Phase-Change-Material Nanoemulsions for Energy Transport and Storage

Masahiro KAWAJI
Department of Mechanical Engineering
City College of New York

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Outline

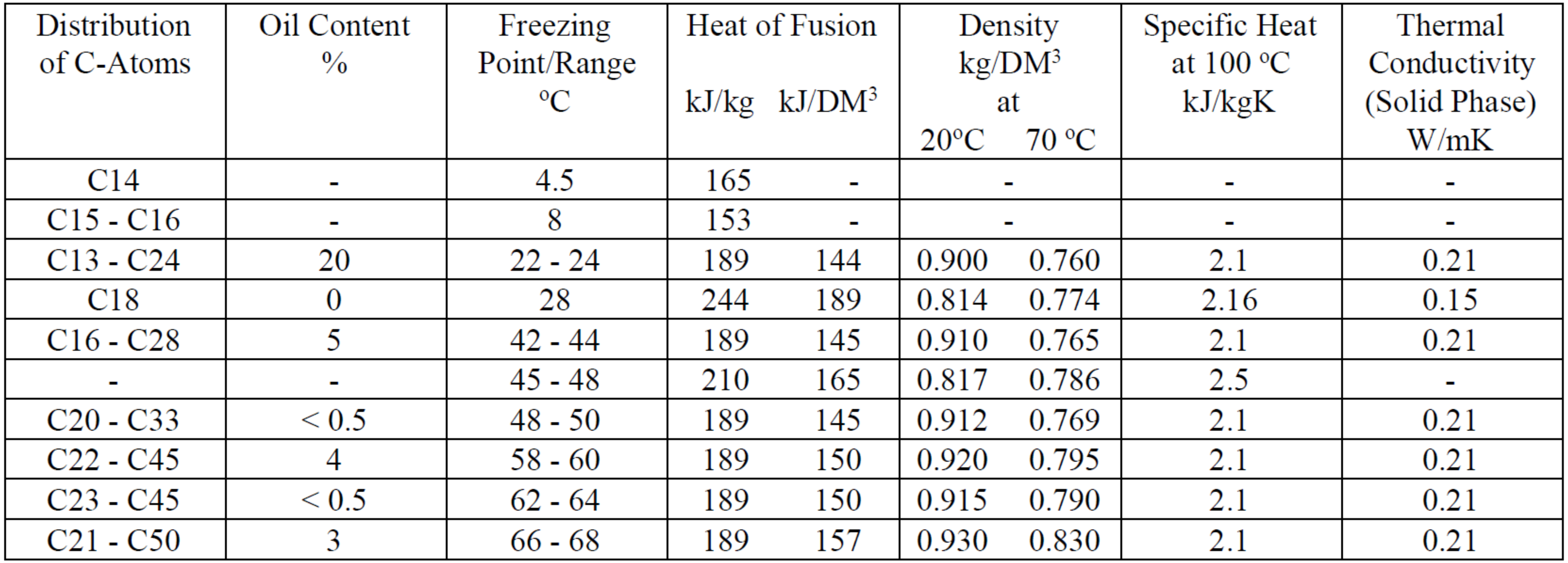
- Introduction and Recent Review Papers
- Phase Change Materials
- PCM Nanoemulsions
  - Synthesis Methods
  - Particle Size and Supercooling
  - Stability
  - Rheology: Viscosity
  - Heat Transfer
- Modeling and Simulation

Recent Review papers

- Kawaji, M., Fournaison, L. and Guilpart, J. (2007). Understanding of Ice Slurry and Low Temperature Phase Change Slurries for Thermal Storage and Transport Applications, Paper ICR07-E1-1068 in Proc. of the International Congress of Refrigeration, August 21-26, 2007, Beijing, China.
- Kawaji, M. (2012). Macroscopic and Microscale Phenomena in Multiphase Energy Storage and Transport Systems. J. Heat Transfer, Vol. 134(3), Article Number: 031010 DOI: 10.1115/1.4005159.
- Delgado, M., Lázaro, A., Mazo, J., Zalba, B. (2012). Review on phase change material emulsions and microencapsulated phase change material slurries: Materials, heat transfer studies and applications, Renewable and Sustainable Energy Reviews, 16 (1) 253-273.
- Youssef, Z., Delahaye, A., Huang, L., Trinquet, F., Fournaison, L., Pollerberg, C., Doetsch, C. (2013). State of the art on phase change material slurries, Energy Conversion and Management, 65, 120-132.
- Shao, J., Darkwa, J. & Kokogiannakis, G. (2015). Review of phase change emulsions (PCMEs) and their applications in HVAC systems, Energy and Buildings, 94, 200-217.

Table 1 Physical Properties of Organic Phase Change Materials

(from Abhat, 1983, Solar Energy 10(4), 313-332)



Distribution of C-Atoms	Oil Content %	Freezing Point/Range °C	Heat of Fusion		Density kg/DM^3 at		Specific Heat at 100 °C kJ/kgK	Thermal Conductivity (Solid Phase) W/mK
			kJ/kg	kJ/DM^3	20°C	70 °C		
C14	-	4.5	165	-	-		-	-
C15 - C16	-	8	153	-	-		-	-
C13 - C24	20	22 - 24	189	144	0.900	0.760	2.1	0.21
C18	0	28	244	189	0.814	0.774	2.16	0.15
C16 - C28	5	42 - 44	189	145	0.910	0.765	2.1	0.21
-	-	45 - 48	210	165	0.817	0.786	2.5	-
C20 - C33	< 0.5	48 - 50	189	145	0.912	0.769	2.1	0.21
C22 - C45	4	58 - 60	189	150	0.920	0.795	2.1	0.21
C23 - C45	< 0.5	62 - 64	189	150	0.915	0.790	2.1	0.21
C21 - C50	3	66 - 68	189	157	0.930	0.830	2.1	0.21

Popular PCMS for HVAC applications

For cooling applications with m.p. < 20 °C: tetradecane (C14), pentadecane (C15) and hexadecane (C16)

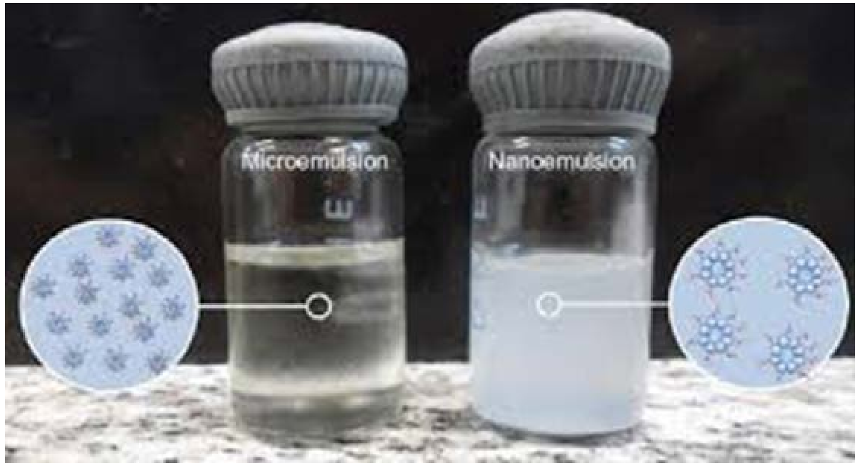
For heating applications with m.p. > 60 °C: Beeswax (m.p. = 62 °C), microsere (m.p. = 70, 83 °C)

Polymers blends such as RT6, RT10 and RT18 from Rubitherm Technologies GmbH (m.p. = -9 to 90 °C)

Emulsions, Microemulsions and Nanoemulsions

- Classification based on Particle Size
  - 10 to 100 nm: Microemulsion, thermodynamically stable.
  - 100 to 1000 nm: Nanoemulsion, thermodynamically unstable but kinetically stable.
  - > 1 μm: Macroemulsion systems, thermodynamically unstable but kinetically stable.

Note: If viscosity of an emulsion remains unchanged after pumping, then it is considered to be kinetically stable.



