A comprehensive review on preparation, dispersion stability and phase change cycling stability of phase change microemulsions

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Abstract: Phase change material emulsions (PCMEs), as novel latent heat storage media, have great potential to advance applications. A comprehensive review of PCMEs is provided in this paper, including preparation methods, dispersion stability, phase change cycling stability, and improvement strategies. Various preparation techniques are presented, emphasizing the important factors that affect the homogeneity and stability of the PCMEs. A detailed analysis of the factors affecting dispersion stability is provided, emphasizing techniques for enhancing it. The dynamics of PCMEs during their solid-liquid phase transitions are investigated, introducing mechanisms of phase change cycling stability. Performance-enhancing methods are suggested, including using surfactants and nano-additives to improve the stability of PCMEs. Challenges and future research directions are also discussed.

Keywords: Thermal energy storage, Dispersion stability, Phase change cycling stability, Surfactant, Nanoparticle

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Abbreviations: EIP, emulsion inversion point; HLB, hydrophilic-lipophilic balance; O/W, oil-in-water; PCM, phase change material; PCME, phase change material emulsion; PIC, phase inversion composition; PIT, phase inversion temperature; TES, Thermal Energy Storage; W/O, water-in-oil.

List of abbreviations

c_p	specific heat, kJ kg^{-1} K^{-1}	T_d	temperature threshold, K
$c(r)$	oil solubility	TES	thermal energy storage
$c(\infty)$	volumetric solubility	T_f	bulk freezing temperature, K
EIP	emulsion inversion point	T_s	surface freezing temperature, K
g	gravitational acceleration, m s^{-2}	V_m	molar volume, m^3 mol^{-1}
HLB	hydrophilic-lipophilic balance	W/O	water-in-oil
O/W	oil-in-water	γ	interfacial tension, N m^{-1}
PCM	phase change material	φ	volume fraction
PCME	phase change material emulsion	η	Viscosity, Pa·s
PIC	phase inversion composition	ρ	Density, kg m^{-3}
PIT	phase inversion temperature	δ	thickness of interfacial layer, mm
r	droplet radius, m	ΔA	change in the surface area, m^2
R	molar gas constant, J mol^{-1} K^{-1}	ΔG	change in the free energy, J
T	absolute temperature, K		

1 Introduction

The sustainability of society is facing serious issues as a result of the influence of growing energy consumption [1-3]. Thermal energy storage (TES), one of the many methods to improve thermal efficiency and reliability, has proven to be a very successful approach with significant promise for energy conservation and pollution reduction [4-6]. TES technologies can be categorized into three types: sensible heat energy storage [7,8], latent heat energy storage [9], and thermochemical energy storage [10,11]. Latent heat energy storage uses phase change materials (PCMs) to absorb and release heat energy at the phase change temperature. Compared to sensible heat storage, this technique offers a greater energy storage density and a lower temperature difference between heat absorption, storage, and release, hence it is widely applied in a number of fields [12-14]. PCMs exhibit great potential in various fields, including solar energy utilization, industrial waste heat recovery, air conditioning and cold storage, aerospace, textile industry, and building energy conservation [15-24]. One of the most effective techniques for TES is generally acknowledged to be PCM-based technology [25].

Phase change material emulsions (PCMEs) are a topic of significant research interest due to their unique properties and wide range of applications [26]. They are prepared by dispersing PCM microdroplets within a conventional thermal fluid through microemulsion technology, which combine the high heat storage density of PCMs [27] with the fluidity of the heat transfer fluid. They also exhibit improved heat transfer efficiency because of the increased specific surface area of the dispersed PCMs [28]. The unique properties of PCMEs make them attractive options for various applications, such as TES and cooling [29]. Oil-in-water (O/W), water-in-oil (W/O), and oil-in-oil are three different forms of PCMEs [1]. Among these, O/W emulsions are often chosen as the first option among these because of their lower viscosity and ease of handling water as the base fluid [30,31].

Currently, research on PCMEs focuses on several hotspots. 1) Researchers are continuously exploring new methods for the synthesis of stable PCMEs. This includes the use of different surfactants and cosurfactants to prepare emulsions with improved dispersion stabilities. 2) Researchers are exploring the incorporation of nanomaterials and additives that can act as nucleating agents to promote crystallization at higher temperatures, thus reducing the degree of supercooling. 3) Another hotspot is enhancing the thermal conductivity of PCMEs. By modifying the PCME structure or incorporating thermal conductive materials, researchers aim to improve the heat transfer properties, which is vital for applications in thermal management and TES. 4) The viscosity of PCMEs directly impacts their effectiveness in applications. Research is focused on optimizing viscosity to enhance the performance and stability of PCMEs. 5) Efforts are made to develop new applications for PCMEs in various fields including TES.

The research difficulties for PCMEs include maintaining long-term stability under various conditions, controlling supercooling and viscosity to ensure efficient heat release and fluid transfer, and understanding the complex relationships between these parameters. These challenges require a deep understanding of the underlying physical mechanisms.

The stability of PCMEs is an important factor since it directly influences the efficiency performance and economic viability of TES systems. PCMEs are in a thermodynamic unstable condition, which means they can suffer from issues such as delamination, flocculation, phase inversion, agglomeration, and Ostwald ripening after a period of standing or multiple phase change cycles. These issues can lead to a loss of the intended properties and effectiveness of the PCME over time. The size distribution, homogeneity, and stability of the PCM microdroplets suspended within the base fluid matrix are significantly influenced by the proper preparation methods chosen. The enhancement of PCME stability is critical for delivering efficient and cost-effective TES solutions.

Supercooling is another issue of PCMEs which may be related to the small PCM droplets [32,33]. Supercooling occurs when the emulsion cools below the melting point of the PCM without crystallization. This effect is undesirable in latent heat storage because it increases the working temperature range of the system. Excessive supercooling causes lower solidification temperature and longer solidification time for PCM during latent heat release. When the degree of supercooling is too high, the stored thermal energy cannot be released in time and the exothermic temperature does not match the endothermic temperature, resulting in a significant reduction in thermal energy utilization efficiency. The most popular technique for mitigating the effects of supercooling is to use nucleating agents. Nucleating agents, often impurities or other chemicals with a higher melting point, are applied to the dispersed phase to induce heterogeneous nucleation of PCMEs [26].

The parameters for evaluating performance of PCMEs include phase change enthalpy, stability, supercooling, thermal conductivity, and viscosity, etc. Current research mainly focus on dispersion stability, thermal conductivity and supercooling of PCMEs. Existing reviews on PCMEs mainly focus on the mechanisms of dispersion stability [34-36], the rheological characteristics [37,38], Pickering emulsions [39-42], and the applications of PCMEs [43-46]. However, there remains a lack of comprehensive analysis on the phase change cycling stability of PCMEs, despite their significance for PCMEs to achieve long-term performance. Furthermore, improving supercooling often has an effect on the stability of PCMEs [47,48] and other properties. As a result, the progress of jointly investigating multiple properties also needs to be reviewed.

This study presents a comprehensive review of the preparation methods, dispersion stability, and phase change cycling stability of PCMEs within the framework of TES. The review begins by discussing the fundamental principles and methods underlying the fabrication of PCMEs. It then conducts a thorough investigation of the important parameters influencing the dispersion stability of PCMEs, clarifying the intrinsic mechanisms. Furthermore, the review looks into recent advances in research on the phase change cycling stability of PCMEs, evaluating the instability mechanisms, thereby laying a theoretical groundwork for improving the cycling stability of PCMEs.

This review is unique in that it focuses on the stability of emulsions, particularly the solid-liquid phase change cycling stability, which has been largely overlooked in earlier reviews. This review provides useful insights for optimizing emulsion qualities by elucidating the mechanisms governing the impact of preparation methods, surfactants, nanoparticle inclusion, and phase change cycling.

2 Preparation methods

The formulation PCMEs is significantly influenced by the emulsification techniques. The strategies for PCME preparation can be classified into high-energy methods, low-energy methods [49], solvent-assisted emulsification, mixing film synthesis, and condensation-emulsification methods. The debate over the best method for preparing micro/nano emulsions continues, with the literature presenting diverse conclusions [50-52].

The high-energy and low-energy emulsification methods are schematically represented in Fig. 1. High-energy methods necessitate significant energy input and specialized equipment, but they often require a relatively low surfactant-to-oil ratio, usually less than 0.1. In contrast, low-energy emulsification methods, make use of the chemical energy inherent in the system and are therefore more energy-efficient. The methods rely solely on basic stirring and have been shown to produce droplets that are smaller than those obtained by high-energy methods [53]. Moreover, low-energy methods produce nano-emulsions with high surfactant-to-oil ratios [51]. For instance, spontaneous emulsification, a low-energy method, requires only basic mixing but requires a higher surfactant-to-oil ratio, which is usually greater than 0.5 [52].

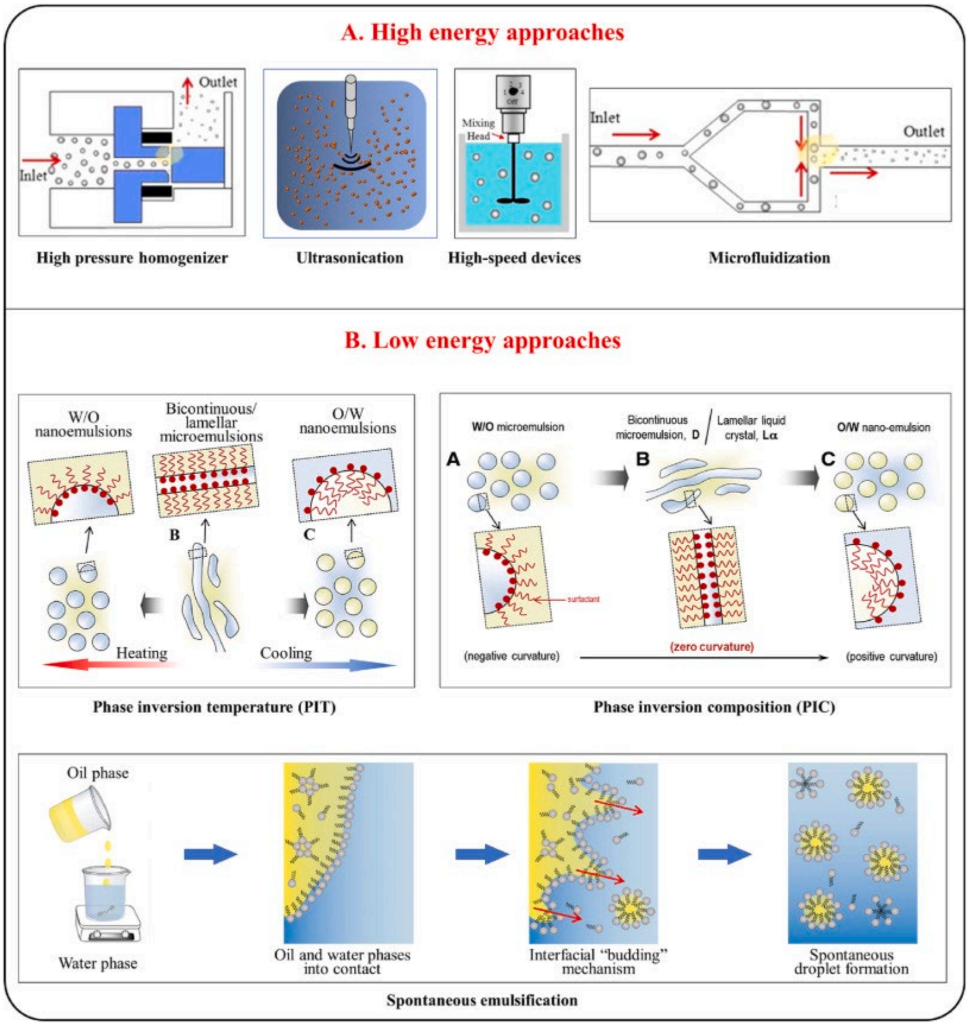


Fig. 1 Nanoemulsion preparation methods and instrument [54].

2.1 High energy methods

High-energy methods typically used for PCME for PCME preparation include high-pressure homogenization [55], phacoemulsification, microfluidic emulsification, and rotor-stator homogenization [56]. These techniques are characterized by their reliance on mechanical devices capable of applying significant shear stresses to facilitate the formation of PCMEs. It has been shown that increasing the energy input during these processes reduces the droplet size [57], which is an important characteristic influencing the stability of PCMEs.

2.1.1 High pressure homogenization

During the high-pressure homogenization process, the mixture of PCM and base fluid is exposed to a confined resistive valve at high pressure, which promotes emulsification by means of shear forces, turbulence, and cavitation [58]. The size and polydispersity of the resultant droplets are influenced by numerous parameters, including the rheological characteristics of the emulsion, such as flow behavior and viscosity, and the number of passes through the homogenizer. In order to successfully avoid droplet coalescence and enable the formation of emulsion droplets with diameters as tiny as 100 nm, a critical concentration of surfactant can generate a dense oil-water interfacial layer with strong adsorption characteristics. High-pressure homogenization is widely acknowledged as a common industrial technique for the fabrication of emulsions with submicron-sized droplets [26], because it consistently produce droplets and can be scaled for large-scale production. Moreover, the application of high-pressure homogenization has advanced the field by making it possible to produce emulsions with improved stability. However, the energy-intensive nature of the process increases the cost of production. Ongoing research aimed at optimizing the procedure to reduce energy consumption and improve effectiveness.

2.1.2 Ultrasonic emulsification

Ultrasonic emulsification captures a substantial amount of energy locally using ultrasonic sound waves that normally operate in the frequency range of 20 to 100 kHz [26]. When acoustic cavitation occurs in the liquid medium, the liquid structure is upset and bubbles are produced, which starts the emulsification and homogenization processes. Initially, the droplet size decreases to a certain degree when the ultrasonic power increases. However, after the droplet size reaches a specific minimum threshold, increasing the power input has insignificant effects on the droplets and raises the temperature of the liquid, which may cause surfactant molecules, particularly non-ionic emulsifiers, to degrade or break down [59]. When it comes to preparing emulsions using high-energy methods, ultrasonic emulsification is the best method. Notably, Jadhav et al. [60] combined ideal formulation and processing parameters to prepare paraffin nanoemulsions under ultrasonication. The nanoemulsions demonstrated higher stability with an average droplet size of 160 nm when compared to emulsions prepared using the same composition via the emulsion inversion point (EIP) method. A detailed summary of ultrasonic emulsification is shown in Table 1.

