak.

2.3 Flocculation and coalescence

Flocculation and coalescence lead to an increase in the size of the dispersed phase (**Figure 9**). The two phenomena can be differentiated in the way that coalescence is irreversible and leads to the fusion of the interfaces, resulting in the creation of one single drop. Flocculation, on the other hand, is only an aggregation of drops and particles. When flocculation is irreversible, it is called coagulation. In some case flocculation can lead to coalescence.

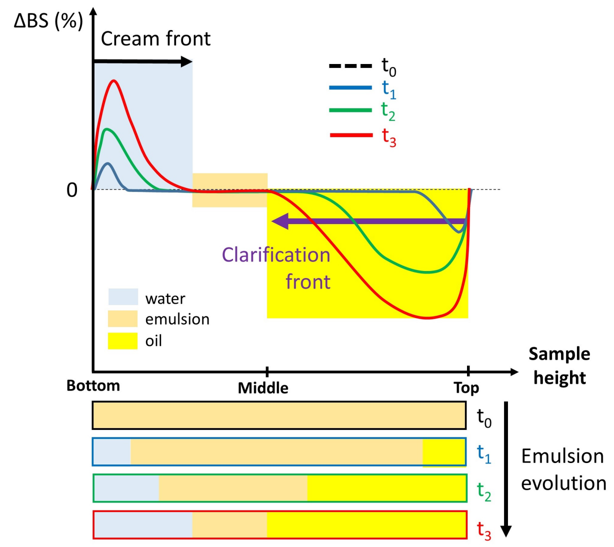

Figure 8. ΔBS profile for sedimentation phenomenon.

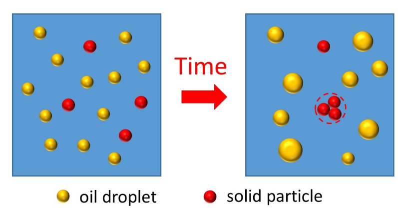

Figure 9. Coalescence of oil droplets and flocculation of particles.

This size variation leads to a decrease of the backscattering over the total height of the sample (**Figure 10**).

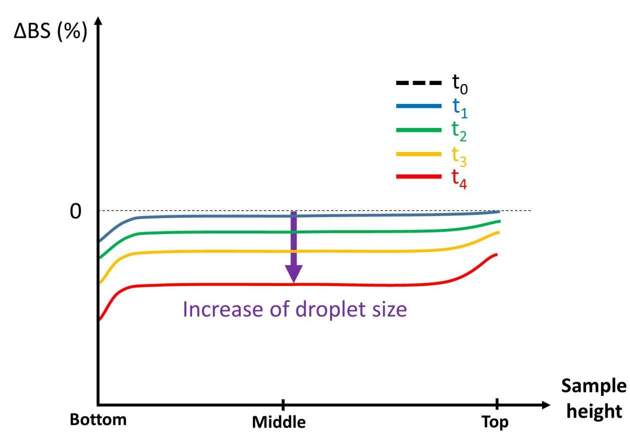

Figure 10. ΔBS profile for coalescence phenomenon.

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The evolution of the mean diameter can be determined knowing the refractive indices and the volume fraction.

2.4 Foam

Foams are mainly subjected to three instability phenomena: coalescence, ripening, and drainage.

Ripening is the increase in bubble size by gas dissolution from smaller to larger bubbles because of Laplacian pressure. Therefore, the evolution of ΔBS will have the same trend that the coalescence phenomenon **Figure 10**.

Foam drainage is the flow of liquid through a foam, driven by gravity and capillarity (**Figure 11**). This phenomenon is especially present for dry foams where the continuous phase flows through the lamella between the bubbles. It is possible to follow the appearance of the water phase at the bottom of the foam by the transmission peak.

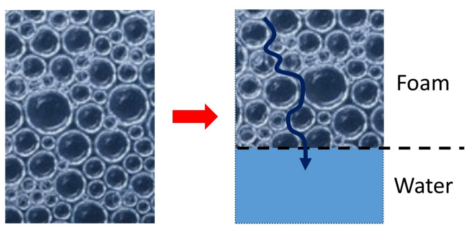

Figure 11. Drainage phenomenon for foam.

2.5 Sum-up

The main instabilities observed in colloidal systems are of two types:

- Migration: local variations (at the top and bottom of the sample) of the concentration of the dispersed phase in the sample, thus local variations of the measured transmission or backscattering level.
- Size increase: global variations (over the total height of the sample) of the particle size, thus global variations of the measured transmission or backscattering level.