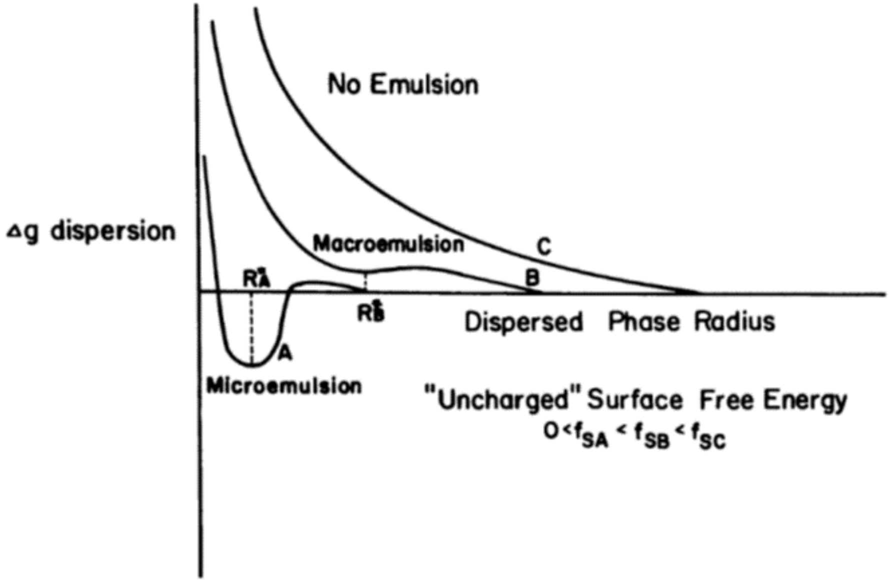


Figure 4. Schematic illustration of free energy change (Δg) as a function of droplet size (R)

Tetradecane Nanoemulsions

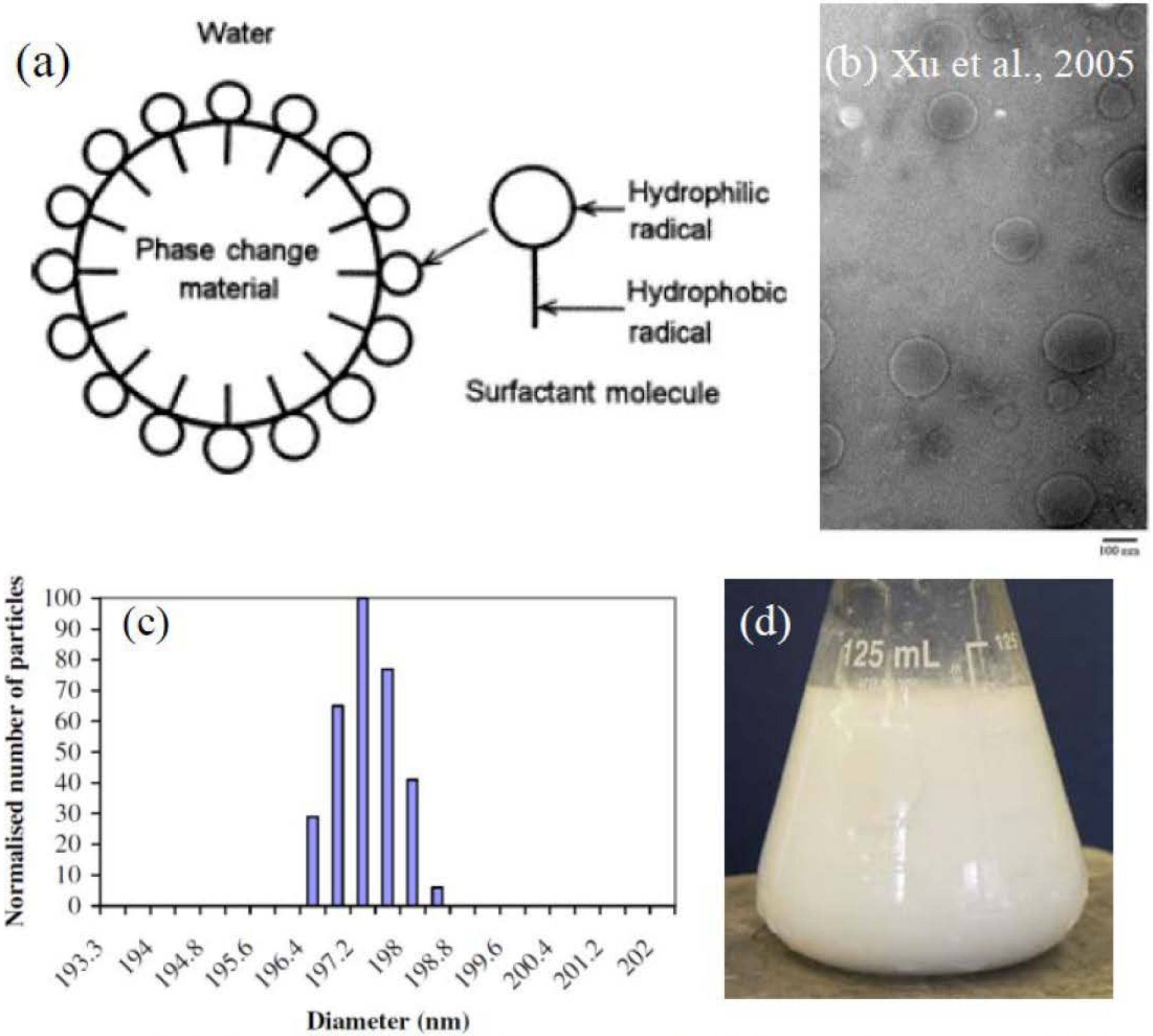
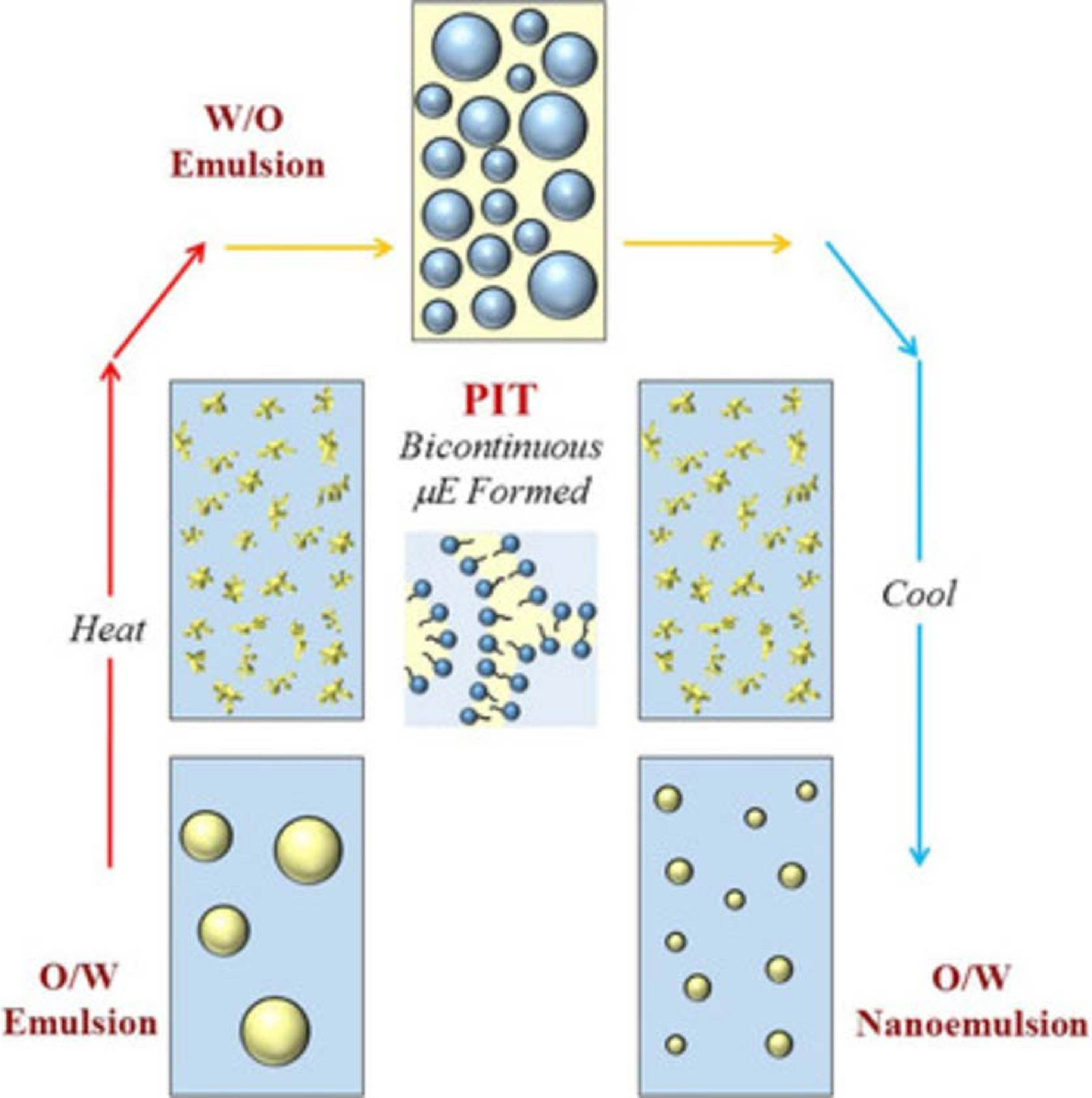


Fig. 1 (a) Micelle structure of a PCM particle, (b) TEM picture of PCM particles of 100 – 200 nm in water (Xu et al., 2005), (c) size distribution and (d) milky appearance of PCM nanoemulsion (Schalbart et al., 2010).