Table 1 Summary of ultrasonic emulsification method

Aspect	Description
Advantages	
High energy localization	Ultrasonic emulsification focuses energy through sound waves, effectively disrupting liquid structures and creating emulsions.
Small droplet formation	Reduces droplet size significantly, beneficial for applications requiring small droplets for optimal performance.
Versatility	Suitable for a wide range of materials, making it a versatile high-energy emulsification method.
Disadvantages	
Energy intensity	Process requires substantial energy, which can be costly and less sustainable.
Thermal degradation	High power can increase temperature, potentially degrading surfactant molecules, especially non-ionic emulsifiers.
Advances	
Optimized parameters	Stable nanoemulsions with droplet sizes as low as 160 nm can be prepared through optimization of formulation and processing parameters.
Combination with other methods	Ability to combine with other techniques enhances overall efficiency and stability of emulsions.
Existing Problems	
Surfactant degradation	High temperatures can lead to degradation of surfactants, essential for emulsion stability.
Optimization challenges	Finding optimal balance between power input and emulsion quality is challenging; excessive power can lead to unwanted side effects.
Effect on Dispersion Stability	Improves stability by creating smaller, more uniform droplets less likely to coalesce.
Effect on cycling stability	Enhances stability during thermal cycling; smaller droplets have larger surface area to volume ratio, improving resistance to temperature changes.
Effect on performance	Small size of droplets enhance performance in applications, where stability is crucial.

2.1.3 Microfluidic emulsification

Microfluidizers are a type of homogenizer that generates and reduces droplet sizes via impact stress, shear forces, and cavitation events. Emulsification is caused by the collision and fragmentation of two immiscible fluids passing through a high-pressure microchannel network. In comparison to other methods, the resultant emulsion droplets are often smaller but but less homogeneous [26]. An overview of the microfluidic emulsification method is shown in Table 2.

Table 2 Overview of the microfluidic emulsification method

Aspect	Description
Advantages	
Precision and Control	Microfluidic emulsification allows for precise control over droplet size and uniformity due to predictable flow patterns in microchannels.
Reproducibility	Consistent geometry of microfluidic devices ensures reproducible emulsion characteristics, crucial for quality control in industrial applications.
Disadvantages	
Cost and complexity	Expensive to manufacture, and complexity may limit scalability for large-scale production.
Material compatibility	Some materials may not be compatible, leading to clogging or material degradation.
Limited throughput	Traditional devices may have limited throughput, disadvantageous for high-volume production.
Advances	
Integration with other technologies	Integration with sensors and actuators for real-time monitoring and control.
Design innovations	New designs like droplet-based microfluidics expand capabilities, enabling complex emulsion structures.
Existing problems	
Scalability	Challenging to scale up processes while maintaining droplet quality and uniformity.
Maintenance and cleaning	Regular maintenance and cleaning required to prevent clogging and ensure consistent performance.
Effect on dispersion stability	Enhances stability by producing monodisperse droplets with narrow size distribution, reducing coalescence and sedimentation.
Effect on Cycling Stability	Uniform droplets contribute to improved cycling stability, less likely to undergo changes in size or distribution over multiple cycles.
Effect on Performance	Controlled droplet formation improves performance in applications like drug delivery, requiring precise dosing and release profiles.

2.1.4 Rotor-stator homogenization

In a high-speed rotor-stator homogenization system, a substantial percentage of the energy input is converted into thermal energy, making it challenging to achieve droplet sizes of 300 nm or smaller [58]. Despite this, rotor-stator devices are widely used to prepare PCMEs with micron-sized droplets [61-64]. When an emulsion cannot form spontaneously, high-energy methods are usually required to prepare it, especially in the case of high viscosity or high dispersed phase content, this preparation method is a good choice [65].

High-energy emulsification techniques require a considerable amount of mechanical energy to break down bigger droplets into smaller ones, resulting in emulsions with finer droplet distributions [66].The energy required to generate nanoscale droplets using high-energy emulsification methods is considerable, with only a small proportion (approximately 0.1%) of the total energy input being effectively utilized for emulsification. Consequently, this represents a significant cost impediment. For comparision, hand shaking is sufficient to generate emulsions with droplet sizes ranging from 40-100 μm, whereas producing nanoscale droplets requires a substantial energy input in the magnitude of 10^8-10^{10} W/kg [49]. Golemanov et al.[67] used a rotor-stator homogenizer, the Ultra Turrax, at 13500 rpm for 5 minutes to achieve droplet sizes of around 10 μm. The high-speed rotor-stator homogenization system may also be emulsified efficiently in a short period of time, decreasing cost input and enhancing efficiency. Table 3 presents a summary of rotor-stator homogenization. Barison et al. [68] used ultrasonication with a power of 65-95 W for 30 minutes to fabricate paraffin emulsions with droplets of 130 nm. Golemanov et al. [67] achieved droplet sizes of approximately 10 μm by using a rotor-stator homogenizer, the Ultra Turrax, at 13500 rpm for 5 min. The high-speed rotor-stator homogenization system may also be emulsified efficiently in a short period of time, decreasing cost input and enhancing efficiency. A summary of rotor-stator homogenization is shown in Table 3.

Table 3 Summary of rotor-stator homogenization method

Aspect	Description
Advantages	
Suitable for high viscosity materials	Rotor-stator homogenizers excel in preparing emulsions with high viscosity PCMs or high dispersed-phase content.
Micron-scale droplets	Effective in producing PCMEs with micron-scale droplets, suitable for applications not requiring nanoscale dispersions.
Widely utilized	Extensively used, indicating reliability and acceptance across various industrial applications.
Disadvantages	
Energy inefficiency	A significant portion of energy input dissipates as heat, leading to inefficiency.
Limited for nanoscale emulsions	Not ideal for nanoscale droplet dispersions.
High energy costs	Requires substantial mechanical energy input, which can be costly, especially for large-scale production.
Advances	
Optimization of parameters	Improved understanding of operational parameters enhances emulsification efficiency and effectiveness.
High-speed rotor-stator systems	Development of high-speed systems facilitates more effective disruption of large droplets, resulting in finer emulsions.
Existing Problems	
Energy dissipation	Majority of energy lost as heat, inefficient and may not suit thermally sensitive materials.
Scalability challenges	Difficulty in scaling up while maintaining emulsion quality, high energy requirements become prohibitive.
Effect on dispersion stability	
Micron-scale droplets	Good dispersion stability for micron-scale droplets.
Nanoscale droplets	May not achieve same level of stability due to energy dissipation as heat.
Effect on cycling stability	Cycling stability may be affected by heat generated during the process, potentially altering droplet size or distribution over cycles.
Effect on Performance	Limited in producing very fine or nanoscale emulsions due to energy inefficiency and potential for thermal degradation.

2.1.5 Overview of high-energy methods

Table 4 presents a comprehensive list of high-energy emulsification techniques. Ultrasound-assisted emulsification is recognized as the most effective method for producing stable oil-in-water emulsions, outperforming high-pressure homogenization and high-speed homogenization [55]. The ultrasonic cavitation technique has been utilized to prepare nanoemulsions that retain exceptional stability throughout long storage periods and many heating-cooling cycles [57]. Furthermore, paraffin/water emulsions prepared by high-speed homogenization have been found to be stable in the absence of additives [60]. Emulsions containing graphene oxide and reduced graphene oxide, when subjected to sonication, are recognized for their enhanced stability and potential to increase the heat transfer capacity of PCM droplets [64].

Table 4 Summary of high-energy emulsification methods

Reference	Preparation method	Stability	Progress
[55]	ultrasound-assisted emulsificationhigh-pressure homogenizationhigh-speed homogenization	During the 7 d storage, no separation was observed for the ultrasound-assisted emulsification -fabricated emulsion, while the emulsions fabricated by high-pressure homogenization and high-speed homogenization were separated after storage for 5 d and 2 h. The turbiscan stability index values of the ultrasound-assisted emulsification -fabricated sample showed the lowest turbiscan stability index values, indicating that the myofibrillar protein -soybean oil emulsion prepared by ultrasound-assisted emulsification was the most stable	Explore the hypothesis that ultrasound showed advantages over traditional methods for preparing oil-in-water emulsions; Ultrasound-assisted emulsification is a better method to fabricate myofibrillar protein stabilized soybean oil emulsions compared to high-speed homogenization and high-pressure homogenization treatment.
[55]	ultrasonic cavitation	No distinct changes observed for 9 mg ml^{-1} MXene-decorated n-tetradecane/water nano-PCME after experiencing long-term storage and 100 heating-cooling cycles.	The self-assembly strategy of MXene nanosheets at the PCM/water interface provides a simple way to construct high-performance nano-PCMEs, which shows important practical significance
[58]	ultrasonic cavitation	Stable for more than 3 months	Ultrasonic emulsification is an excellent method for formulation of paraffin wax nanoemulsion. This process is environmental benign.

[62]	high-speed homogenization	The paraffin/water emulsions without graphite is very stable, while the graphite of paraffin/water emulsions is gradual subsidence after 7 days of storage; layering is occurring slowly in the emulsion containing 0.1 wt% graphite after 300 heating–cooling cycles. Subsiding and creaming in paraffin/water/graphite emulsions reach stable in about a week and they can be avoided by stirring.	Developing a novel working fluid with excellent energy storage capacity, good optical absorption property, and high thermal conductivity
[65]	sonicated	The stability with time was investigated for 2 months and showed a slight increase in size with time to a size of about 240 nm and stabilization afterwards; no significant coalescence or sedimentation occurred; DLS performed after freeze-thaw cycles did not alter the values.	Graphene oxide and reduced graphene oxide are effective on producing stable emulsions, they can reduce supercooling and increase heat transfer capacity of PCM droplets

The specific requirements of the emulsion and the intended application will determine which of the high-energy emulsification techniques is best. A comparison to assist identify which method could be better suited for various applications is shown in Table 5.

Table 5 Comparison among high-energy emulsification methods

Technique	Suitability	Advantages
High-pressure homogenization	Best for applications requiring very fine and uniform droplet sizes.	Provides control over droplet size and distribution, leading to highly stable emulsions. Scalable and suitable for industrial production.
Ultrasonication emulsification	Ideal for laboratory-scale preparations and for formulations that require gentle processing to avoid damaging sensitive materials.	Offers control over emulsion characteristics and can produce droplets in the nanoscale range. Adaptable to a variety of materials.
Microfluidic emulsification	Suited for applications where precise control over droplet size and monodispersity is critical.	Can generate highly uniform emulsions with droplet sizes down to the nanoscale. Compatible with a wide range of materials and can be designed for specific emulsification needs.
Rotor-stator homogenization	Best for large-scale industrial applications, particularly for products that do not require extremely fine droplets.	Cost-effective for high-volume production and can handle high viscosities and high dispersed-phase contents. Robust and suitable for a variety of materials, including those that are difficult to emulsify.

2.2 Low energy methods

Low-energy emulsification techniques are a strategy that uses the inherent chemical energy of the dispersion medium to facilitate emulsion formation. These approaches significantly lower energy expenditure, using 3 to 5 orders of magnitude less energy than their high-energy counterparts [26]. A notable characteristic of emulsions made through low-energy emulsification is that they are more stable over long periods of time. However, the concentration of the surfactant required for these emulsions is considerably higher than that needed for high-energy emulsification procedures.

The classification of low-energy emulsification methods is based on the dynamics of surfactant spontaneous curvature during the emulsification process. "Self-emulsification" is the process by which emulsions are formed when surfactant and solvent molecules quickly diffuse from the dispersed phase to the continuous phase without changing the surfactant's spontaneous curvature [69]. On the other hand, the "phase inversion" technique is used when the spontaneous curvature of the surfactants changes from negative to positive, or vice versa, during the emulsification process. There is also a "D-phase emulsification method" that is comparable to self-emulsification; however, when surfactants are used,, its fundamental characteristics differ greatly from those of the self-emulsification process.

2.2.1 Self-emulsification

Self-emulsification, also known as spontaneous emulsification, is a method that uses the chemical energy released during the dilution of the system, rather than changes in the curvature of surfactant molecules. This method is also known as a phase inversion or isothermal emulsification technique [70]. The preparation of O/W nanoemulsions requires the dilution and subsequent diffusion of water-miscible constituents, such as solvents, surfactants, and/or co-surfactants, from the organic phase to the aqueous phase. This diffusion process results in a significant expansion of the interfacial area, which induces a metastable emulsion state [70]. Fig. 2 displays the so-called Pastis or Ouzo effect [71,72], which aids in the self-emulsification of free surfactant systems. The alcoholic beverage Pastis becomes turbid when water is added, due to the low solubility of trans-anethole, the chemical responsible for the anise flavor in Pastis and Ouzo, in the aqueous solution. This solubility difference results in the formation of micrometer-sized droplets, which gradually increase in size over time, extending the shelf life of the anise-flavored beverage.

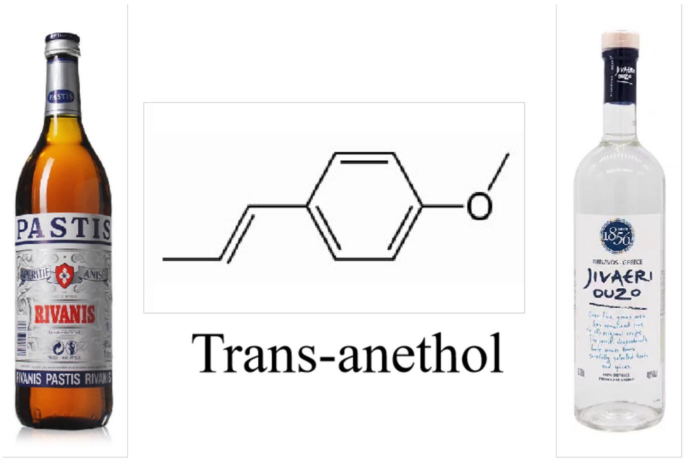


Fig. 2 The Pastis or Ouzo effect is caused by the self-emulsification process found during the dilution of aniseed (the oil phase is mainly trans-anisol) [72].

Self-emulsification methods are highly valuable in the pharmaceutical industry. O/W nanoemulsions, which are formed in water at a low energy cost, are widely used as carriers for lipophilic medicines. These technologies are also known as self-nano-emulsifying drug delivery systems [73]. According to research [74], the transition in structural configuration occurs when the average spontaneous curvature of the surfactant reaches zero (such as in bicontinuous microemulsions or layered liquid crystal phases), and it is a critical factor in the preparation of nanoemulsions.

Achieving nanoemulsions with small droplet and a low polydispersity index depends on the particular phase of the emulsification process. Nevertheless, it is important to note that the kinetics of the emulsification process may also have a substantial influence on the properties of the resulting nanoemulsion, particularly when a highly viscous emulsion forms during the process.

Furthermore, the self-emulsification method offers som advantages over other methods, as shown in Table 6. Specifically, the preparation method requires neither temperature change nor energy compensation, and may complete emulsification in the absence of surfactant. This method is suitable for practical applications because of its ease of scalability and low energy usage. It is used to prepare nanocapsules and nanoparticles that are smaller than typical particles prepared using traditional methods (such as solvent-assisted emulsification). This technique is commonly used to produce nanocapsules and nanoparticles, and it can also be used to make small nanospheres, liposomes, and vesicles. However, because the microemulsion domain has been extensively studied and characterized, current research focuses on various dilution procedures. The stability of the emulsion is determined by droplet development on short time scales, whereas droplet emulsification affects emulsion stability on longer timescales. Stability studies in the emulsification process suggest that Ostwald ripening is the primary mechanism. Instead of droplet coalescence, the process of Ostwald ripening is used to achieve droplet growth following oil nucleation is obtained. For growth on short time scales, The stability of the emulsion is determined by droplet growth on short time scales; whereas droplet emulsification affects emulsion stability on longer time scales.

