



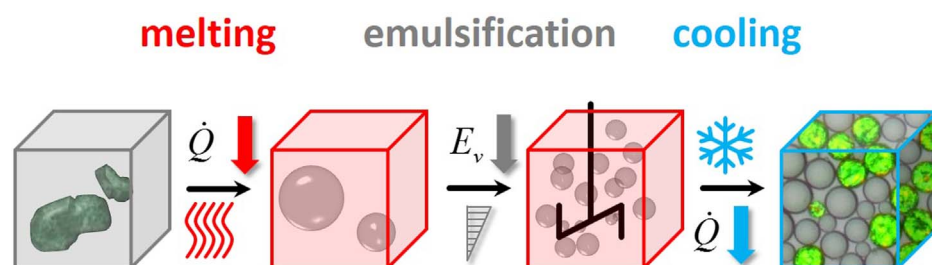
## Investigation of the influence of mean droplet size and shear rate on crystallization behavior of hexadecane-in-water dispersions



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### GRAPHICAL ABSTRACT



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### ABSTRACT

In this contribution, we used our thermo-optical method to characterize the quiescent crystallization behavior of hexadecane-in-water dispersions and to determine the number based crystallization index  $CI_N$  as a function of supercooling and mean droplet size. We observed two crystallization regimes in our model dispersion: (1) individual and stochastic crystallization of droplets at low supercooling and (2) mean droplet size dependent crystallization of droplets at high supercooling. We then applied shear (shear rates between 50 and  $1250 \text{ s}^{-1}$ ) in a shear cell and compared the quiescent crystallization to the crystallization under defined shear. We could not observe any shear-induced acceleration of nucleation during cooling. At low shear rates (between 50 and  $250 \text{ s}^{-1}$ ) we detected aggregation of the dispersed droplets/particles during cooling. Applying a shear rate of  $1250 \text{ s}^{-1}$  even completely suppressed the crystallization and the hexadecane-in-water emulsions remained in supercooled liquid state.

**Abbreviations:**  $CI$ , crystallization index;  $CI_N$ , number based crystallization index; DLS, dynamic light scattering; DSD, droplet size distribution;  $E_v$ , volumetric energy input; IP, image processing; LD, laser diffraction; PLM, polarized light microscopy; PSD, particle size distribution

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## 1. Introduction

Emulsions with crystalline dispersed phase have a wide field of applications in chemical, pharmaceutical and life science industry [1–4]. They act as high performance lubricants or mold release agents, are used as targeted delivery systems with site-specific and controlled release kinetics or increase the bioavailability and biocompatibility in food- and feedstuffs [5–8]. Due to the distinctive viscoelastic behavior of the dispersed phase and the required particle size, these dispersed systems are usually produced in a two-step melt emulsification process [9,10]: In the first step, the dispersed phase is emulsified above its melting temperature and crystallized during cooling in the second step [11–13].

While bulk crystallization is quite well understood today, crystallization in molten droplets in dispersions is still challenging. Different to bulk crystallization, organic droplets show individual crystallization behavior, which differs from droplet to droplet [14]. During cooling, droplets in dispersions can remain as supercooled liquid, form amorphous particles, or crystallize to single or poly crystalline structures. The formation of individual structures within dispersions depends on nucleation and colloidal processes [3,12,13,15–17], both being influenced by the formulation and process parameters [18–21]. Ideally, liquid droplets are transformed into spherical particles of the same size. Incomplete crystallization or colloidal processes, such as aggregation or partial coalescence, often occur during cooling and destabilize the dispersion [22,23].

The first step in any crystallization process is nucleation due to supersaturation or supercooling. Usually, the formation of nuclei proceeds by a heterogeneous nucleation mechanism due to catalytic impurities in the bulk [24]. In emulsion, the volume of individual droplets is comparatively low and the number of catalytic impurities is usually much smaller than the number of droplets [25]. Consequently, nuclei formation in emulsion may approach the homogenous nucleation mechanism, which requires higher supercooling [26]. Since the droplets in emulsions are commonly polydisperse and the nucleation in emulsions is strongly droplet size dependent, individual and stochastically distributed crystallization often occurs during cooling in oil-in-water dispersions. Inhomogeneous crystallization leads to the presence of supercooled liquid and crystallized solid droplets within one dispersion and thus to incomplete crystallization [14]. Consequently, supercooled droplets may collide with crystallized particles, wet their surface and crystallize/coalesce with those particles leading to an increase in the particle size distribution.