Low Energy Phase Inversion Method



Effect of Surfactant on Emulsion Stability

- Stability of PCME is closely related to surfactants used.
- Surfactant forms an absorption layer around oil droplet. If the layer is not strong enough, droplets will cream.
- Therefore, surfactant selection is the top priority to produce small and even paraffin droplets.

Particle size and shape

- Mean particle diameters in PCEs have ranged from 43.6 nm (Zhao and Shi, 2005) to 3.4 μm (Inaba and Morita, 1995) depending on the surfactants used and their concentrations.
- Fumoto et al. (2014) showed a minimum average particle diameter at surfactant (Span 60 and Tween 60) concentrations between 6 and 10 wt.% for tetradecane (20 wt.%) PCE.
- Niedermaier et al. (2016) have observed both spherical and rod-like particle shapes depending on the surfactants used.
- Irregularly shaped crystals could significantly destabilize the system during the freezing-thaw cycles.

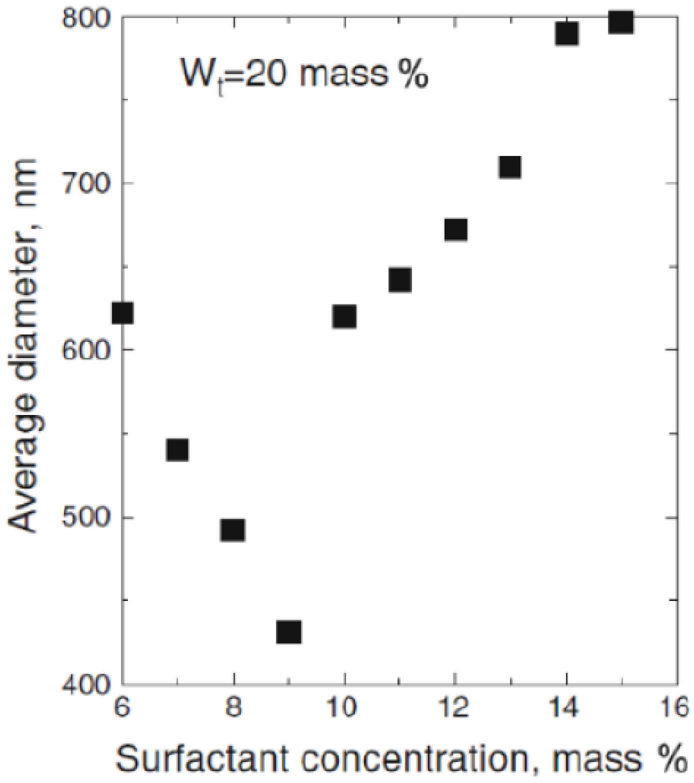
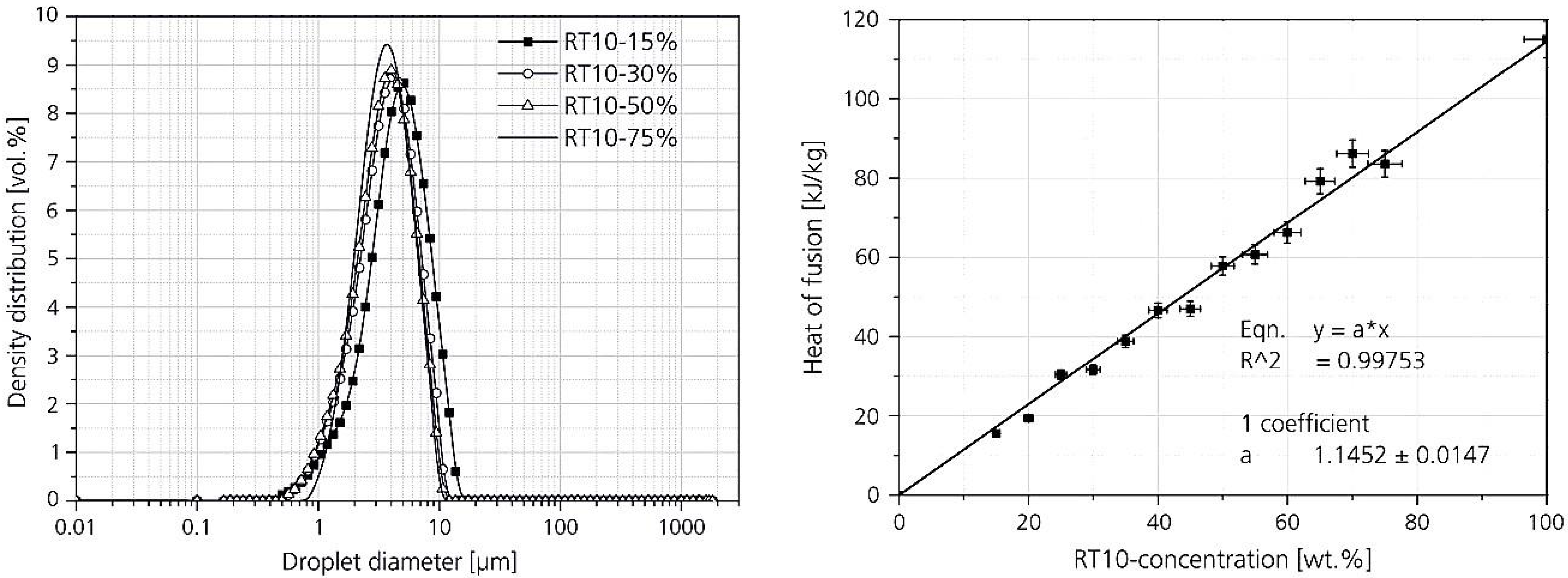


Fig. 2 Effect of surfactant concentration on particle size (Fumoto et al., 2014)

Effect of PCM Concentration on Droplet Size and Latent Heat Capacity of Emulsions



Relationships between heat of fusion and droplet distribution with different PCM concentrations

[L. Huang, M. Petermann, C. Doetsch, Evaluation of paraffin/water emulsion as a phase change slurry for cooling applications, Energy, 34 (2009) 1145-1155.]

- Latent heat capacities increased with PCM concentration for RT10 emulsions (15, 30, 50 and 75 wt%) with a mean diameter d_{50} of 3–5 mm.
- Increasing PCM concentration has little or no effect on the droplet size.

Supercooling Phenomena in Tetradecane Nanoemulsions

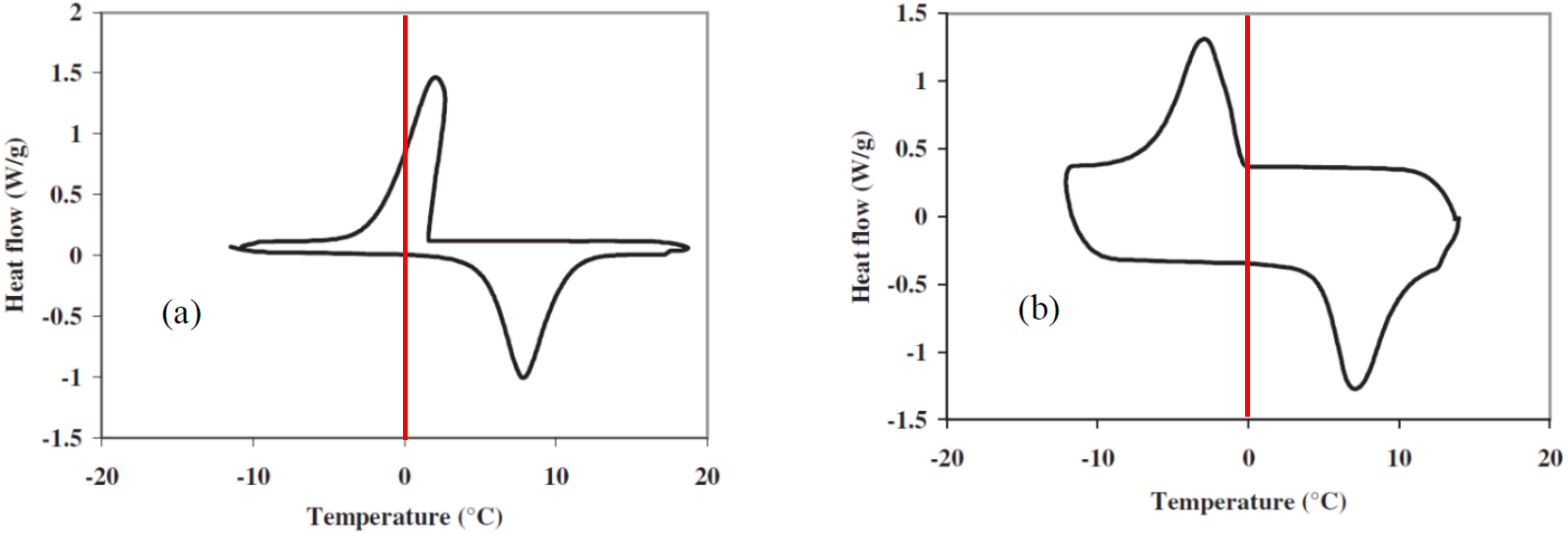


Fig. 5 DSC curves for (a) pure tetradecane and (b) tetradecane nanoemulsion (Schalbart and Kawaji, 2013)

Nucleation agents can reduce supercooling effect, e.g., paraffins of higher m.p.