Table 6 Summary of the self-emulsification method

Reference	Characteristics	Progress	Stability	Application
[70]	Easy to scale, low energy consumption.	Focus on the different dilution procedures.	Ostwald ripening is the principal mechanism.	The method can be used to develop practical applications.
[72]	No emulsifier, and does not require any mechanical energy.	/	Remain stable for days to months.	Often used in the production of nanocapsules, nanoparticles, liposomes and vesicles.

2.2.2 Phase inversion methods

The variable lipophilic and hydrophilic properties of distinct surfactants at the interfacial area can cause interfacial bending, resulting in intrinsic curvature. When temperature or composition adjustments cause spontaneous curvature changes in surfactants, techniques such as the phase inversion temperature (PIT) or the phase inversion composition (PIC) method, also known as the EIP method [26], are used. As shown in Fig. 3, changing the concentration or temperature of the PCMEs can affect the intrinsic curvature of the surfactant molecules. At the point where the curvature approximates zero, surface tension decreases significantly, resulting in the formation of a bi-continuous phase. This phase change facilitates droplet fragmentation, which eventually leads to the formation of nano-scale droplets [70]. Research has emphasized [75,76] the significance of structural transitions involving surfactant membranes with an average zero curvature, such as double continuous microemulsions or stratified liquid crystal phases, in the formation of nanoemulsions.

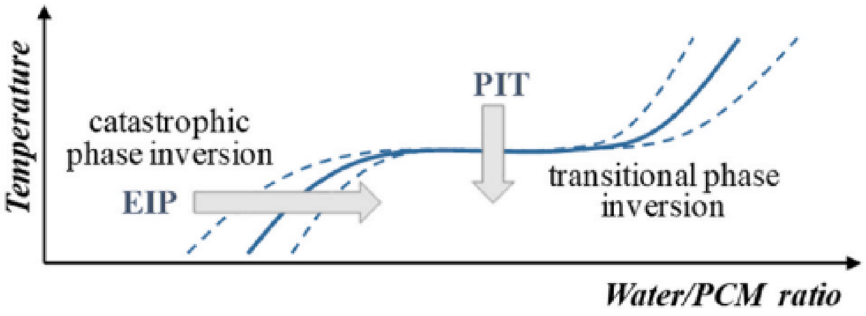


Fig. 3 Formulation-composition diagram with constant surfactant concentration (the thick line is the phase inversion boundary) [26]

The PIT method, which is based on the temperature-dependent variation in molecular curvature or solubility of nonionic surfactants [77], is most suited to polyoxyethylene-type nonionic surfactants [26]. Typically, the preparation process begins by heating a mixture of surfactants, water, and oil from room temperature. When the phase change temperature is reached, the molecular curvature of the surfactant becomes zero, bringing in the hydrophilic-lipophilic balance (HLB) value of the system to equilibrium and the interfacial tension to a minimum. Under these conditions, stirring facilitates the formation of a fine emulsion[26], as shown in Fig. 4. However, due to the zero molecular curvature, the coalescence rate is high [78], making the emulsion highly unstable around the PIT point. To mitigate this, the temperature must be quickly adjusted, either lower or higher, to produce an emulsion with small droplets and good dispersion.

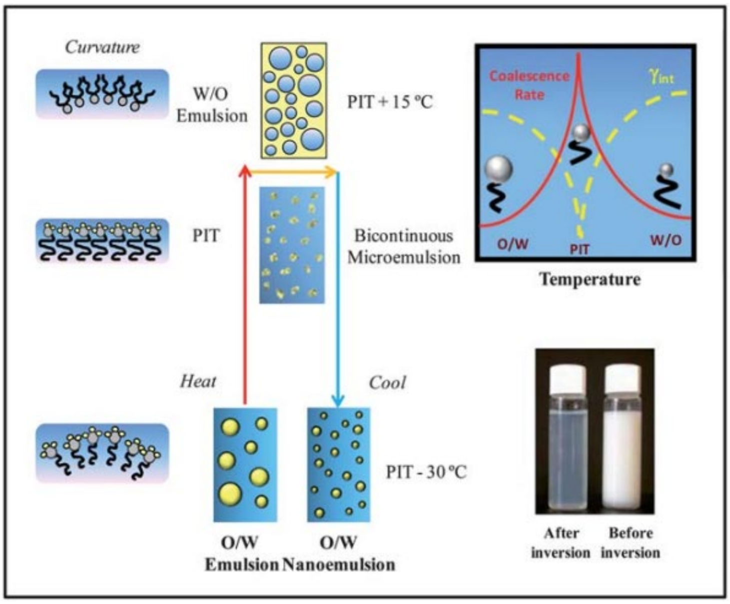


Fig. 4 Schematic diagram of emulsion preparation by PIT method [79].

Schalbart et al. [80] compared three low-energy preparation methods: EIP, PIT, and the mixing film synthesis method. Their findings indicate that the PIT method produced droplets with a size of 206 nm, outperforming the other two methods. Zhang [81] used a combination of the PIT and PIC methods to prepare a cetane emulsion. The PIT method achieved a minimum droplet size of 60 nm at a fixed PCM content by cooling the emulsion from 60 °C to 20 °C. In contrast, the EIP method involved adding water dropwise to the oil phase at a rate of 1 ml/s, resulting in an emulsion with a minimum droplet size of 120 nm. Vasile [82] also discovered that the PIT method performs better than the PIC method for preparing emulsions with high dispersed phase content and small droplet sizes. To prevent the droplets from re-coalescing, the PIT method must rapidly lower the temperature of the emulsion in a short period of time. However, the PIC method less effective than the PIT method since it entails gradually adding droplets and keeps the emulsion in the phase-inverted state for an extended period of time.

The PIT method has various advantages and disadvantages, as detailed in Table 7. This technique primarily attempts to reduce interfacial tension, allowing for the formation of minute droplets. However, emulsions with low interfacial tension are inherently unstable and prone to rapid coalescence. Consequently, the method demands rapid cooling or heating to produce a kinetically stable and fine emulsion.

Table 7 Summary of the PIT method

Reference	Advantages	Disadvantages	Stability	Surfactant effect	Application
[81]	This method can achieve high deformation resistance.	Rapid cooling or heating is required to produce a kinetically stable and fine emulsion.	The nanoemulsion is more stable in space because the thickness of the adsorbed emulsifier layer is equivalent to the droplet size.	When the concentration of emulsifier reaches the critical micelle concentration, its molecules begin to aggregate into supramolecular structures such as micelles, while critical micelle concentration is sensitive to temperature, and the critical micelle concentration of non-ionic emulsifiers decreases with increasing temperature.	/
[79]	Nanoemulsions can greatly improve the bioavailability of highly lipophilic substances encapsulated in them.	When the temperature of the system increases, droplet coalescence tends to occur easily.	/	The dependence of packing parameters or the solubility of non-ionic surfactants on temperature determines the ability to form nanoemulsions using the PIT method.	It can be used to create products with novel textural properties or reduced calories. At the same time, also can be used to extend the shelf life of commercial products.

Furthermore, the solubility of non-ionic surfactants varies with temperature. Therefore, the capacity to prepare nanoemulsions using the PIT approach depends on the temperature sensitivity of the filling parameters or the solubility of nonionic surfactants. This temperature dependence is a critical factor in the emulsification process, influencing both the preparation and stability of the nanoemulsions.

The PIC method is a methodical process that involves gradually adding a new component to a a system that contains a surfactant at a steady temperature. Emulsion formation depends on structural changes and rearrangements that occur during the dilution process [54]. A detailed procedure involves adding water progressively, drop by drop, to a mixture containing a surfactant and an oil phase. When a small amount of water is injected at first, a W/O emulsion is formed. As the volume of water gradually increases, a partially continuous phase emerges within the mixture, characterized by a surfactant interface that separates the water and oil in a non-uniform manner. The emulsification process goes through a critical transition after the aqueous phase accumulates further, resulting in the formation of an O/W emulsion structure. This structure achieves equilibrium when the volume of the aqueous phase reaches a specific threshold [83]. The transition from a W/O to an O/W emulsion is a pivotal point known as the phase inversion point, which is an important parameter in the PIC method.

PIC methods just require the addition of one component to another, as opposed to PIT methods that require a sudden temperature change. This makes the preparation procedure simpler and more convenient for operations. Consequently, PIC methods have more potential for large-scale production. Additionally, when working with components that have temperature stability issues, PIC methods are often the best option [70].

Unlike PIT procedures, where the droplet size distribution of the resulting emulsion is essentially independent of the HLB value of the surfactant mixture [84], the HLB value and temperature are typically crucial factors in the PIC process for producing emulsions with small droplet sizes. For instance, Yu et al. [85] produced an emulsion with an average droplet diameter of approximately 10 nm at 70 °C, which is much smaller than that obtained at 25 °C.

The advantages and disadvantages of the PIC method are shown in Table 8. The PIC method has the advantages of being simple to implement and requiring little energy, making it ideal for amplification applications. Furthermore, the nanoemulsion can be prepared in variety of temperatures. This method increases emulsification efficiency while also allowing for quick preparation. However, obtaining highly dynamically stable nanoemulsions with tiny droplet sizes using low-energy methods is more challenging than using high-energy methods with input energy.

Table 8 Summary of the PIC method [85]

Advantages	Disadvantages	Surfactant effect
Easy to form and low energy costs. Wide preparation temperature range. High emulsification efficiency.	Ostwald ripening is a major limitation in developing practical applications	The use of industrial-grade surfactants and oil phases in this system makes it less meaningful to study phase behavior at different temperatures.

2.2.3 D-phase emulsification

The D-phase emulsification method, proposed by Sagitani [26], is a low-energy emulsification approach in which an oil/gel emulsion is formed within a surfactant matrix and then diluted during the droplet generation process. This method is distinguished by the lack of requirement for precise adjustment of the HLB value [86], which simplifies the emulsification procedure. The introduction of alkyl polyols as additional constituents facilitates the emulsification process by promoting a unique arrangement among the surfactant, dispersed phase, and polyol solution [87]. The methodological processes involved in the D-phase emulsification process are shown in Fig. 5.

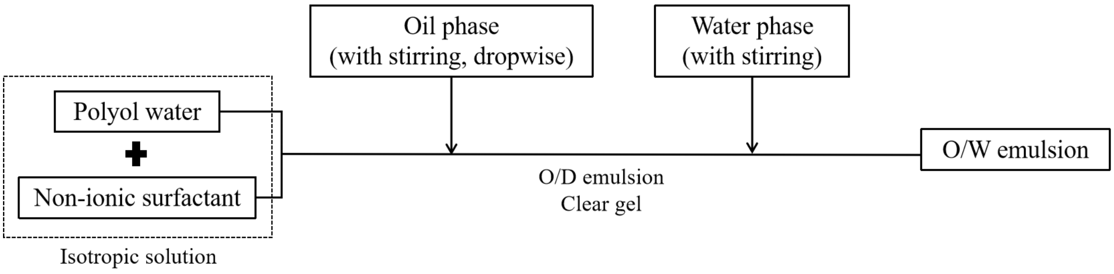


Fig. 5 Process of preparing emulsions by D-phase method [88].

Takashi et al. [86] used the D-phase emulsification method to prepare emulsions of n-hexadecane and n-octadecane with typical droplet size ranging from 200-300 nm. Similarly, Kawanami et al.[88] used the D-phase emulsification method to prepare nanoemulsions with hexadecane and tetradecane as PCMs, despite the fact that they experienced significant supercooling (17 °C). Chen and Zhang [89] used the D-phase emulsification method to fabricate nanoemulsions with n-hexadecane and n-octadecane as PCMs, attaining average droplet sizes of 290 nm and 320 nm, respectively.

Table 9 summarizes the properties of the D-phase emulsification method. Compared to other emulsifying methods, This method uses less energy than other emulsifying methods because it does not involve any energy-intensive processes. It can also be prepared at room temperature, with no further heating or cooling. In this method, the kinetic stability of emulsion storage is determined by surfactant action. Currently, the phase inversion method is the most commonly used in prior studies, whereas D-phase emulsification method has received little attention.

Table 9 Summary of the D-phase emulsification method [89]

Characteristics	Progress	Stability	Surfactant effect
It can minimize energy consumption and can also be prepared at room temperature without heating or cooling.	This approach has not been extensively researched.	Creaming is one of the most common causes of unstable lotions	The melting temperature and latent heat of emulsion are much lower than that of pure water due to the influence of surfactant.

2.3 Solvent-assisted emulsification

The solvent-assisted emulsification approach was first reported by Agresti et al. [90]. In the early stage, ultrasonic is used to mix the PCM, surfactant and auxiliary solvent before adding the water phase to emulsify. After emulsification, the solvent is removed out and only the needed emulsion is left, as illustrated in Fig. 6.

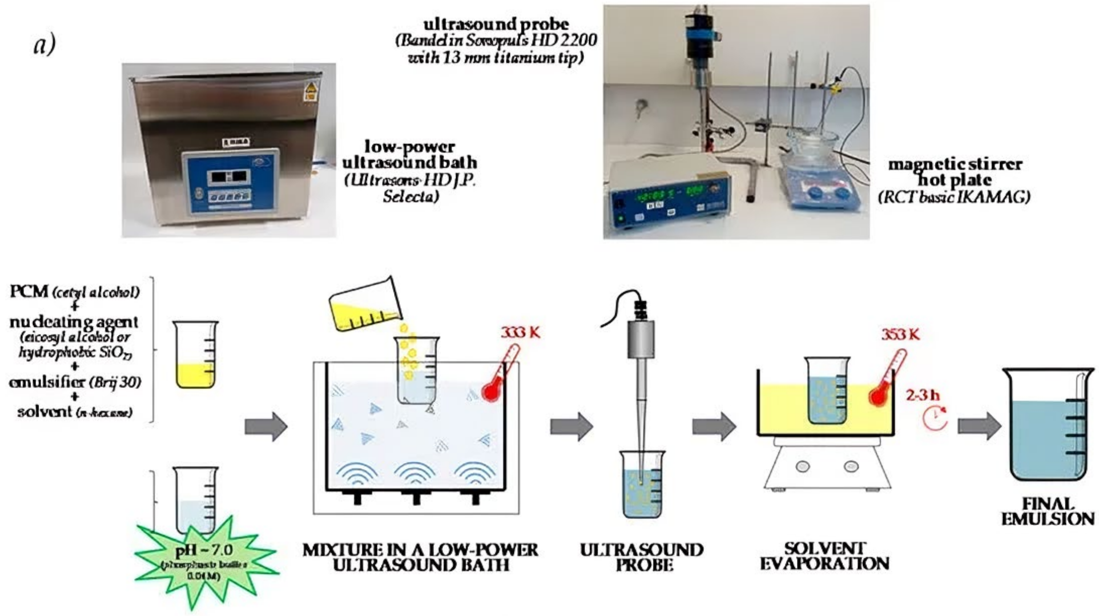


Fig. 6 Main steps of solvent-assisted preparation of cetyl alcohol-in-water nanoemulsion [25].