The following table sums-up the different observable and measurable kinetics as a function of the destabilization phenomena:

Phenomena	Kinetics
Creaming	Left peak : clarification Right peak : creaming Mean value at the top and bottom
Sedimentation	Left peak : sedimentation Right peak : clarification Mean value at the top and bottom
Flocculation Coalescence Ripening	Mean value at the middle

For example, for a creaming phenomenon, the interesting parameters to compute are:

- The variation of backscattering (ΔBS) at the top and the bottom of the cell to compare quickly various formulations.
- The phase thickness of the cream layer and/or the clear phase, in order to be able to follow its formation.
- The migration velocity of the clarification front, in order to follow the kinetics of the creaming phenomenon.

3. Measurement limits

3.1 Meniscus

The quality of the meniscus is crucial for a good data interpretation, to ensure that movement of the meniscus is not interpreted as a change in the sample.
If the meniscus moves over time (bubbles breaking, shaking, evaporation) a peak at the top can be interpreted as a phase, therefore it is not recommended to calculate parameters in this area.

3.2 Model limit

Small particles The physical model predicts that the BS flux decreases with the mean diameter of the dispersed phase. However, experimental values show that below 800 nm, the BS flux increases with the mean diameter (**Figure 12**).

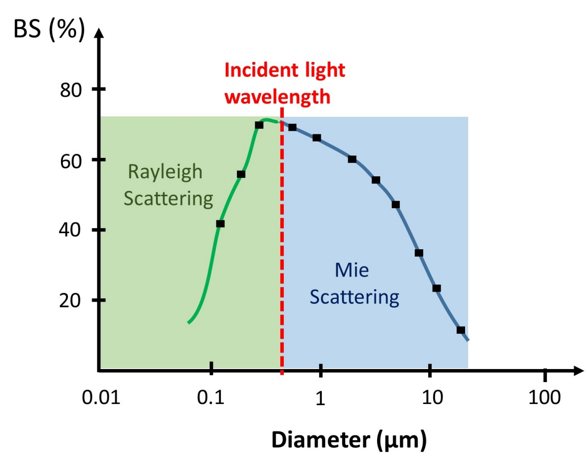

Figure 12. Evolution of the backscattering with the diameter.

Indeed, when the dispersion size is smaller than the wavelength of the incident light ($< 800\ nm$), Rayleigh scattering takes place. In this case, the scattering is isotropic and Mie theory can not be used to estimate the mean free path l^*.

Volume fraction Consistent with the physical model, experimental values show an increase in BS with volume fraction for $\Phi_c < \Phi < \Phi_s$ (**Figure 13**). However, a saturation of the BS signal is obtained for high volume fraction values (Φ_s). Indeed, when the dispersion is very concentrated, the neighbouring particles scatter the light with destructive interferences.

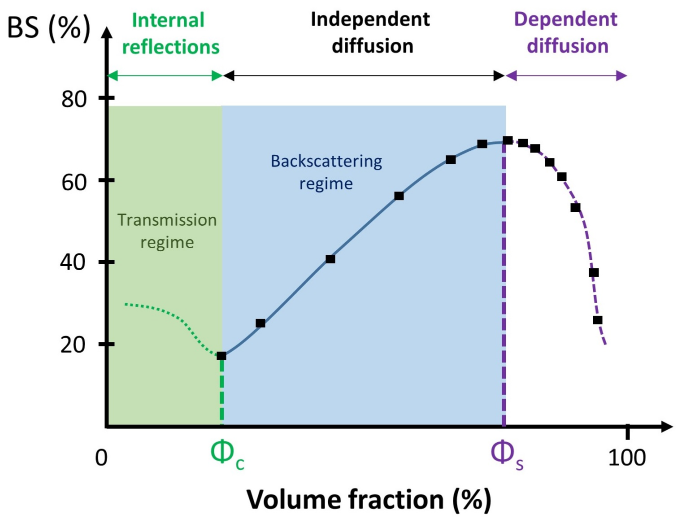

Figure 13. Evolution of BS as a function of volume fraction (%).

These interferences induce an increase of the mean photon transport l^*, thus a decrease of the BS flux. When $\Phi > \Phi_s$, BS flux decreases as the volume fraction increases. This is a dependent scattering region.

Likewise, there is a minimum volume fraction Φ_c which corresponds to the concentration at which photons begin to be transmitted in backscattering. For $\Phi < \Phi_c$, it is recommended to work with the transmission signal only, even if an increase of the BS flux can be observed.

This increase can be explained by internal reflections in the cell, which become more and more important as the volume fraction decreases: these reflections induce an increase of the BS signal. This means that for the creaming, there will be a decrease of the BS flux at the bottom (normal clarification phenomenon) and at the top (dependence phenomenon in the cream phase) and vice-versa for sedimentation.

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