Rheological Behavior of Nanoemulsions

- Significant differences exist in the apparent viscosity, which generally decreases with temperature but increases with the mass fraction of PCM.
- More than one order of magnitude differences exist possibly due to different particle sizes, PCM weight fractions and types of paraffins used.
- Tetradecane emulsions: as a Newtonian fluid at low shear rates even at a particle concentration of 30 wt.% or a shear thinning fluid.
- Viscosity tends to increase as the droplet size decreases.

Various Viscosity Correlations for non-PCM emulsions

- Einstein's Equation for Viscosity: $\eta = \eta_w(1 + 2.5\phi)$, where ϕ is the volume fraction of PCM. (good for small values of ϕ)
- Taylor's formula: $\eta = \eta_w\left(1 + \frac{5k+2}{2(k+1)\varphi}\right)$ where $k = \eta_{pcm}/\eta_w$
- Doughery-Krieger formula $\eta = \eta_s\left(1 - \frac{\phi}{\phi_m}\right)^{-2.5\phi_m}$ Reliable forϕ up to 0.6
- Yaron, Gal-Or formula:

$$\eta = \eta_w\left(1 + \frac{5.5\varphi\left[4\varphi^7 + 10 - \frac{84}{11}\varphi^2 + \frac{4}{k}(1-\varphi^7)\right]}{10(1-\varphi^{10}) - 25\varphi^3(1-\varphi^4) + \frac{10}{k}(1-\varphi^3)(1-\varphi^7)}\right)$$

- Non-spherical particles $$\eta = \eta_s\left(1 + \left(\frac{(a/b)^2}{5(\ln(2a/b) - 0.5)} + \frac{(a/b)^2}{15(\ln(2a/b) - 1.5)} + \frac{14}{15}\right)\phi\right),$$ for prolate ellipsoids

$$\eta = \eta_s\left(1 + \left(\frac{(16/15)(a/b)}{\arctan(a/b)}\right)\phi\right),$$ for oblate ellipsoids

Viscosity Variation with PCM Volume Fraction

- PCE viscosity relative to water (Fig. 3) shows a sharp increase at a paraffin concentration above 30 wt.% (or 40 vol.%) due to the rising importance of particle interactions.

  Due to high viscosity, the pressure drop in a pipe flow could be 100 times higher than that for water at PCM concentrations of 40~50 wt.%.

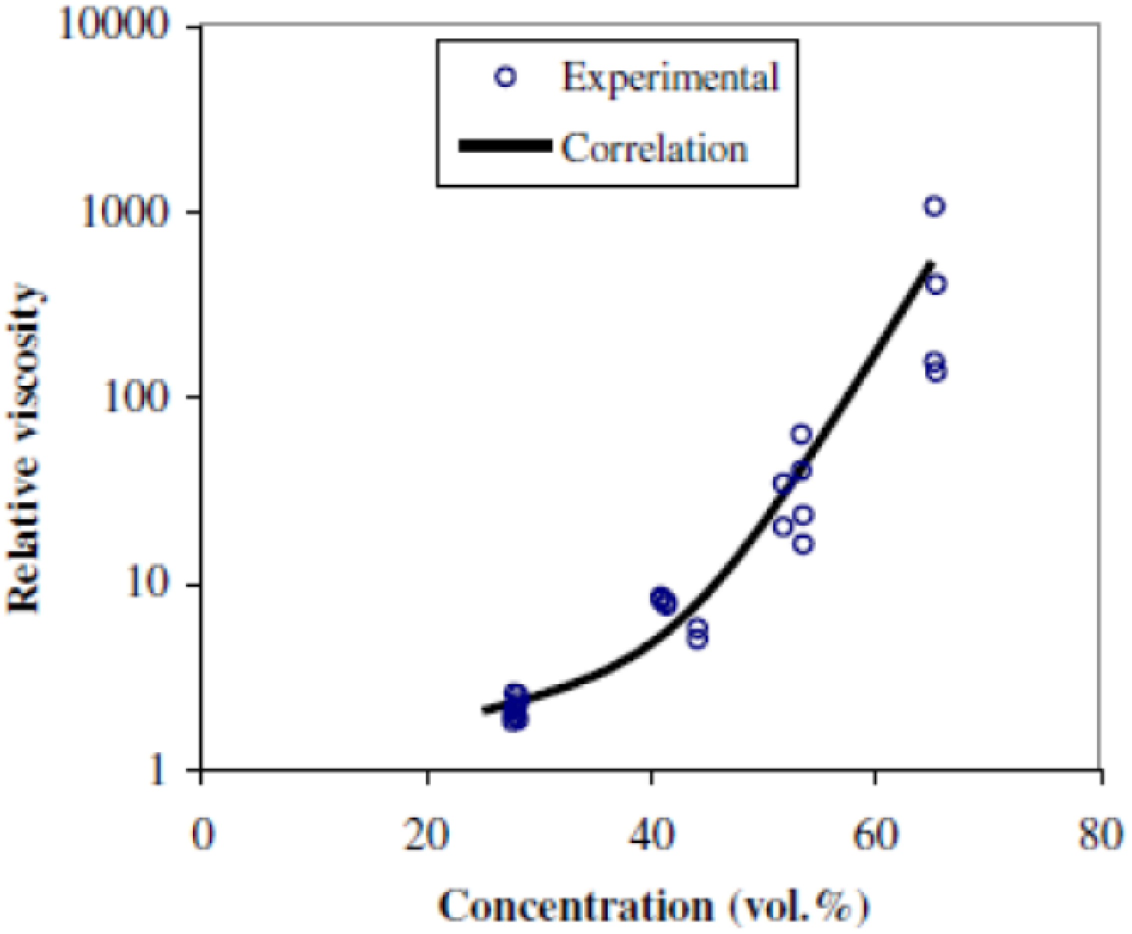


Fig. 3 Viscosity variation with surfactant concentration for RT-10 and Parafol emulsions (Schalbart and Kawaji, 2013)

Viscosity Variation with Thermal Cycling

- Niedermaier et al. (2016) measured viscosity variations of a PCE with 35 wt.% n-octadecane in water during thermo-mechanical stability tests in a rheometer with and without a nucleation agent.
- Large differences in viscosity at temperatures above and below the melting point can be observed, increasing with the number of thermal cycles.
- As the PCE is heated and cooled repeatedly, a shear-thinning behavior is also observed, but nucleation agents in the PCM particles have a strong effect.
- Physical reasons for these results are unclear.