Agresti et al. [90] prepared paraffin-in-water emulsions with PCM concentrations ranging from 2 to 10 wt%. When the PCM-to-surfactant ratio was low, the resultant emulsion had droplet sizes smaller than 100 nm. Building upon this method, Cabaleiro et al. [91] expanded on this approach to produce water-based nanoemulsions with n-heptadecane and commercial paraffin, obtaining droplet dimensions in the 90-150 nm range and demonstrating remarkable stability. David et al. [25] utilized a synergistic combination of anionic and nonionic surfactants within the solvent-assisted emulsification paradigm, augmented with ultrasonication. This methodology effectively generated cetyl alcohol nanoemulsions that exhibited commendable stability.

The features of the solvent-assisted emulsification method are shown in Table 10. This method enables the use of multiple PCMs with varying melting temperatures in the same emulsion, broadening the range of feasible operating temperatures. Additionally, nanoemulsions containing fine PCM droplets can be efficiently produced. Notably, no evidence of phase separation or considerable expansion of PCM droplets in the nanoemulsions was detected over time, or when the samples were subjected to freeze-thaw cycles or mechanical shear stress. The samples a have also been shown to be resistant to many freeze-thaw cycles, even nine months after preparation.

Table 10 Summary of the solvent-assisted emulsification method

Reference	Advantages	Progress
[90]	Possible to use a variety of PCMs in the same emulsion.	/
[91]	Nanoemulsions with fine PCM droplets can be efficiently produced. Good freeze-thaw cycle stability and shear stability	The difference between the predicted latent heat and the experimental latent heat of the crystal-rotating phase transition may be due to the deformation of the alkane chain.

2.4 Mixing film synthesis method

The mixing film synthesis method [92], as illustrated in Fig. 7, begins with the inclusion of a lipophilic surfactant into the oil phase to form mixture A, followed by the introduction of a hydrophilic surfactant into the aqueous phase to produce mixture B. Following the application of heating and vigorous mixing, mixture of A and B are agitated for a predetermined period, resulting in the formation of a preemulsion. This preemulsion is then undergoes homogenized and emulsified to yield the final emulsion.

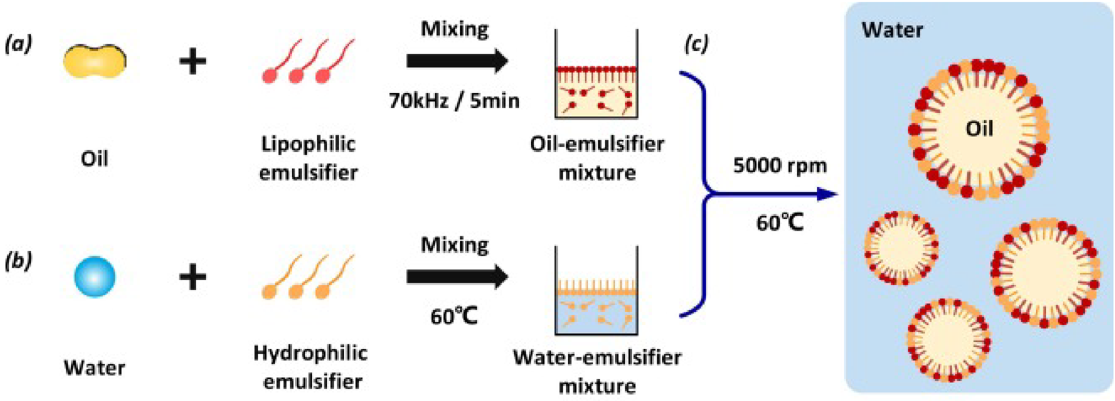


Fig. 7 Mixing film synthesis method [93].

Yang et al. [94] utilized this technique to produce tetradecane-in-water emulsions with consistent droplet size. In another study, Shao et al. [92] developed a paraffin-in-water emulsion with a droplet size of 3 microns that demonstrated exceptional storage stability over a 9-month period and withstood over 500 phase change cycles within a pumping system, without any significant changes in droplet size or heat storage capacity.

Zhong et al. [93] prepared an anti-volatile emulsion template using the mixing film synthesis method. They emphasized that in the pursuit for stable PCMEs, three essential factors were examined: the water-oil ratio of the composite emulsifier, the emulsifier-to-oil ratio, and HLB.

The characteristics of the method is highlighted in Table 11. At present, There are currently just a few research on volatile oil phase in emulsion stability. The method can serve as a template for anti-volatile emulsions. This volatility inhibition is mainly due to the aggregation of emulsifiers at the interface of the two phases, forming microlayers that increase mass transfer resistance. This aggregation prevents the oil phase from escaping from the liquid-liquid interface and into the liquid-gas interface, a process known as the interface obstruction effect.

Table 11 Summary of the mixing film synthesis method [93]

Characteristics	Stability	Progress	Surfactant effect
Anti-volatile emulsion template can be prepared.	In the study of emulsion stability, the volatile oil phase is seldom considered.	High water phase decreases the effective energy storage and delays the phase transition temperature. This greatly weaken the reliability of the emulsion.	Emulsifier accumulates at the interphase interface to increase the mass transfer resistance and form an interphase obstruction effect.

2.5 Condensation-emulsification

Guha et al. [95] developed a unique "condensation-emulsification" method for producing emulsions with droplet sizes. This technique process involves generating nanoscale water-in-oil emulsions by condensing water vapor on a supercooled oil-surfactant solution. The nucleation of nanoscale water droplets at the oil/air interface is induced by the diffusion dynamics of oil on water, which then spontaneous disperse within the oil phase. During the emulsification process, the surfactant has two functions: it stabilizes the neighboring droplets and facilitates the diffusion of the oil phase at the water/air interface, encapsulating the condensed water droplets. Following that, the dispersed phase, or aqueous phase, is evaporated and transferred into a continuous phase that already contains the emulsifier. This final phase results in the production of a W/O emulsion.

Notably, this method does not rely on shear forces or matching equipment; nonetheless, the boiling temperature of the continuous phase must be much higher than that of the dispersed phase (in this case, water). Furthermore, particular emulsifier formulation and concentration parameters must be satisfied to enable the generation of small droplets with a limited size distribution.

Fischer et al. [96] also succeeded in preparing emulsions suitable for application at -30 °C. The specific equipment and underlying principles are illustrated in Fig. 8. Both condensation-emulsification and rotor-stator homogenizers produced emulsions with identical diameters of around 1 μm.

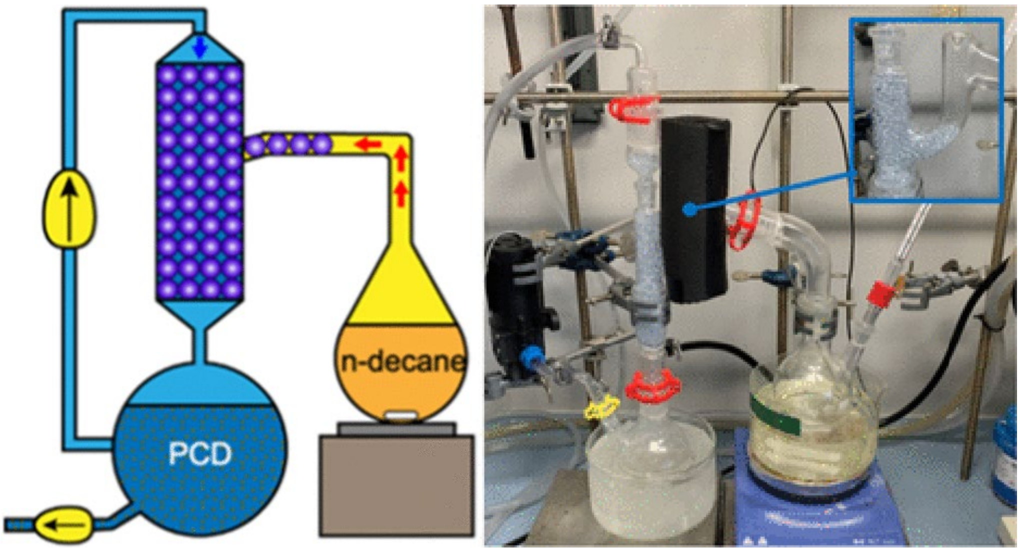


Fig. 8 Left: schematic diagram of the instrument. Right: photo of the apparatus. Top right: details of the inlet connector before thermal insulation.[96]

Table 12 displays the characteristics of the method, which is based on bottom-up assembly to produce nanoscale emulsions. This method is conceptually simple, scalable and adaptable to a variety of liquids. The technique can be expanded to prepare more complex emulsions (e.g., w/o/w or o/w/o emulsions). This method allows for precise control over the dispersion size and polydispersity of nanoscale emulsions while ensuring long-term stability. However, the operation of this method is more complicated, which indicates that the boiling temperature of the continuous phase should be much higher than that of the dispersed phase. Furthermore, the emulsifier system and its concentration must meet specified parameters in order to maintain small droplet sizes and narrow particle size distributions.

Table 12 Summary of the condensation-emulsification method [95]

Reference	Characteristics	Progress	Surfactant effect	Application
[95]	This method is conceptually simple, scalable and suitable for a variety of liquids. It maintains long-term stability.	New methods are needed to expand the range of possible material formulations and operating conditions.	Since surfactants affect the oil/water interfacial tension, their presence affects the diffusion coefficient. This affects the diffusion behavior of the oil at the water/air interface.	Potential to have a broad impact on the pharmaceutical, cosmetic and processed food industries.
[96]	Boiling temperature of the continuous phase should be significantly higher than that of the dispersed phase. Specific requirements need to be made for the emulsifier.	The literature on lotions that work below zero is very lacking. Future work will also study the long-term stability of emulsions.	Emulsifiers serve two purposes. First, stabilize the oil/water interface. Second, one phase is allowed to be hidden by another, especially in the case of condensing-emulsification.	The system is currently used for sub-zero applications.

The technology is now used for sub-zero applications, instead of introducing a completely new continuous phase. However, since pure ethylene glycol can dissolve most organic phase change materials, this method may have limits at lower temperatures or with other PCMs. New emulsification methods are therefore needed to broaden the range of material compositions and operating circumstances.

Surfactant is a key ingredient in the emulsification process. Emulsifiers have two purposes. First, stabilize the oil/water interface. Second, one phase is allowed to be obscured by another, especially in the case of condensing-emulsification. The second effect of surfactants is unique to this emulsification method. When oil is supercooled below the dew point in a humid environment, water droplets form at the oil/air interface. The subsequent droplet growth process is substantially determined by the diffusion behavior of the oil at the water/air interface. However, surfactants can affect the interfacial tension of oil/water, influencing its diffusion behavior, as seen in Fig. 9.

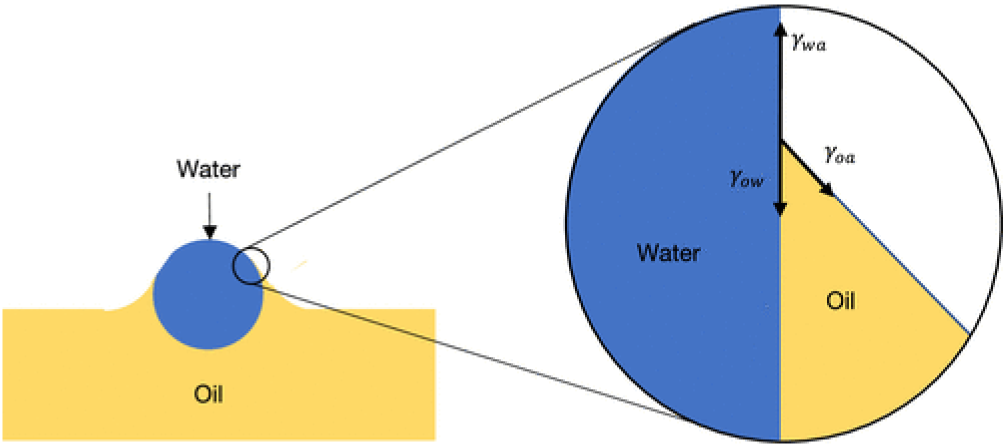


Fig. 9. In the case of an oil-in-water emulsion prepared by condensation - emulsification, the oil phase diffuses over water droplets [96].

2.6 Comparison of emulsion preparation methods

Among the methods for PCME fabrication, high-energy emulsification techniques have high energy cost, reduced efficiency, and need advanced experimental equipment. In contrast, low-energy emulsification approaches require a more conservative surfactant usage relative to high-energy methods. However, while the low energy method is more energy efficient than the high energy method, it restricts the types of materials that can be used for emulsification. Moreover, the solvent-assisted emulsification method allows for the incorporation of PCMs with different operational temperature ranges into a single emulsion. The mixing film synthesis method is practical for creating templates for volatile-resistant emulsions, although it is hindered by a complex preparatory procedure. The condensation-emulsification technique is versatility, accommodating a wide range of materials while producing emulsions with excellent dispersibility and stability. However, this method requires a high level of precision in the operational equipment. A comprehensive comparison is presented in Table 13.

Table 13 Comparison of emulsion preparation methods

Methods	Advantages	Disadvantages
High energy methods	Use less surfactant than low energy methods	High energy consumption and low efficiency
Low energy methods	More energy efficient than high-energy methods	Materials for emulsification is limited [95].
Solvent-assisted emulsification	Allows the use of multiple PCMs in the same emulsion. The use of solvents increases the incorporation of nucleating agents, reducing supercooling [90]	The evaporation process is time-consuming [97]
Mixing film synthesis method	Anti-volatile emulsions can be prepared.	Usually a combination of high-energy method and low-energy method is used, and the preparation process is complicated.
Condensation-emulsification	The method is scalable and suitable for various materials. The dispersion size and polydispersity of nanoemulsions can be controlled while maintaining long-term stability [95].	Operating equipment connection requirements are high.

3 Dispersion stability

Dispersion stability is a critical factor in the development and application of emulsions. The stability of an emulsion is often determined by assessing the degree of its instability tendencies. The uniformity and durability of the dispersed droplets within a base fluid determine the stability of an emulsion. Fig. 10 depicts five major instability phenomena observed in emulsions. These instability phenomena are often interrelated and can occur concurrently. Therefore, comprehensive methods are required to adequately evaluate and address these challenges.