In the past decades, many researchers investigated the crystallization in emulsions with the focus on the acceleration of the nucleation in emulsions. Different approaches, like surface-initiated nucleation using surface-active substances [20,21,27] or collision-mediated nucleation [28] were considered. One of the most promising approaches being still not fully understood yet is shear-controlled nucleation in emulsions [23,29–34]. The influence of shear on bulk crystallization is well known and already industrially applied during e.g. cocoa butter crystallization in chocolate or confectionery industry [28,29,35,36]. Also in dairy products such a whipped cream, ice cream, milk and butter defined shear is applied to influence the crystallization process in dispersions and thus to adjust the morphology, texture or mouthfeel of those products [23,37,38]. However, the impact of shear on nucleation in emulsion droplets is still a subject of many investigations.

## 2. Materials and methods

### 2.1. Materials

All substances were commercially available and used as purchased without further purification or processing. Hexadecane (purity 99%, melting point at 18 °C) was purchased from Sigma-Aldrich® (St. Louis,

MO, USA) and polyoxyethylen-20-sorbitanmonolaurat (Tween® 20) from Carl-Roth® (Karlsruhe, Germany). Water was purified in a Milli-Q® instrument Q-POD® at 18.2 MΩ (Darmstadt, Germany).

### 2.2. Emulsion preparation

Every emulsion consisted of 1 wt% or 10 wt% hexadecane (dispersed phase), 1 wt% Tween® 20 (surfactant) and 98 wt% or 89 wt% purified water (continuous phase). First, Tween® 20 was dissolved under continuous stirring in tempered purified water at 28 °C in a glass vessel. Afterwards, hexadecane was added to the surfactant solution and tempered with the rotating part (tooth-rim dispersing element, or propeller stirrer) for another 15 min at 28 °C without stirring. Then, hexadecane was homogenized at different volumetric specific energies ( $E_v$ ) to prepare emulsions with different mean droplet diameter:

- (1) 1 wt% hexadecane emulsions: ‘High’  $E_v$  was applied with a tooth-rim dispersing machine (IKA® T25 digital, ULTRA-TURRAX®, Staufen im Breggau, Germany) at 6.8 m/s tangential speed (10,000 rpm, 13 mm outer diameter of the rotating part) 10 K above hexadecane melting temperature for 10 min in a glass vessel of 60 mm inner diameter.
- (2) 1 wt% hexadecane emulsions: ‘Medium’  $E_v$  was applied with a tooth-rim dispersing machine (IKA® T25 digital, ULTRA-TURRAX®, Staufen im Breggau, Germany) at 2.2 m/s tangential speed (3200 rpm, 13 mm outer diameter of the rotating part) 10 K above hexadecane melting temperature for 10 min in a glass vessel of 25 mm inner diameter.
- (3) 10 wt% hexadecane emulsions: Medium  $E_v$  was applied with a colloid mill dispersing machine (IKA® magic Lab, Staufen im Breggau, Germany) at 8.0 m/s tangential speed (5000 rpm, 30 mm outer diameter of the rotating part, 0.48 mm gap) at room temperature (above hexadecane melting temperature) for 10 min in a stainless steel tank in continuous mode.
- (4) 1 wt% hexadecane emulsions: Low  $E_v$  was applied with a four blade propeller stirring machine (IKA® EUROSTAR digital, Staufen im Breggau, Germany) at 1.7 m/s tangential speed (750 rpm, 50 mm outer diameter of the rotating part) 10 K above hexadecane melting temperature for 10 min in a glass vessel of 60 mm inner diameter.

After emulsification, samples were taken for droplet size distribution measurements (laser diffraction and dynamic light scattering, 1 wt% and 10 wt% emulsions), thermo-optical analysis (cryo-polarizing microscopy, only 1 wt% hexadecane emulsions) and rheological investigations (rotational rheology, 1 wt% and 10 wt% emulsions). Between emulsification and analysis, the emulsions were continuously stirred above the melting temperature of hexadecane (18 °C) to avoid creaming, crystallization and inhomogeneous sampling. During the sample preparation for the analytical part, emulsions did not show any sign of instability.

### 2.3. Emulsion characterization and crystallization behavior

#### 2.3.1. Laser diffraction and dynamic light scattering droplet size measurements

The droplet size distributions of emulsions were determined by a laser diffraction particle analyzer (HORIBA LA-940, Retsch Technology, Haan, Germany) in a stirred fraction cell. The measuring range of the instrument is between 0.01 and 3000 μm. The refractive index used for hexadecane was 1.434 + 0.000i. Emulsions were strongly diluted and measured three times above melting temperature of hexadecane. All droplets were in liquid state during the measurement.

#### 2.3.2. Thermo-optical analysis: quiescent crystallization

The thermo-optical observation of quiescent crystallization behavior of hexadecane in water dispersions was investigated using a

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