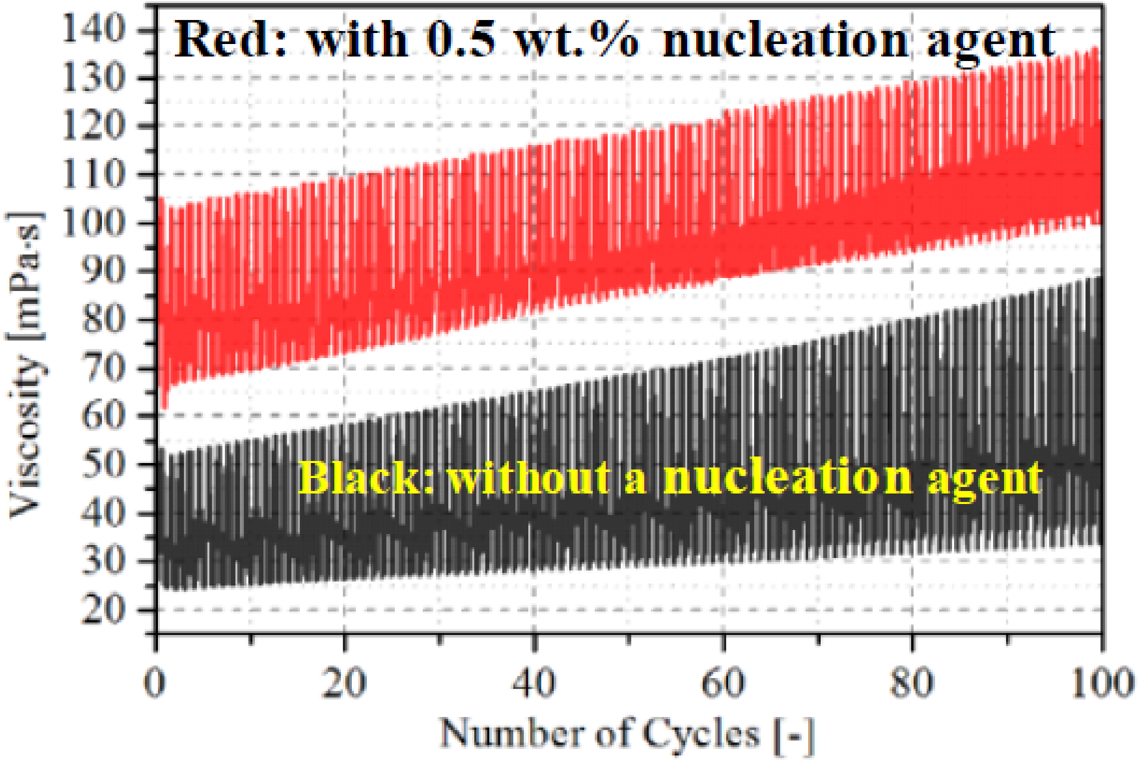


Fig. 14. Viscosity variation during thermo-mechanical cycles (5-35 °C)

Shear Thickening or Shear Thinning?

- Zhao and Shi (2005) found their tetradecane-water emulsion to behave as a shear thinning fluid like an ice slurry and used the following equation to correlate the apparent viscosity data.

$$\eta_a = k \cdot \left(\frac{dv}{dy} \right)^{n-1} \qquad (1)$$

- From 10 to 50 ^{o}C, the consistency index, k, decreased from about 0.13 to 0.06 and power law index, n, decreased from about 0.84 to 0.82, indicating a shear-thinning behavior.

Viscosity Variation with Temperature and Phase Change

"Sudden jump in viscosities of emulsions were witnessed at corresponding peak freezing point. The most likely cause was that at the freezing point, PCM got frozen and solid PCM particles deformed little under shear stress and thus caused higher viscosities." (Shao, Darkwa and Kokogiannakis, 2015)

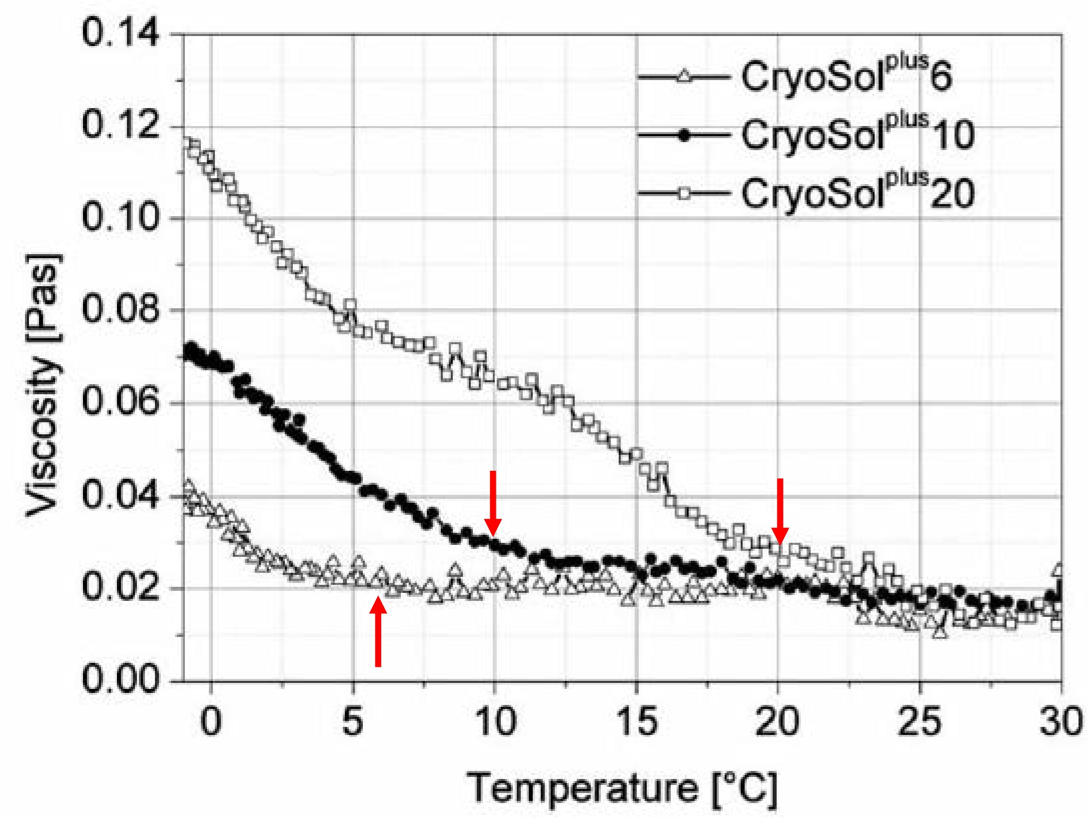


Figure 18: Viscosity of Cryosol 6, 10 and 20 versus temperature at 50s-1 [66]