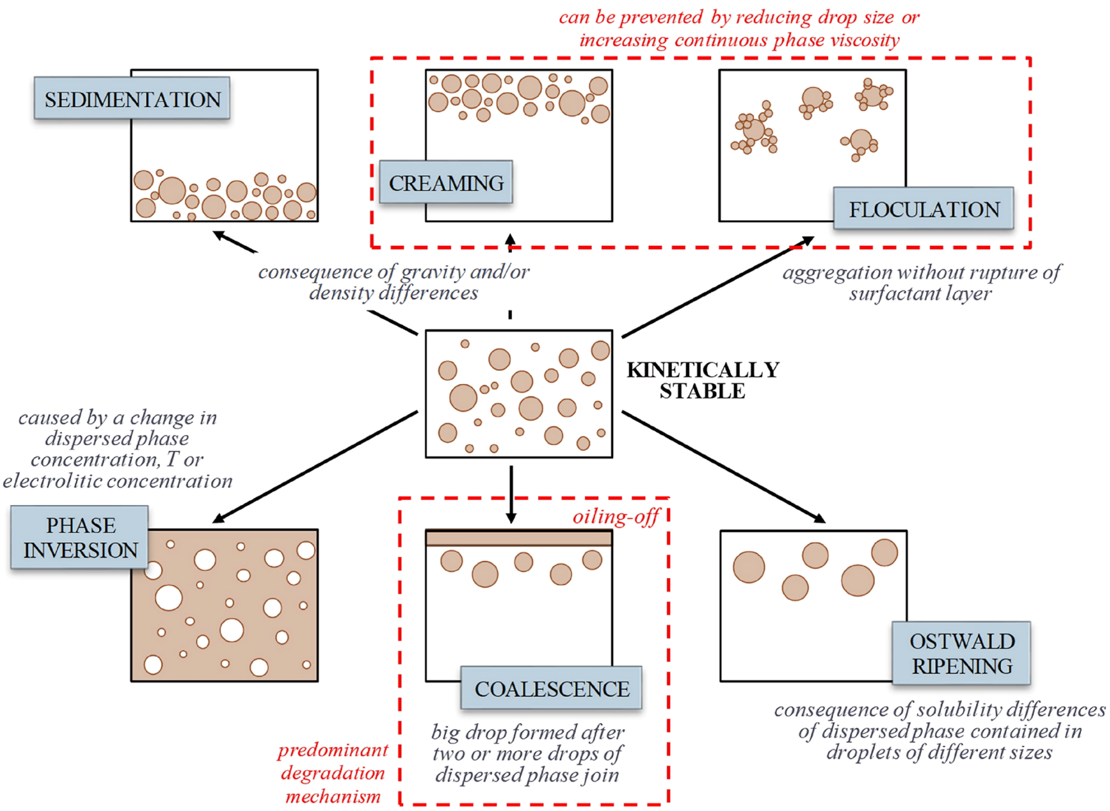


Fig. 10 Primary mechanisms of emulsion instability [26,98].

3.1 Unstable behavior of emulsions

3.1.1 Creaming and precipitation

Stokes' law defines the creaming or precipitation rate ($v_{\min}$) of spherical droplets in a dilute emulsion [99] with a volume fraction of $\varphi < 0.01$ [65].

$$v_{min} = -2gr^2(\rho_2 - \rho_1)/(9\eta_1) \tag{1}$$

where (ρ_2-ρ_1) is the density difference between the continuous phase and the dispersed phase, r is the droplet radius, g is the gravitational acceleration, and η_1 is the viscosity of the continuous phase.

When the emulsion volume fraction is between 0.1 and 0.2, the hydrodynamic interaction between the droplets can reduce the Stokes velocity [100] to the value v. This value v is described by the following Eq. (2) [79]:

$$v = v_0(1 - k\varphi) \tag{2}$$

where hydrodynamic interactions are taken into consideration by the constant k.

In a concentrated emulsion, the sedimentation or creaming rate of droplets is complexly dependent on the volume fraction. During the homogenization process, the surfactant in the emulsion system has a significant impact on the size of the produced droplets. Owing to the diverse structures of surfactants, The adsorption capacity of droplets varies as a result of surfactant structure, influencing droplet coalescence and emulsion stability [101].

Furthermore, the density and volume fraction of the inner core material and surfactant layer that make up the droplet determine its effective density. Notably, a significant amount of surfactant is adsorbed at the oil-water interface layer, changing the effective density of the droplets [59]. The effective density of emulsion droplets can be calculated using Eq. (3) [79]:

$$\rho_3 = (r\rho_{PCM} + 3\delta\rho_{surfactant})/(r + 3\delta) \quad (3)$$

where δ is the thickness of interfacial layer, r is the radius of the droplet, and ρ_{PCM} and $\rho_{\mathrm{surfactant}}$ are the densities of the PCM and surfactant, respectively.

3.1.2 Unstable behavior of droplets

Flocculation, the process by which two or more droplets combine into a flocculated mass, occurs when droplet fusion does not occur. This phenomenon occurs when the attractive forces between emulsion droplets, such as van der Waals forces, hydrophobic interactions, and depletion attractions, surpass the repulsive forces, which include steric and electrostatic interactions.

Coalescence, or the merging of two or more droplets to form a bigger droplet, can occur quickly when the attractive forces between the droplets exceed the repulsive forces [102]. This process can be slowed by altering the surfactant to form an interfacial layer that is robust enough to resist rupture [103]. However, the precise mechanisms by which emulsifiers decrease droplet coalescence remains unknown and is being investigated. Controlling droplet coalescence and maintaining emulsion stability are frequently dependent on the strength and thickness of the interfacial layer, as well as the amount of surfactant coverage on the droplet surface.

Ostwald ripening is a diffusion-driven mass transfer phenomenon in emulsions that causes larger droplets to grow at the expense of smaller ones. This mechanism is mediated by the diffusion of oil molecules from smaller droplets to larger ones through the continuous phase [104] Ostwald ripening is commonly observed in polydisperse emulsions, where the limited mutual solubility of the two liquids can compromise the dispersion stability of the emulsion [105].

As droplet interfacial curvature increases, so does the solubility of the dispersed phase in the continuous phase. This tendency promotes the occurrence of Ostwald ripening. This state can be mathematically expressed using the Kelvin equation, which is shown in Eq. (4) [106]:

$$c(r) = c(\infty)\exp(2\gamma_i V_m/(rRT)) \tag{4}$$

where $c(r)$ represents the oil solubility proximal to the droplet with radius r, $c(\infty)$ signifies the volumetric solubility, γ_i denotes the interfacial tension of the droplet, V_m represents the molar volume of the dispersed phase, R stands for the molar gas constant, and T designates the absolute temperature.

Various factors, including droplet composition, solute solubility, and interfacial tension, can inhibit the Ostwald ripening of emulsions. One approach for stabilizing emulsions is to introduce components with poor or no solubility in the oil phase before homogenization [107,108]. Alternatively, in emulsions containing flavorful oils, the addition of amphiphilic polysaccharides, such as gum Arabic, can generate a dense and mechanically robust interfacial layer, preventing droplet deformation and effectively reducing Ostwald ripening [109,110].

The interchange of continuous and dispersed phases is a unique phenomenon known as phase inversion. Changes in the molecular geometry of surfactants are usually the cause of this inversion [111,112]. During the phase inversion process, a phenomenon called incomplete phase inversion has been observed [113], which causes emulsion droplets to expand and their droplet size distribution to widen. Consequently, this causes the stability of the emulsion to decline. Furthermore, the reverse rotation is significantly impacted by the properties of the surfactant. For instance, the turbidity point problem arises when non-ionic surfactants are used in the phase inversion method. The two phases eventually separate as a result of tendency of the emulsion droplets to combine and form larger droplets as the temperature rises.

3.2 Characterization of emulsion stability

Emulsion stability is a multidimensional property that may be evaluated by examining a variety of parameters. These include droplet diameter, droplet size distribution, and the degree of phase separation. To determine stability under defined conditions, these parameters should be evaluated following exposure to particular tests, such as extended storage, repeated phase change cycles, and shearing stress. Such evaluations reveal changes in droplet diameter, the degree of phase separation, and the visual appearance of the emulsion, among other qualitative characteristics.

A variety of methods can be used to characterize emulsion stability [114], including nuclear magnetic resonance, near-infrared spectroscopy, optical microscopy, droplet size analysis, zeta potential measurements, acoustic and electrical techniques, bottle tests, light scattering diffraction, electrical conductivity measurements, and turbidity analysis. By using these methods, stability may be precisely measured, which is essential for the improvement and application of emulsions in a variety of industrial and research settings.

The sedimentation of emulsions under the action of gravity can be tracked through periodically photographing emulsions in transparent test tubes. Zhang et al. [115] used this technique to investigate the long-term behavior of paraffin-in-water emulsions over a six-month period. They found t that some samples showed creaming at the interface after just 15 days.

One useful analytical technique for accelerating the separation process of emulsions is centrifugation. Samples in a centrifuge are subjected to a centrifugal force that is significantly greater than the gravitational acceleration, which significantly speeds up the separation of droplets. This method provides a quick and accurate assessment of emulsion stability. Fischer et al. [62] used centrifugation to investigate the shelf-life of a number of paraffin-in-water emulsions. The long-term stability of these model emulsions was assessed using multisample analytical centrifugation [116]. Fischer et al.[117] prepared an emulsion using fatty acid esters as the PCM in a related investigation. The emulsion was found to have a 300-day service life at 25 °C and a 25-

day service life at 60 °C.

The dynamic stability of emulsions can be better understood by high-frequency viscosity analysis. As demonstrated by Ataeian et al. [118], complex viscosity measurements under oscillatory frequency sweeps are an effective way to evaluate the stability of emulsion samples under dynamic conditions. In particular, improved dynamic stability is shown by a sample's ability to tolerate higher shear rates.

Lorusso et al. [119] proposed a unique application of diffusing wave spectroscopy analysis that takes into account the distribution of optical path lengths inside the sample. This technique measures the velocity distribution of scattering centers and calculates their variance by a specific equation. Diffusing wave spectroscopy provides a more detailed insight of emulsion stability by exploring the internal structure of the emulsion, including the average droplet radius, size distribution, emulsification rate, and even the dynamic behavior of emulsion droplets. The combination of diffusing wave spectroscopy and other analytical techniques is recommended for characterizing transient and unstable processes in emulsions, which has significant practical implications.

3.3 Factors that influence dispersion stability

During emulsification, the interfacial area increase significantly, from 1 to 100 m^2/ml [65]. This significant expansion can be thermodynamically described by the required free energy change, which is shown in Eq. (5).

$$\Delta G = \gamma \Delta A \tag{5}$$

where ΔA represents the change in the surface area between oil and water phases, while γ denotes the interfacial tension [120]. However, despite the fact that emulsions are made up of two or more surfactants distributed between two distinct phases, they are fundamentally thermodynamically unstable. Nonetheless, after homogenization, emulsions can achieve a state of kinetic stability, which can remain for a certain duration [121].

Dispersion stability of emulsions is influenced by various factors which can be divided into two categories: preparation conditions and emulsifiers. These factors have a significant impact on the properties and performance of the resulting emulsion. Droplet sizes have an important influence in the dispersion stability of PCMEs, which are categorized as microemulsions, nanoemulsions and macroemulsions. Microemulsions are typically characterized by droplet sizes ranging from 10 to 100 nm, nanoemulsions from 20 to 500 nm, and macroemulsions from 1 to 100 μm [54,122]. Details of the specific classification of PCMEs are shown in Table 14. Microemulsions are thermodynamic and kinetic stability, whereas nanoemulsions have some kinetic stability but low thermodynamic stability. Macroemulsions exhibit low thermodynamic and kinetic stability [49]. Smaller droplets are generally more resistant to gravity-induced creaming or sedimentation due to their enhanced Brownian motion, which improves emulsion stability.

Table 14. Different properties of nanoemulsions, microemulsions, and macroemulsions [54].

Types	Nanoemulsions	Microemulsions	Macroemulsions
Morphology investigation method	Optical microscopy	Phase diagram	Optical microscopy
Droplet diameter	20–500 nm	10–100 nm	1–100 μm
Appearance	Transparent, milky, translucent	Transparent, translucent	Turbid
Stability	Kinetically stable	Kinetically and thermodynamically stable	Weakly kinetically stable;thermodynamically un-stable
Microstructure	O/W, W/O	O/W, W/O, bicontinuous, lamellar	O/W, W/O
Surfactant concentration	Low	High	Low

The droplet size in emulsion is influenced by a variety of factors, including operating temperature, emulsification time, and equipment power e. This eventually influences the stability of the emulsion. In the context of ultrasonic emulsion preparation [60], increasing the ultrasonic power from 200 W to 400 W resulted in a significant reduction in the droplet size of the paraffin emulsion, from 250 nm to 150 nm. Furthermore, at constant ultrasonic power, increasing emulsification time resulted in a gradual decrease in droplet size. However, after a certain amount of ultrasonic time, the effect on droplet size reduction was insignificant.

Within the emulsion preparation process, a higher operating temperature during the emulsion preparation process helps to reduce droplet size, which improves emulsion stability. In a study conducted by Liu et al. [123] used a low-energy method to prepare emulsions. A series of experiments demonstrated that droplet size decreased as the working temperature increased from 30 °C to 50 °C.

Zhang et al. [115] and Wang et al. [124] investigated how rotational speed affects the emulsification of paraffin. For relatively large droplets, Increasing the rotational speed of big droplets can reduce their size from 24 µm to 4 µm. However, reducing droplet size beyond 1 µm is challenging, even at rotational speeds of up to 24000 rpm.

The dispersion stability of emulsions are significantly influenced by surfactants. The properties of the surfactants themselves are crucial for emulsion stability, as the continuous and dispersed phase in emulsions depend on the surfactant layer between them to remain stable. By lowering the surface tension between the oil and water phases, Surfactants help to generate a stable emulsion structure by reducing the surface tension between the oil and water phases. According to Cai et al. [65], differences in the molecular structures of emulsifiers cause variations in molecular adsorption and rearrangement at the interface, which have a significant impact on the formation and properties of the interface layer. Fig. 11 shows how different emulsifiers are categorized.