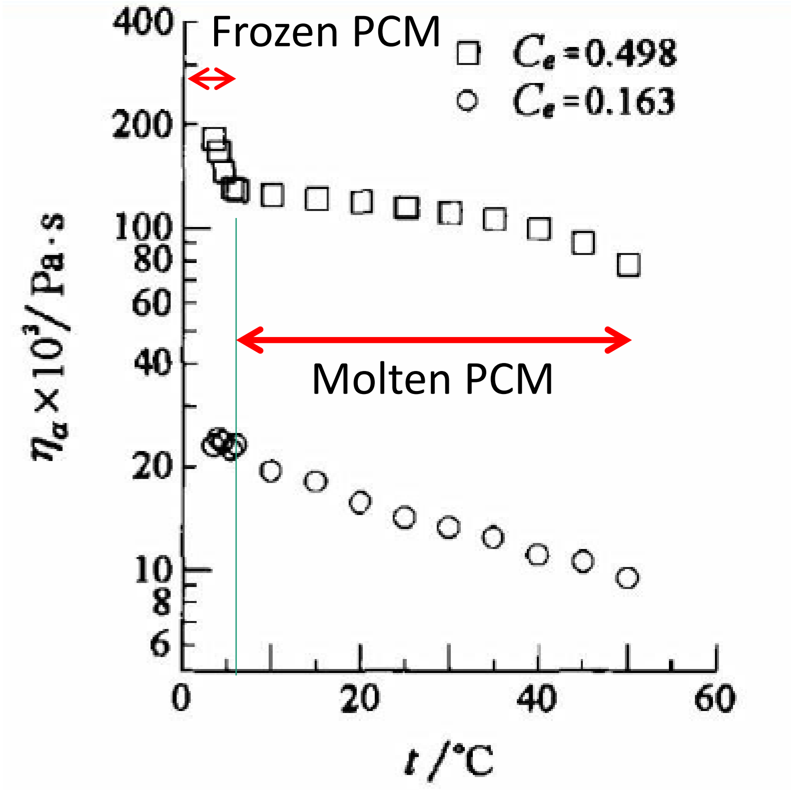


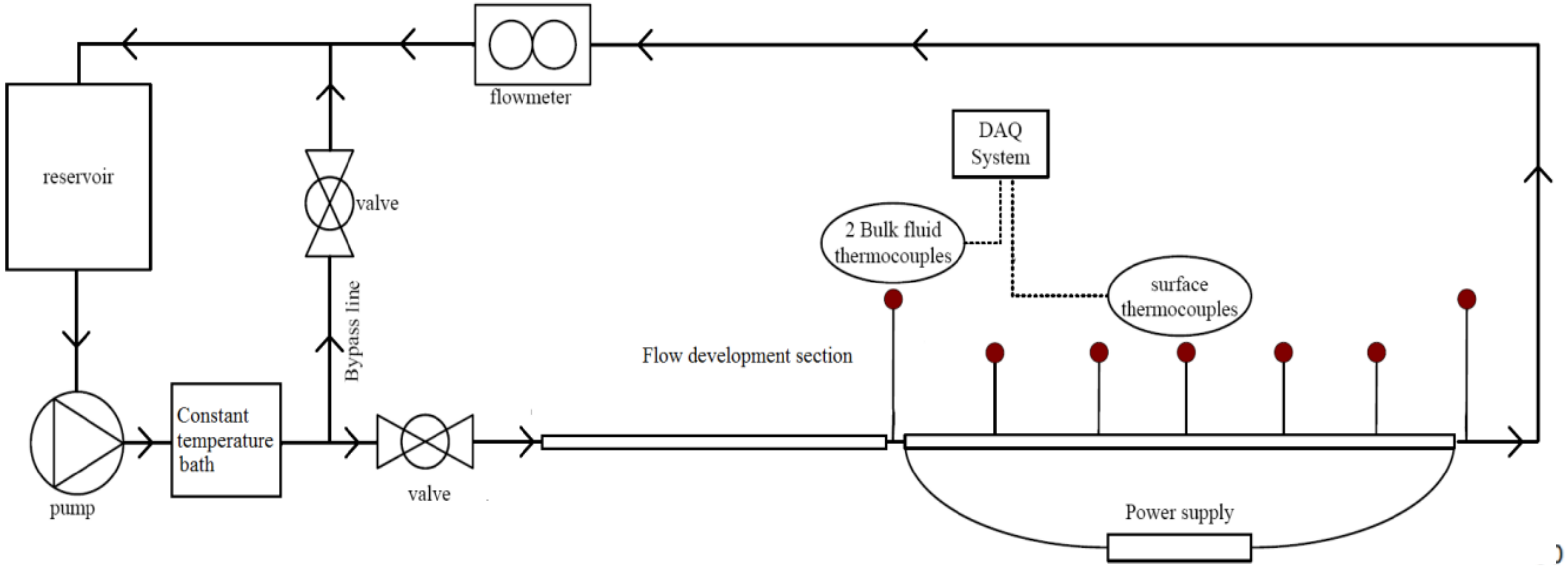
Figure 19: Viscosity against temperature phase change emulsions [9]

Viscosity Variation of PCM Nanoemulsion with Temperature and Phase Change

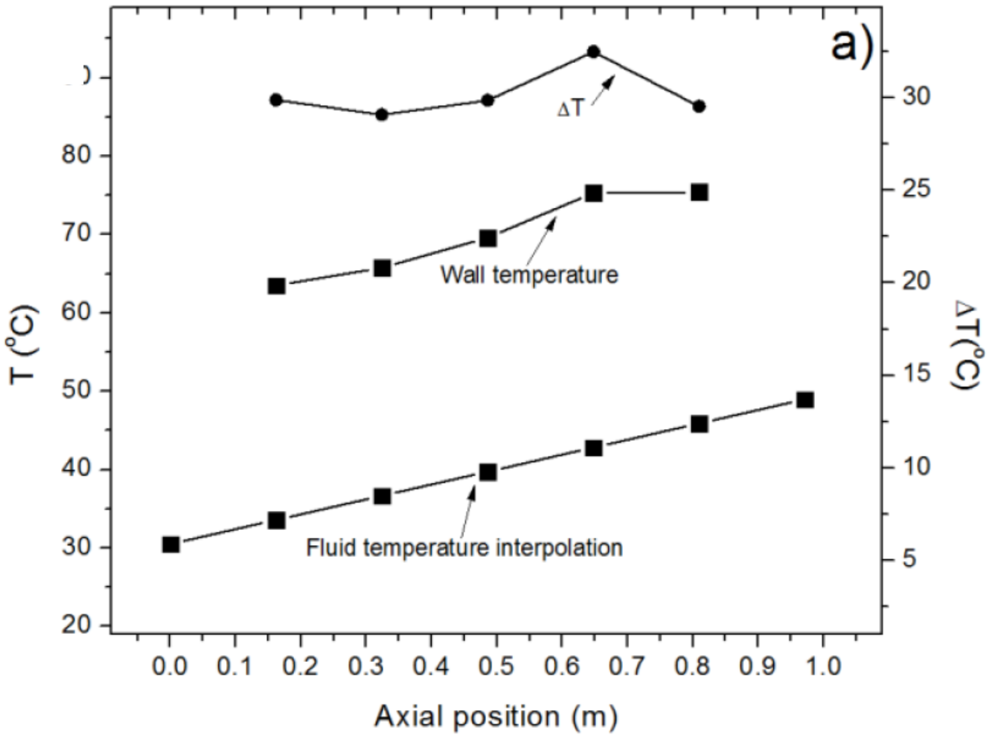
- Anderson et al. (2013) tested a nanoemulsion of beeswax ($C_{15}H_{31}COOC_{30}H_{61}$) which is a natural organic PCM with a melting point of 61.8^{o}C and a latent heat of fusion of 177 kJ/kg.
- A nanoemulsion was formed with surfactants (SPAN 60 and TWEEN 60) and water with an average particle size of ~100 nm.
- Viscosity variation with temperature showed a large jump from approximately 20 cP at 40 ^{o}C and 23 cP at 60 ^{o}C (solid PCM particles) to over 70 cP above 62 ^{o}C (PCM droplets).
- These data were opposite to the rheological properties of other nanoemulsions.