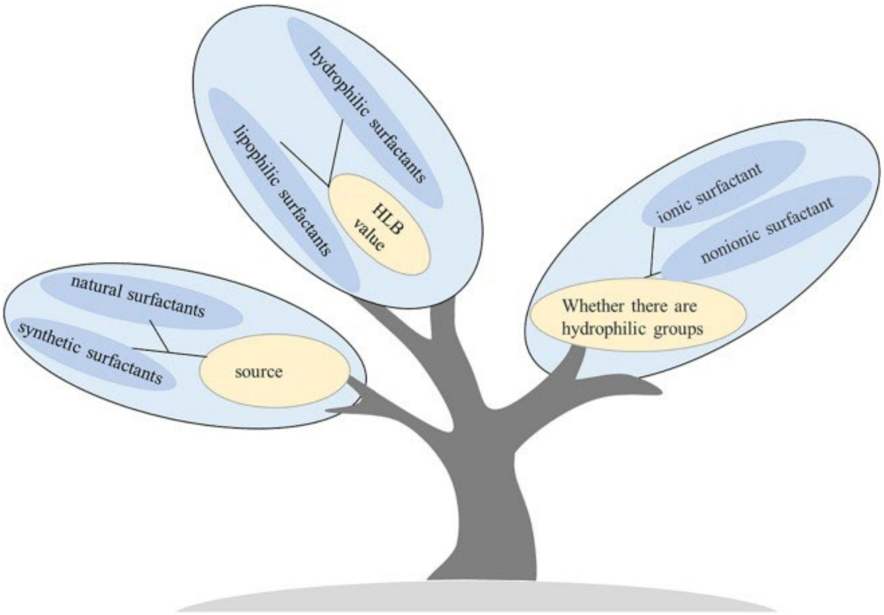


Fig. 11 Classification of surfactants [45].

The HLB value is an important guideline for emulsion preparation. The HLB value, which is a relative metric, is determined by calculating the corresponding value of the molecular group. This value provides information about the hydrophilicity or lipophilicity of a surfactant, with a higher HLB value indicating greater hydrophilicity. The HLB value of a surfactant is inextricably tied to its intended application; for instance, surfactants with HLB values ranging from 3 to 6 are well-suited for W/O emulsions, whereas those with HLB values between 8 and 18 are appropriate for O/W emulsions [125].

Surfactants with appropriate HLB values can significantly reduce the interfacial tension between oil and water phases, which has a considerable impact on preparation and stability of the nanoemulsion [126]. Moreover, it has been found [127] that surfactants such as Tween and Span with HLB values around 12 are effective emulsifiers for alkanes. Notably, HLB value primarily predicts surfactant properties at room temperature. Temperature influences the degree of hydrophilicity or lipophilicity in nonionic surfactants.

Zeta potential value is critical for emulsion stability. This potential provides repulsion between droplets, and when the absolute value of the potential is high enough, dispersion stability is ensured. Specifically, if the absolute value of the zeta potential exceeds 30 mV, it can be concluded that the electrostatic repulsion among droplets is sufficient to prevent phase separation. Furthermore, the zeta potential value correlates with the pH value. For instance, when the pH value of the emulsion is between 10 and 12, the potential is -60 mV, whereas at pH 4, the potential approaches 0 mV [123,128].

In alkane emulsions, the ethoxy group on the nonionic surfactant forms a hydrogen bond with water, enabling the generation of negative potentials. Furthermore, the potential value is influenced by salt concentration. Vilasau et al. [129] tested alkane emulsions with both ionic and nonionic surfactants. Their findings indicated that the stability of emulsions prepared solely with ionic surfactants followed the DLVO hypothesis, which considered only electrostatic repulsion and ignored steric interactions.

3.4 Strategies to improve dispersion stability

The choice of emulsifier is an important aspect in determining dispersion stability. Single emulsifiers have been used to stabilize emulsions, but their efficacy is low. Multiple emulsifiers has been demonstrated to greatly improve dispersion stability [81].

Co-surfactants are extra chemicals used in conjunction with primary surfactants in a surfactant system to improve emulsion performance. Often, these co-surfactants exhibit structural and property complementarity with the primary surfactants, allowing for a synergistic effect. The stability of an emulsion is determined by the interfacial layer generated by surfactant adsorption on the surface of the droplets [130]. When emulsion droplets come into contact with each other due to motion or long-range interactions, the deformable interface of the adjacent droplets flattens, forming a continuous phase film. This film is discharged until it reaches a critical thickness, which normally ranges between 50 and 100 nm. The resistance to additional thinning and cracking determines whether it coalesces or forms more durable droplet aggregates. As a result, the interfacial layer must be thick and elastic enough to withstand easy disruption. Co-surfactant formulations aid in increasing the thickness and flexibility of this film, both of which play important roles in enhancing emulsion stability. Liu et al. [131] found that nanoemulsions prepared with a mixture of Brij and polyethylene block poly (ethylene glycol) P-2250 were more stable than those made with Brij and P-1400.

The utilization of composite surfactants in emulsions provides considerable advantages over single surfactants. Firstly, the mixed surfactants facilitate the formation of an interface film through directional self-assembly, effectively limiting the coalescence of emulsion droplets and therefore enhancing the stability and performance of the emulsion. Secondly, using composite surfactants more efficiently reduces interfacial tension, strengthening the emulsion against various instability mechanisms, as shown in Fig. 12. Liu et al.[131] used a dual surfactant technique to prepare stable n-hexadecane phase change nanoemulsions, with Brij L4 served as the primary surfactant and polyethylene-b-PEG or Tween 60 as the co-surfactant. This method allowed for effective control of the droplet size of the nanoemulsion, maintaining it within 100 nm.

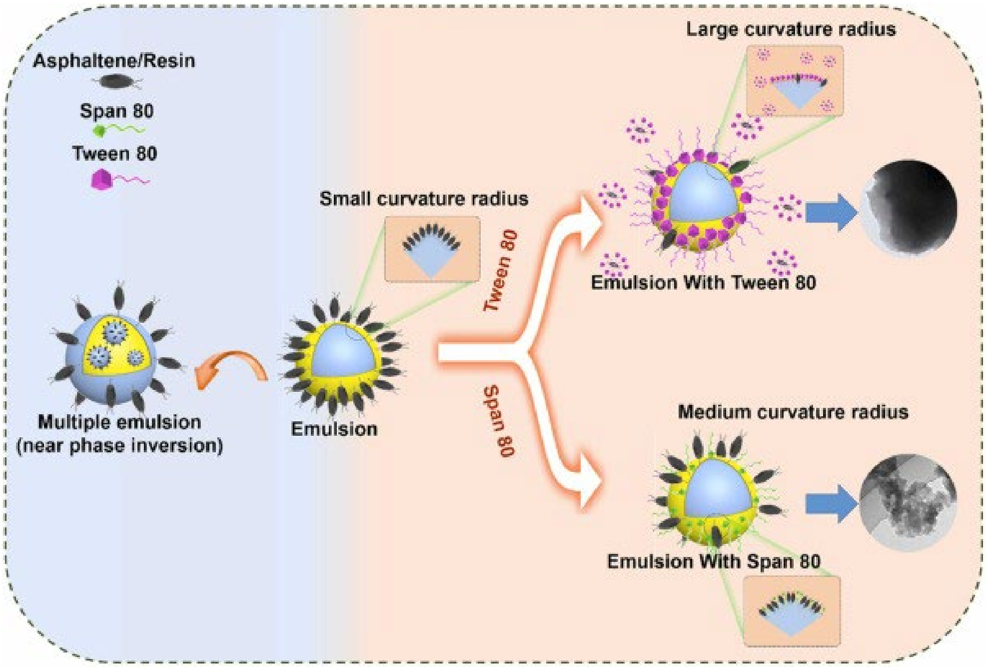


Fig. 12 Schematic diagram of the interaction between PCM and nonionic surfactants [132].

Surfactant content has a substantial influence on emulsion stability. The morphology of the emulsion varies with the concentration of surfactant, as shown in Fig. 13. Droplet leakage is caused by insufficient surfactant concentration, which lowers droplet surface coverage. In contrast, too much surfactant might stimulate micelle formation in the emulsion, increasing the overall viscosity [115]. According to Liu et al.[131], droplet size decreases as the surfactant content increases, from 92.5 nm at 8% to 45.6 nm at 12%. Moreover, an increase in viscosity correlates with surfactant content, promoting greater stability. An excess of emulsifiers over the critical value required to coat the droplet surface can reduce emulsion stability [133].

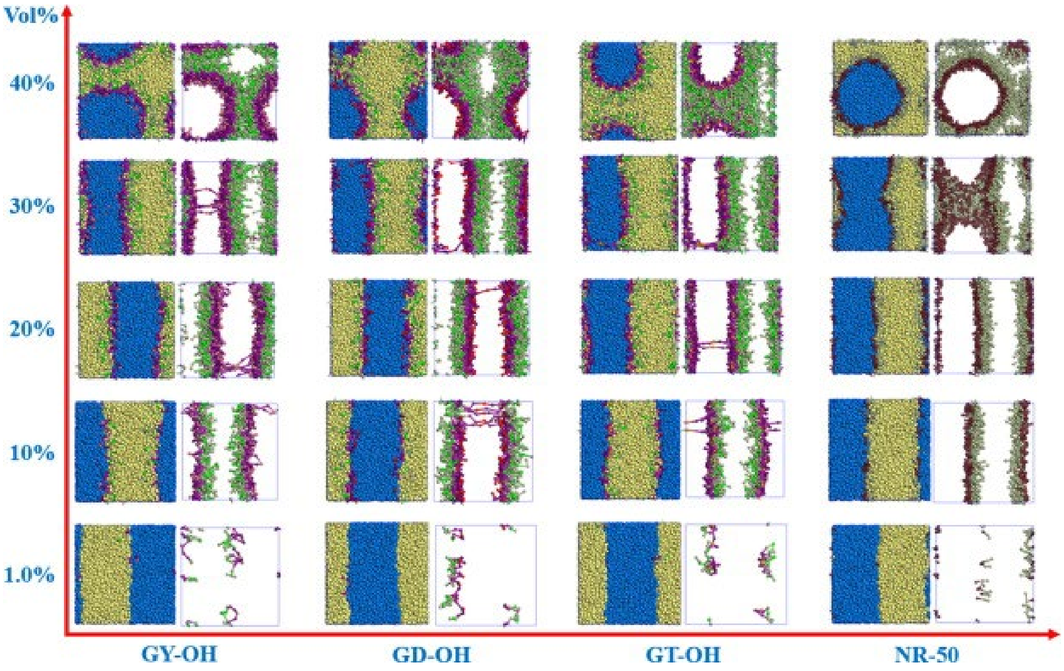


Fig. 13 Changes in emulsion morphology with surfactant concentration [134].

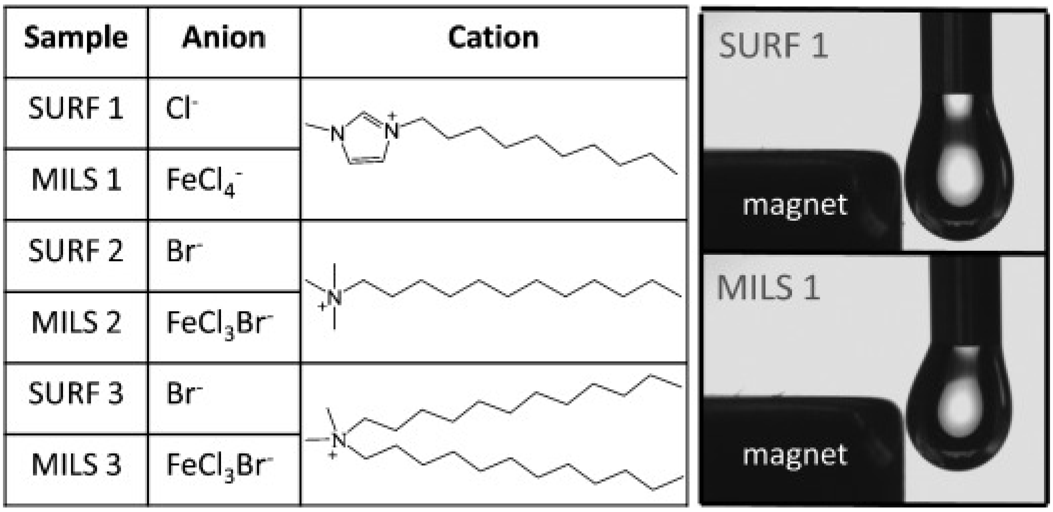
In addition to conventional surfactants, there are new varieties such as bio-based surfactants, polymeric surfactants, non-molecular surfactants, and other surfactants that offer distinct advantages in emulsification and dispersion stability of PCMEs.

Bio-based surfactants are extensive, renewable, environmentally friendly and are the best alternative to petroleum-based surfactants [135]. They exhibit unique amphiphilic structure, surface/interface properties and self-assembly behavior different from conventional small molecule surfactants [136]. The structural diversity of these surfactants derived from nature determines their functional diversity, which has good dispersion, emulsification, and unique physiological properties [137]. Saponins are a class of non-ionic bio-based surfactants mainly found in plants, composed of hydrophobic glycosides and hydrophilic glycochains, with amphipathicity [138]. The unique adsorption layer and interface membrane formed at the interface (oil-water interface and gas-water interface) make it commonly used as emulsifier, showing a completely different effect from the conventional small molecule surfactants [139].

Polymer surfactants have the structural characteristics of long molecular chain and high molecular weight, which can effectively reduce the possibility of molecular migration. Furthermore, this dense molecular layer can also provide a spatial stability [140]. In the synthesis of polymer surfactants, random copolymers are simple, cost-effective, and have a large range of monomer selection and composition compared with complex and high-cost processes [141,142]. Acrylic acid pressure sensitive adhesive emulsion is widely used in the industry, which is mainly made by emulsion polymerization method and using polymer surfactants [143]. Qin et al. [144] used a continuous polymerization process and found that polymer surfactants could effectively stabilize the emulsion. They have better binding properties and heat resistance than conventional low molecular weight surfactants.

The aforementioned surfactants are classified as molecular surfactants, which are typically amphiphilic compounds composed of both hydrophilic and hydrophobic groups [145]. The adsorption and desorption of molecular surfactants on the interface tend to become unstable under thermal motion [146]. As a result, non-molecular surfactants have gained interest. Typical non-molecular surfactants are solid particles, also referred to as colloidal surfactants [147]. Pickering emulsions are emulsions stabilized by solid particles. Solid particles, as opposed to molecular surfactants, limit droplet interaction by volume repulsion and improve stability at the oil-water interface through irreversible adsorption [148,149]. Interestingly, the solid particles do not significantly alter interfacial tension, indicating that the mechanism for Pickering emulsions to remain stable is not due to decrease in interfacial tension [150]. Additionally, the particles create three-dimensional networks in the continuous phase, which increases the viscosity and slows down the motion and coalescence of emulsion droplets [151]. For stable emulsions to form, suitable particles must be chosen as surfactants [152]. The stability of Pickering emulsions depends on a number of factors, including size, amphiphilicity, concentration, and shape of particles [145].

Additionally, there are some novel surfactants for the preparation of PCMEs. For preparing long-acting, low- or non-corrosive emulsions with stable dispersion characteristics, magnetic surfactants hold great promise [153,154]. The magnetic field may be easily adjusted and is less intrusive [155]. As illustrated in Fig. 14, Brown et al. [156,157] synthesized magnetic ionic liquid surfactants for the first time by mixing $FeCl_3$ with appropriate cationic surfactants, as shown in Fig. 14. Magnetically sensitive emulsions were produced by effectively combining Gd^{3+} and Fe^{3+} with dodecyl trimethyl ammonium bromide. Liu et al. [158] prepared emulsions with magnetic responsiveness using ZnO nanoparticles modified by magnetic surfactants.



Sample	Anion	Cation
SURF 1	Cl^-	
MILS 1	$FeCl_4^-$	
SURF 2	Br^-	
MILS 2	$FeCl_3Br^-$	
SURF 3	Br^-	
MILS 3	$FeCl_3Br^-$	

Fig. 14 Left: Inert (SURFs) and magnetic surfactants (MILSs) studied. Right: Response of liquid droplets to the field from a 0.4 T NdFeB magnet [157].

Furthermore, alcohols include both lipophilic and hydrophilic components in their molecular structure, making them potential for surfactant applications. Zeng et al. [159] investigated the effect of short-chain alcohols on the stability of emulsions produced through spontaneous emulsification and discovered that ethanol significantly improved the stability of nanoemulsions when compared to 1-propanol and 1-butanol. Similarly, Zeeb et al. [160] nvestigated the effects of short-chain alcohols on droplet size in protein-stabilized emulsions. The results indicated that at a 10% concentration, ethanol, 1-propanol, and 1-butanol all reduced droplet size. However, at higher concentrations, there was a substantial increase in droplet size, which exceeded that of alcohol-free samples.

Nanoparticles significantly influence dispersion stability, functioning as emulsifiers due to their unique physical and chemical features that reduce oil-water interfacial tension and facilitate the formation of stable, homogeneous emulsions [133]. Liu et al. [97] investigated the effects of various nucleating agents on the stability of commercial paraffin (OP44E) nanoemulsions. The study included solid nanoparticles (SiO_2, TiO_2, nano-Al_2O_3), n-alkane dodecane, and two polymers: polyethylene and polyethylene acrylate. The results indicated that SiO_2 and TiO_2 caused precipitation in the OP44E nanoemulsion, reducing its stability. The combination of nano-Al_2O_3 and dodecane significantly reduced supercooling in the OP44E nanoemulsion, enhancing its stability, as shown in Fig. 15.

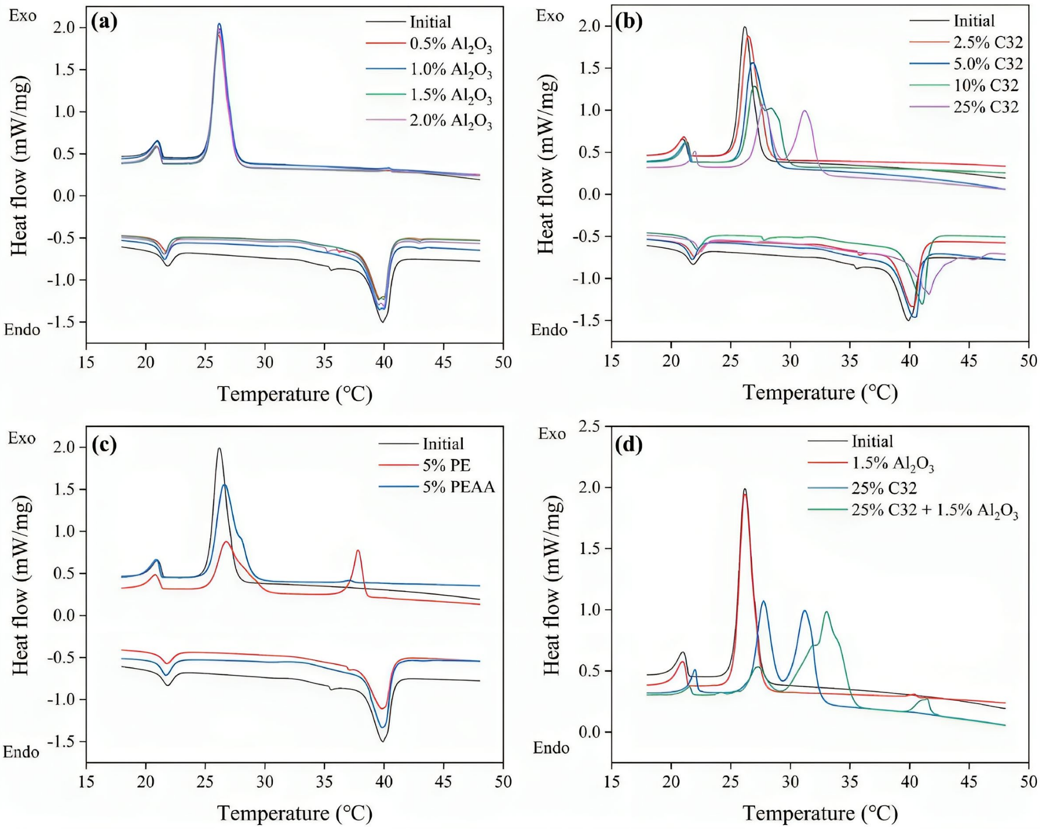


Fig. 15 Differential scanning calorimeter curves of OP44E nanoemulsions with various nucleating agents: (a) nano-Al_2O_3; (b) dodecane; (c) polyethylene and polyethylene acrylate; (d) nano-Al_2O_3 and dodecane (all percentage values refer to the mass ratio of nucleating agent to PCM) [97].

3.5 Influence on supercooling and viscosity

Generally, controlling the dispersion stability of PCMEs influences other emulsion characteristics, including crucial variables like viscosity and supercooling degree. Therefore, it is important to jointly investigate these aspects. The supercooling degree of the emulsion is usually impacted by surfactants applied to increase the dispersion stability of the PCME. Certain surfactants can induce PCME nucleation and decrease the supercooling degree. Golemanov et al. used surfactants like Brij 52 whose carbon chain length was comparable to the PCM in order to improve the stability and supercooling properties of paraffin-in-water PCMEs [67]. Günther et al. found that surfactants significantly affect the supercooling of cetane emulsions [33]. In order to facilitate the heterogeneous nucleation of hexadecane-in-water emulsions, Sakai et al. chose surfactants with carbon chain lengths comparable to PCM [161]. Wang et al. virtually eliminated PCME supercooling by combining two polymeric surfactants [124].

Dispersion stability of PCMEs can be improved by regulation of rheology properties [162]. Rheological properties are primarily determined by the relationship between viscosity and shear rate, which classifies PCMEs as Newtonian or non-Newtonian. Lei et al. [162] investigated the stability of PCMEs through interface rheology and determined that improved dilational rheology properties is associated with enhanced stability. The stability of PCMEs was investigated at microscopic level through assessing the interfacial rheology on the oil-water interfacial film. Adjusting the oil-water ratio was found to be the key to achieving the optimal rheology and ensuring that PCMEs have outstanding stability [163]. Wang et al. [124] studied the relationship between viscosity and stability and found that stability would be improved within a specific viscosity range. Chatterjee et al. [164] investigated the rheology and stability of three different concentrations of "Pickering" emulsions and discovered that the emulsions are susceptible to destabilization under flow, with sensitivity varied with the magnitude of shear forces applied. Delgado et al. [165] investigated the physical stability of four PCM slurries with the help of controlled stress rheometer. This study provides an important research basis for the stability study of PCM slurries.

4 Phase change cycling stability

During phase change processes, the crystallization and expansion of water and PCM within the emulsion exert pressure on its structure, resulting in destabilization characterized by possible stratification, creaming, or precipitation. Generally, the frequency of phase change cycles is proportional to the degree of demulsification, with repeated cycles usually resulting in poorer stability. Severe phase separation during phase change processes has been observed to decrease the heat storage capacity of the emulsion.

The stability issue caused by solid-liquid phase change cycles of the PCM droplets/particles in emulsions has been studied by some research. Emulsified droplets often separate into bulk PCM following phase change cycles, with some separations occurring after only one cycle [67]. The unstable behavior of emulsions after phase change cycles is reviewed in this section, followed by an analysis and discussion on the instability mechanism during the process from four perspectives: droplet collision, yield stress, rotator phase crystallization, and droplet self-planarization.

4.1 Characterization of phase change cycling stability of PCMEs

The impact of various factors on the phase change cycling stability of PCMEs can be evaluated through systematic experiments that subject the PCMEs to multiple solid-liquid phase change cycles. Droplet size distribution, rheological changes, phase transition characteristics, and visual assessment are some of the key parameters evaluated. A full description of these parameters is presented in Table 15.

Table 15 Assessment of emulsion stability through cycling tests

Parameter	Description
Droplet Size Distribution	Measurements before and after cycling can show changes in droplet size, which may indicate coalescence or Ostwald ripening. An increase in droplet size variance suggests reduced stability.
Viscosity Changes	An increase in viscosity after cycling may indicate an increase in droplet aggregation, which can hinder phase change efficiency.
Phase Change Temperature	Tracking the phase change temperature before and after cycling can reveal changes in the thermal properties of the emulsion. A shift in phase change temperature suggests altered droplet interactions and potential stability issues.
Visual Inspection	Observations of phase separation, creaming, or sedimentation can provide qualitative data on the stability.
Cycling Efficiency	The efficiency of the phase change process (e.g., the amount of heat absorbed or released) can be quantified. A decrease in efficiency over cycles may indicate instability.

Lu et al. [166] developed a PCME specifically for cooling applications, incorporating a high-melting-point paraffin wax to reduce supercooling effects. The stability of this PCME was evaluated throughout an eight-month storage period and 50 heating-cooling cycles, during which the emulsion consistently demonstrated an effective reduction in supercooling. In another study, Zhang et al. [115] used n-eicosane for thermal energy storage. The stability of the resulting emulsion was tested over a six-month storage period and five phase change cycles. During the thermal cycling experiment, the presence of separated oil layers indicated a lack of emulsion stability. Gschwander et al. [167] studied the impact of 100 solidification-melting cycles under mechanical stress on emulsions, measuring changes in viscosity, droplet size, and phase change behavior. While no obvious phase separation or creaming was observed following thermal-mechanical cycling experiments, significant changes in viscosity and droplet size distribution were recorded.

4.2 Mechanism of phase change cycling stability of emulsions

The mechanisms governing the phase change cycling stability of PCMEs are summarized in Table 16, with emphasis on the interactions between droplets, the significance of yield stress, the consequences of rotor phase crystallization, and the occurrence of droplet self-planarization. It has been determined that droplet coalescence, which is usually caused by droplet collisions, is a critical factor leading to PCME instability. Yield stress, which occurs when the volume fraction of dispersed droplets increases, can cause e structural changes and precipitate instability within the PCME. The crystallization process, which is controlled by the degree of supercooling, can result in either complex shape formations or direct crystallization, both of which have implications for PCME stability. Furthermore, droplet self-planarization, a phenomenon in which droplets change morphology in response to temperature fluctuations, can be regulated by the addition of specific additives to improve the overall stability of the PCME. These findings provide a comprehensive framework for understanding the various factors that influence PCME stability during phase change cycling.

Table 16 Summary of mechanism of phase change cycling stability in emulsions

Mechanism	**Key findings**
Interaction between droplets	Coalescence is a primary instability mechanism. Solid droplets typically do not coalesce due to limited contact area. Surfactants prevent direct contact, stabilizing emulsion films Irregularly shaped crystals can destabilize emulsions. Collisions between solid particles and supercooled droplets can cause crystallization and partial fusion.
Yield Stress	Yield stress occurs when droplet volume fraction exceeds close-packed concentration. High concentration leads to a jammed state, affecting stability. Unstable emulsions with high yield stress are prone to structural changes. Stable emulsions maintain stability despite yield stress.
Rotator phase crystallization	Degree of supercooling influences PCM crystallization. Low supercooling leads to shape transformations and rotator phase formation. High supercooling skips the rotator phase, directly forming true crystals. Surfactants guide phase transition towards the rotator phase, minimizing supercooling.
Droplet self-planarization	Droplets exhibit complex shapes due to self-planarization. Transformation from spherical to polyhedral geometry occurs at specific temperatures. Interfacial freezing and elasticity drive shape changes. Alcohols and salts can modify self-planarization conditions, affecting emulsion stability.

4.2.1 Interaction between droplets

Droplet coalescence is a common problem that directly causes emulsion instability during phase change cycles. Coalescence usually occurs when two semi-liquid droplets collide; solid droplets are less likely to coalescence. Strong adhesion is prevented by the small contact area between two solid particles, as shown in Fig. 16A, which often results in a rebound after collision. As illustrated in Fig. 16B, an emulsion film parallel to the plane is created when two droplets collide. However, the protrusion of PCM crystals can cause collisions between semi-liquid droplets to break this film, as depicted in Fig. 16C. Variations in crystal shapes during the freezing process can have a substantial impact on emulsion stability. The "pin effect" caused by sharp edges in irregularly shaped crystals can destabilize emulsions; this phenomenon is also observed in fat crystals in food emulsions [168].

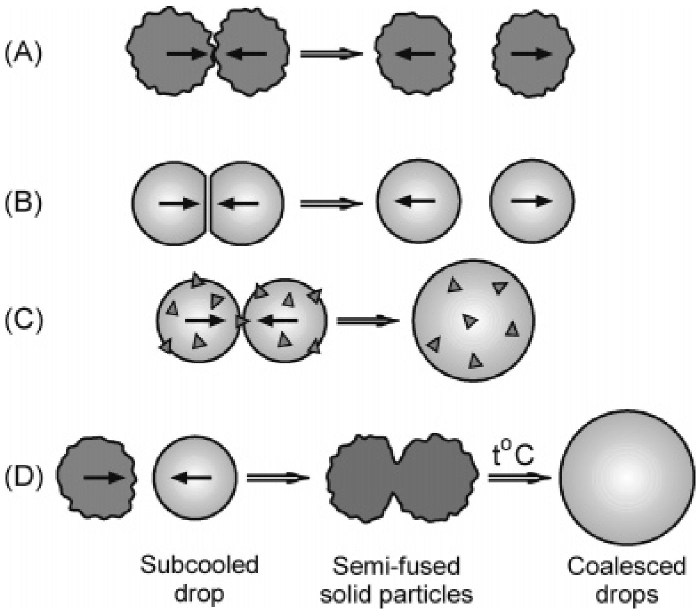


Fig. 16 Possible scenarios of phase change leading to dispersion instability: (A) two solid particles collide and bounce; (B) two droplets collide to form a stable emulsion film; (C) solid crystals break the film between droplets, and droplets coalesce; (D) solid particles contact with supercooled droplets causing crystallization [67].

In addition, collisions between solid particles and supercooled droplets are a crucial instability mechanism, as shown in Fig. 16D [169]. This often occurs when emulsion droplets undergo homogeneous nucleation and crystallization [170]. The polydispersity of emulsion droplets causes a range of crystallization temperatures, up to 10-15 °C, in which collisions between solid particles and supercooled droplets are likely. Such collisions might cause droplet crystallization and partial fusion, increasing the average droplet size in subsequent cycles and potentially leading to creaming of some PCM droplets.