Convection Heat Transfer

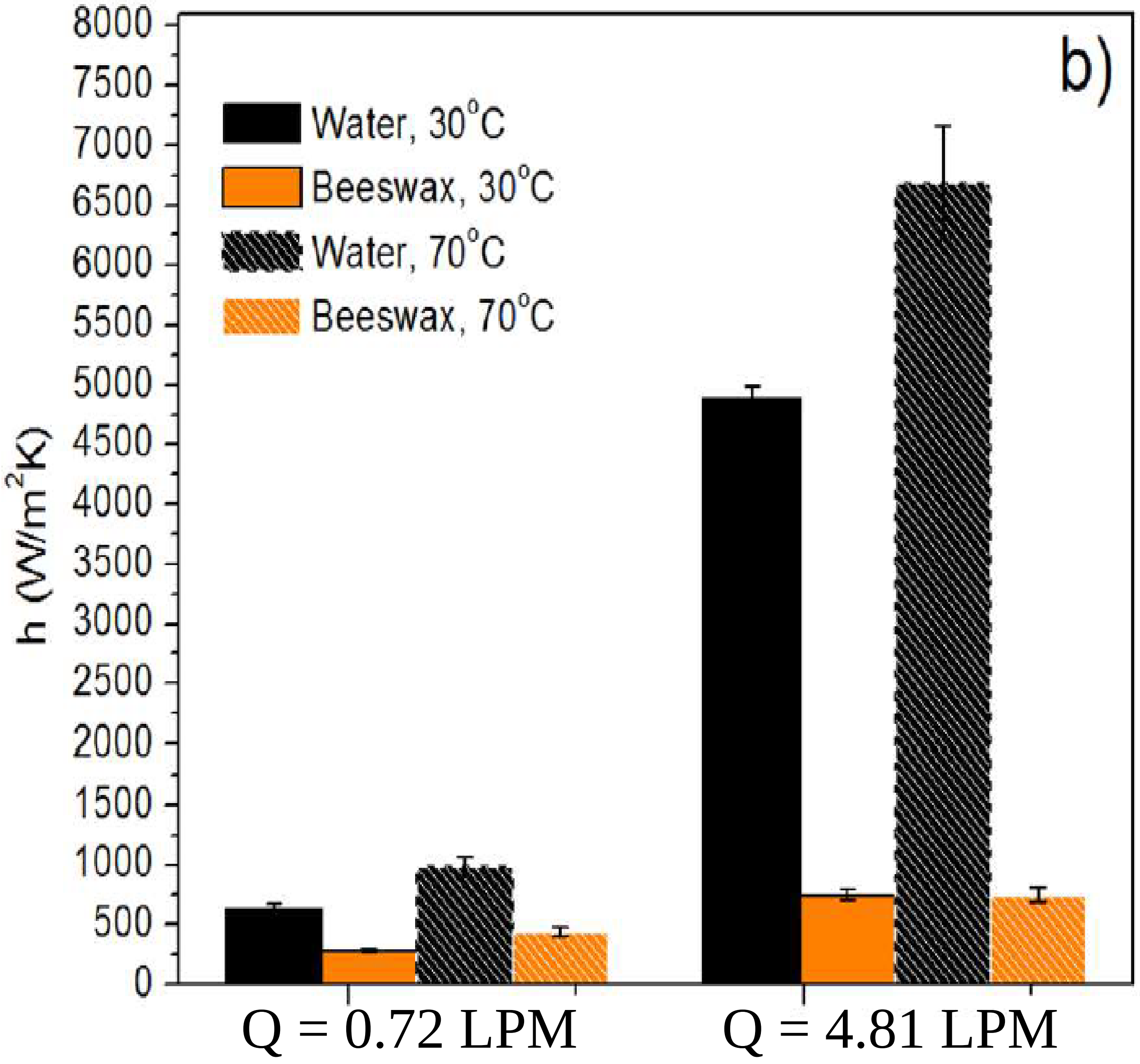
Beeswax Nanoemulsion Flow Loop



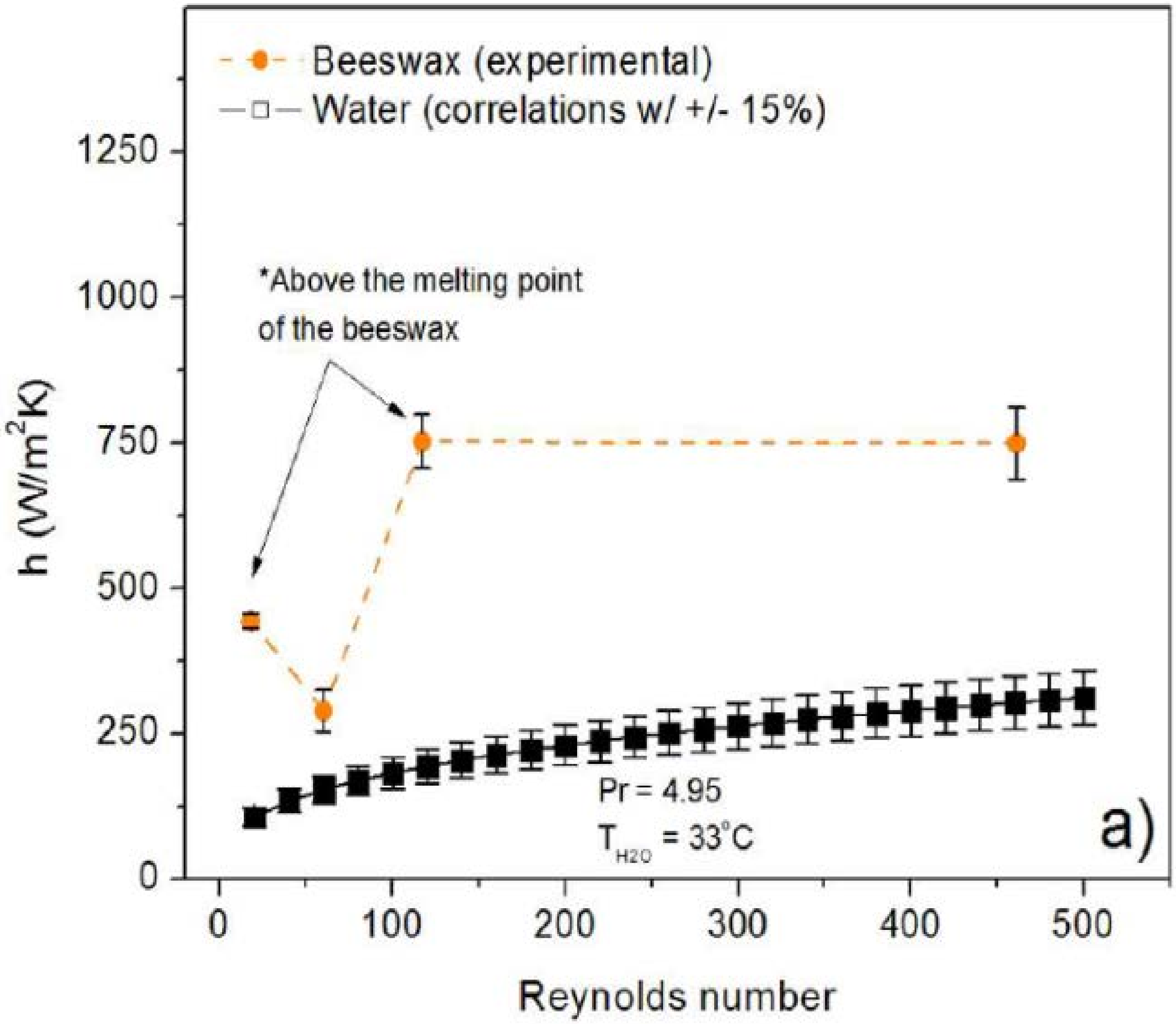
- A 0.97 m long stainless-steel tube with a 11.3 mm inner diameter (12.7 mm outer diameter) was heated by Joule-heating and externally insulated.
- A 2 m long unheated stainless steel tube allowed velocity profile development.
- Wall heat flux, tube wall and bulk fluid temperatures allow determination of heat transfer coefficient.



- At the same volumetric flow rate, water has a substantially higher heat transfer coefficient than beeswax due to substantially lower viscosity and higher Reynolds number.
- The Reynolds number ranged from approximately 1,700 - 22,000 for water and approximately 15 - 460 for the beeswax nanoemulsion.



- At the same Reynolds number, beeswax nanoemulsion has a higher heat transfer coefficient than water.
- The average heat transfer coefficient of the PCM nanoemulsion was 3.1 times higher than that of water.
- For the nanoemulsion, viscosity greatly increases after the phase change, leading to a lower Reynolds number and a higher Prandtl number, ranging from 40 - 200.



Instability in Forced Convection Heat Transfer

- Anderson et al. (2013) observed unusual instabilities (large amplitude oscillations in the flow rate and heated tube surface temperatures) at the phase change temperature.
- When the tube is heated, a radial temperature gradient would exist causing non-uniform melting of the PCM particles.

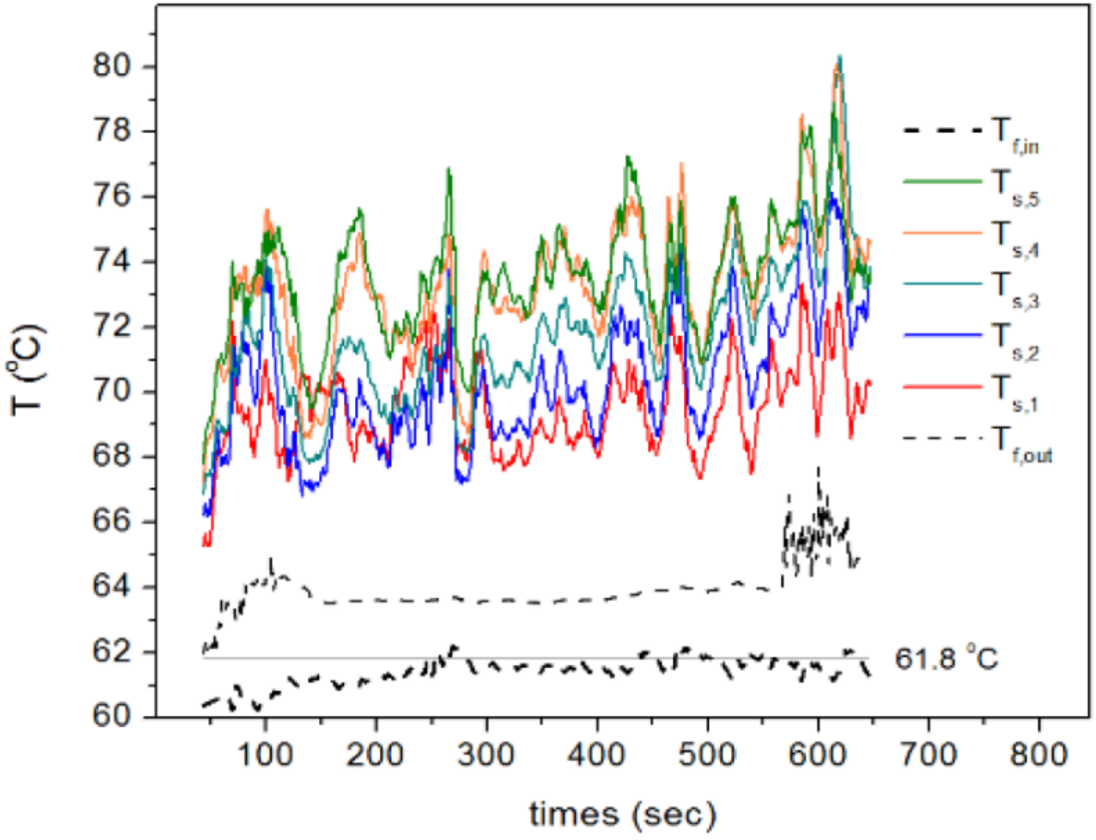
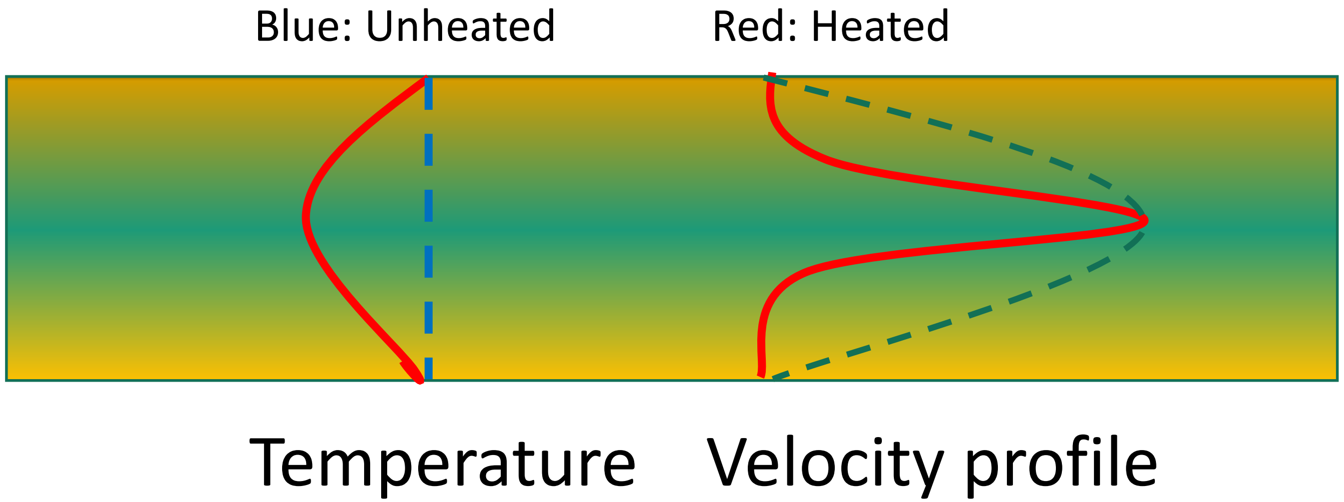