The interactions between droplets have a substantial impact on phase change cycling stability, including coalescence, crystal shape, and collisions with solid particles. These interactions are governed by the balance of forces at the droplet-continuous phase interface, the presence of surfactants and other stabilizers, and Van der Waals forces. Lower interfacial tension reduces the energy barrier for droplet mergers, potentially affecting stability. Surfactants and stabilizers generate repulsive forces between droplets, preventing close contact and coalescence, especially during phase changes when interactions are more common. Van der Waals forces, which are attractive intermolecular forces, can cause droplet aggregation and must be balanced by repulsive forces from surfactants or other stabilizers to keep the emulsion stable.

4.2.2 Yield stress

Yield stress in emulsions is a critical factor influencing phase change cycling stability. It typically occurrs when the volume fraction (φ) of dispersed droplets exceeds 74%, leading to a state where droplets are immobile without applied stress [67]. After the solidification of droplets during phase change cycles, emulsions exhibit a significant yield stress and a colloidal appearance, distinguishing between unstable and stable dispersions.

Unstable emulsions, characterized by low stability and high yield stress, are prone to structural changes during phase change. A partially molten particle network causes these emulsions to form a gelatinous structure [67]. Solidification can cause collisions between supercooled droplets and solid particles, resulting in partial merging and the formation of a three-dimensional PCM network infiltrated by the aqueous phase, which creates a double continuous structure that hinders flow and stability. In these circumstances, yield stress results in a gelatinous structure that traps the continuous phase, resulting in a loss of fluidity and instability upon melting.

In contrast, stable emulsions, remain stable even when subjected to significant yield stress below the freezing point of the droplets. Elongated droplet morphologies during freezing contribute to yield stress while inhibiting coalescence through short-range repulsive interactions. These droplets can form three-dimensional structures without making direct contact, maintaining stability through electrostatic or steric repulsions and reducing aggregation-induced instability [67].

The effect of yield stress on stability is assessed by comparing the flow behavior, structural integrity, and resistance to droplet coalescence of the emulsion before and after phase change cycles. Unstable emulsions may transition to a bulk oil phase when melted, indicating a high level of instability. Stable emulsions, however, exhibit only geometric limits on flow, with no structural collapse or significant changes in droplet interactions, suggesting a lower impact on stability.

4.2.3 Rotator phase crystallization

Supercooling has a significant impact on the crystallization of PCMs. In PCMEs with low supercooling (≤10 °C), PCM droplets exhibit complex shape transformations during freezing, as observed by Phipps et al. [171]. Paraffin droplets changed from spherical to rod-like or flake-like structures before crystallizing. In situations with higher supercooling (≥10 °C), paraffin droplets directly form into real crystals, bypassing the mesophase state [170,172], as shown in Fig. 17. Cholakova et al. [173] classed rotator phases as thermodynamically stable or metastable, with the most unstable transient rotator phase occurring during a brief cooling period [174].

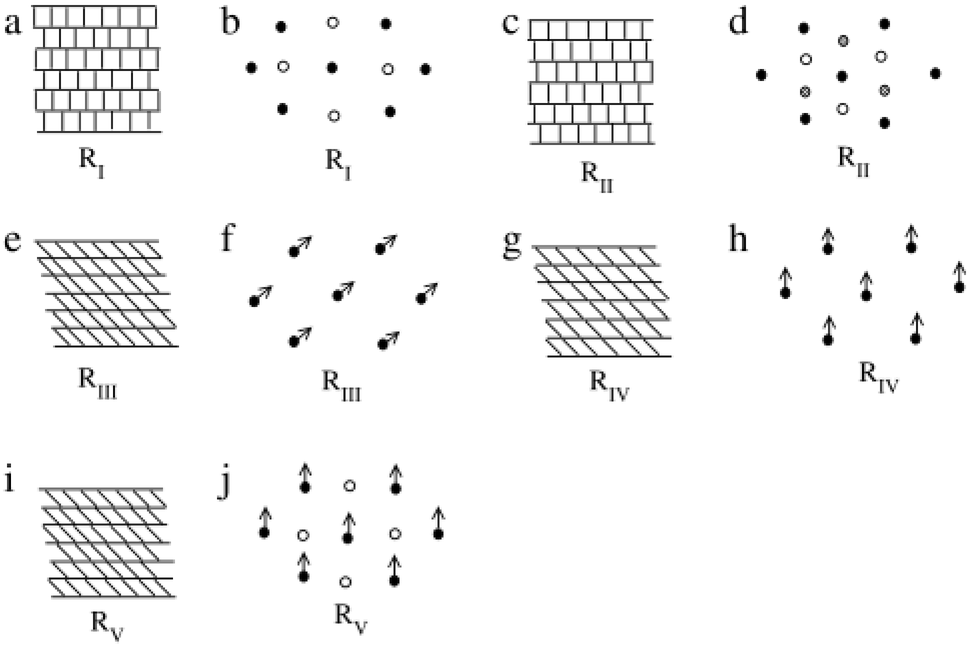


Fig. 17 Molecular arrangement of rotator phases of n-alkanes: Schematic of symmetries and structural representations [172].

The degree of supercooling affects the crystallization process, which includes the rotator phase; high supercooling systems tend to crystallize without the rotator phase, but low supercooling systems often pass through this phase [174]. Surfactants serve an important function in facilitating the phase transition to the rotator phase, increasing nucleation, and reducing supercooling.

In emulsions, PCM crystallization occurs gradually and involves a variety of crystal forms [175]. Metastable soft crystals develop and evolve into stable, rigid structures over 10 hours [176,177], providing at least 15 hours of low-temperature storage. However, the crystal form transitions in emulsion droplets vary across systems, needing individual investigation.

The emergence of the rotator phase is critical for emulsion phase change cycling stability. Crystal structures formed during PCM solidification may break the surfactant film, resulting in droplet coalescence. Therefore, selecting and applying surfactants is critical for initiating the PCM phase transition to the rotator phase, facilitating nucleation, and reducing supercooling.

4.2.4 Droplet self-planarization

Droplets are assumed to be spherical in the absence of external forces according to classic droplet equilibrium theory [178]. However, temperature-regulated liquid emulsion droplets have complex shapes such as icosahedral and cylindrical morphologies, which is caused by droplet self-planarization [179].

Droplet self-planarization is the process by which a spherical shape transforms into a polyhedral geometry with distinct vertices and ridges on a flat surface while it is still liquid [180]. This is often observed in surfactant-emulsified droplets after cooling below a specific temperature threshold, T_d, as shown in Fig. 18. The transition is driven by the tensile elasticity of the crystalline monolayer that forms on the droplet surface [181,182].

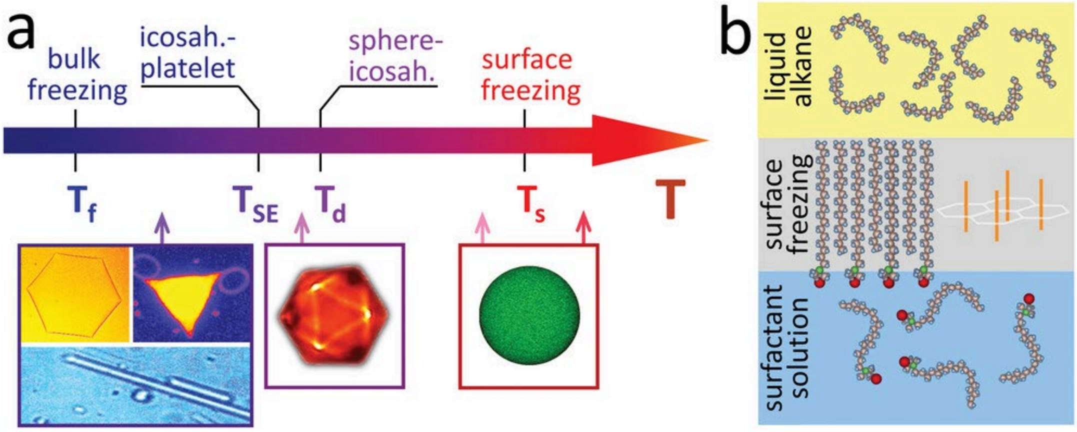


Fig. 18 (a) Droplet shape transition sequence; (b) In an alcohol-free emulsion, there is only a single layer of freezing at the droplet interface [180,183], alkanes (no head group) and surfactants (only red and green head group atoms) [184]. (Figure from Hacmon et al [184] without modification.)

Interfacial freezing occurs at $T=T_s$, reducing interfacial tension (γ) significantly below its value at T_s [185]. Above T_d ($T>T_d$), interfacial tension is sufficient to maintain spherical droplets. At $T=T_d$, droplets change to an icosahedral shape, governed by interfacial elasticity below T_d ($T<T_d$). Further cooling below a second threshold causes negative interfacial tension, resulting in the transition to plate- or rod-like geometries.

Academically, droplet self-planarization is classified as rotator phase crystallization [173]. To overcome capillary pressure during surface deformation, a thicker surface multilayer film is often required. Hacmon et al. [184] used alcohols to control the T_d value of O/W emulsion droplets. Both pure emulsions and those with alcohol additives had similar self-planarization morphologies, albeit with differences in the probability of alternative shapes and transition temperature. Pilkhaz et al. [186] investigated the effect of NaCl and CsCl salts on emulsion stability by adjusting ion adsorption at the interface and electrostatic repulsion between droplets. This approach was designed to reduce surfactant precipitation-induced self-planarization, thereby enhancing emulsion stability, as depicted in Fig. 19. To summarize, temperature significantly influences droplet self-planarization, with droplet morphology and stability varied across temperatures. The addition of alcohols or salts can alter self-planarization conditions, influencing droplet shapes and emulsion stability.

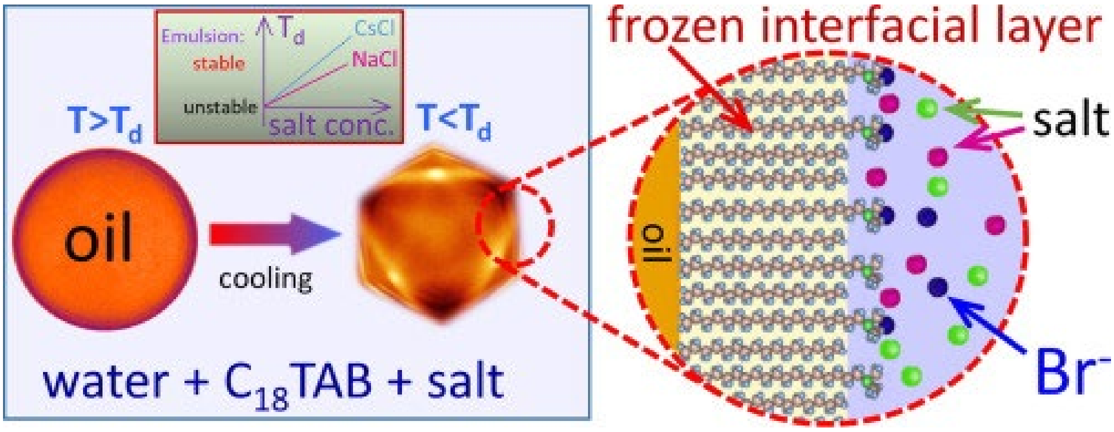


Fig. 19 Salt-induced droplets overcome self-planarization phenomenon [186].

Enhancing phase change cycling stability of emulsions is critical since it has a direct impact on their performance and service life. Emulsion stability is essential for practical applications. Achieving cycling stability during phase change remains a challenge. Current strategies to improve cycling stability primarily focus on enhancing dispersion stability. Despite the significance of this topic, empirical research into understanding and enhancing the cycling stability of PCMEs is limited. Consequently, more research is needed to have a better understanding of phase change dynamics for improving the cycling stability of PCMEs.

5 Conclusions and future research directions

Following a comprehensive analysis of the preparation methods, dispersion stability, and phase change cycling stability of PCMEs, the following conclusions and challenges have been obtained:

(1) Empirical data indicates that it is possible to prepare PCMEs that maintain their stability across multiple thermal cycles and long periods of time by optimizing emulsification settings and choosing suitable surfactants.

(2) The development of multi-component surfactants and nano-composites may enhance long-term stability. Notably, dispersion stability has significantly improved as a result of the addition of stabilizers, such as surfactants and nanoparticles. These additives have been demonstrated to significantly improve the dispersion stability and thermal properties of PCMEs. Maintaining the dispersion stability of PCMEs for extended periods of time under various operating conditions is a major challenge.

(3) The dispersion stability of PCMEs may somewhat deteriorate after multiple phase change cycles. The factors controlling the phase change cycling stability of PCMEs include the interactions between droplets, the yield stress, the rotor phase crystallization, and the droplet self-planarization.

(4) There are difficulties in scaling up laboratory-formulated emulsions and procedures to industrial production, particularly when it comes to large-scale emulsification methods and the maintaining emulsion stability.

This review focuses on principles and mechanisms linked to dispersion stability and phase change cycling stability of PCMEs. The following innovations distinguish this review article from others:

(1) Emphasize the emulsion's stability, particularly the principle and mechanism of solid-liquid phase change cycling stability. Emulsion instability is connected with

two phenomena: rotator phase crystallization and droplet self-planarization. The possible causes of emulsion instability are analyzed from a novel crystallization perspective.

(2) When examining the influence on dispersion stability, supercooling and viscosity are jointly taken into account.

(3) The advantages and disadvantages of new and classic preparation methods were compared, as well as the development and use of novel surfactants.

In addition to the unique insights, this paper has certain limitations. The study on the mechanism is insufficient. More constructive and inventive ideas for the problems in the research should be provided. Future research on this topic might focus on the following areas:

(1) More research is needed to develop of innovative emulsification methods that produce smaller, more homogeneous droplets to improve PCME stability. Further research is required on innovative emulsifiers, stabilizers, and useful additives to improve the preparation process of PCMEs.

(2) Comprehensive cycle stability tests of PCMEs are required to evaluate their reliability and identify areas for improvement. It is necessary to develop strategies to improve phase change cycling stability, especially with relation to microscopic interface crystallization. An in-depth analysis of the relationship between the microstructure and properties of the emulsion will offer a theoretical basis for improving PCME performance.

(3) Because there is currently little information available on how alcohols affect emulsions, more research is required to fully understand the physical and chemical properties of emulsions that are influenced by alcohols.

(4) It is crucial to improve performance evaluation and optimization of PCMEs for real-world applications. This includes a comprehensive a comprehensive assessment of dispersion stability and phase change cycling stability. These assessments can be used to systematically apply specific improvements to the emulsion system.

(5) The development of suitable surfactants that can enhance PCME stability and other characteristics like supercooling and viscosity is essential.

CRediT authorship contribution statement

Yufen Chen & Yuxin Yu: Investigation, Writing-original draft. Songping Mo: Conceptualization, Funding acquisition, Project administration, Supervision, Writing-review & editing. Junhao Chen: Investigation. Yanping Du: Writing-review & editing. Lisi Jia: Writing-review & editing. Ying Chen: Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this review.

Data availability

No data was used for the research described in the article.

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