Fig. 15. Heated tube surface and PCE inlet and outlet temperatures [E10].

Radial variations of temperature and viscosity

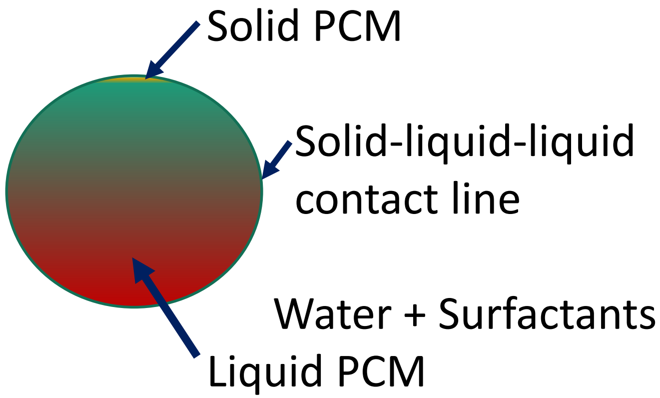
- High viscosity near the heated tube wall and low viscosity in the core.



Viscosity

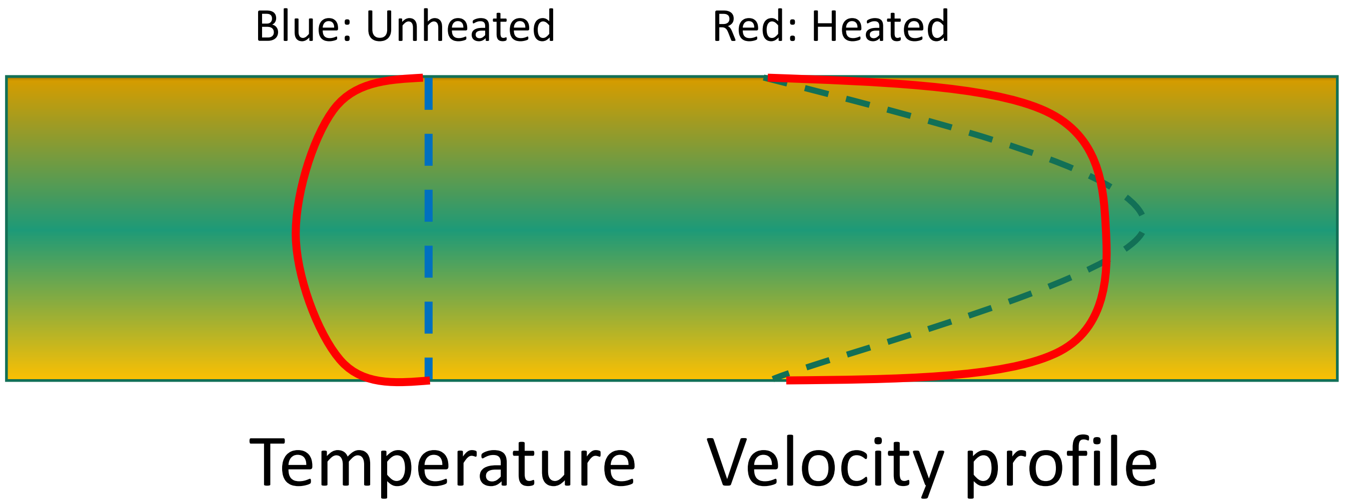
- 70 cP above 62 °C
- 23 cP below 60 °C
- 70 cP above 62 °C

- Also, partial melting of the solid particle surface would lead to a three-phase contact line on the particle surface, affecting the particle-to-particle interactions and particle behavior.



Radial variations of temperature and viscosity

- Low viscosity near the heated tube wall and higher viscosity in the core.



Viscosity

- Low above 62 °C
- Higher below 60 °C
- Low above 62 °C

Advanced Diagnostics and Simulation Methods

- Advanced diagnostics methods will be used to investigate the compositions, structures, and melting processes of the phase-change nanoemulsions at both molecular, mesoscale and macroscales.
  - **An X-ray imaging system** for the agglomeration and formation of droplet or particle clusters as well as solid fraction distributions in heated flow channels.
  - **Multidimensional NMR measurements** to characterize the chemical compositions and molecular structures of the nanoemulsion liquid phases and the surfactants.
  - **Variable-temperature NMR measurements** to study the three-phase contact line among the solid and melted PCM and the aqueous phase.
  - **Variable-temperature Rheo-NMR** to study how shear flow affects molecular-level properties and bulk rheology.
  - **Variable-temperature pulsed-field-gradient (PFG)/magnetic resonance imaging (MRI) velocimetry** experiments under shear flow to reveal how the melting process affects the local velocity profile and causes thermal and hydrodynamic instabilities.

Modeling of a PCM nanoemulsion

1. LBM prediction of PCM nanoemulsion's viscosity variation with temperature from below to above the melting point.

- Temperature dependency of the beeswax nanoemulsion viscosity was measured by Dyanlene Laboratory Services. Note the large jump in viscosity from approximately 20 cP to over 70 cP after the phase change.

Phase change at 62 ^{o}C

T (^{o}C)	Viscosity (cP)
40	20
60	23
70	73

- To study the destabilization processes computationally, we could consider the liquid droplet phase of a PCM and solve a lattice Boltzmann equation along with equations for the bulk and interfacial surfactant concentrations.

- A non-linear equation of state could be used to relate the surface tension to the interfacial surfactant concentration.

Various Viscosity Correlations for non-PCM emulsions

- Einstein's Equation for Viscosity: $\eta = \eta_w(1 + 2.5\phi)$, where ϕ is the volume fraction of PCM. (good for small values of ϕ)
- Taylor's formula: $\eta = \eta_w\left(1 + \frac{5k+2}{2(k+1)\varphi}\right)$ where $k = \eta_{pcm}/\eta_w$
- Doughery-Krieger formula $\eta = \eta_s\left(1 - \frac{\phi}{\phi_m}\right)^{-2.5\phi_m}$ Reliable forϕ up to 0.6
- Yaron, Gal-Or formula:

$$\eta = \eta_w\left(1 + \frac{5.5\varphi\left[4\varphi^7 + 10 - \frac{84}{11}\varphi^2 + \frac{4}{k}(1-\varphi^7)\right]}{10(1-\varphi^{10}) - 25\varphi^3(1-\varphi^4) + \frac{10}{k}(1-\varphi^3)(1-\varphi^7)}\right)$$

- Non-spherical particles

$$\eta = \eta_s\left(1 + \left(\frac{(a/b)^2}{5(\ln(2a/b) - 0.5)} + \frac{(a/b)^2}{15(\ln(2a/b) - 1.5)} + \frac{14}{15}\right)\phi\right),$$

for prolate ellipsoids

$$\eta = \eta_s\left(1 + \left(\frac{(16/15)(a/b)}{\arctan(a/b)}\right)\phi\right),$$

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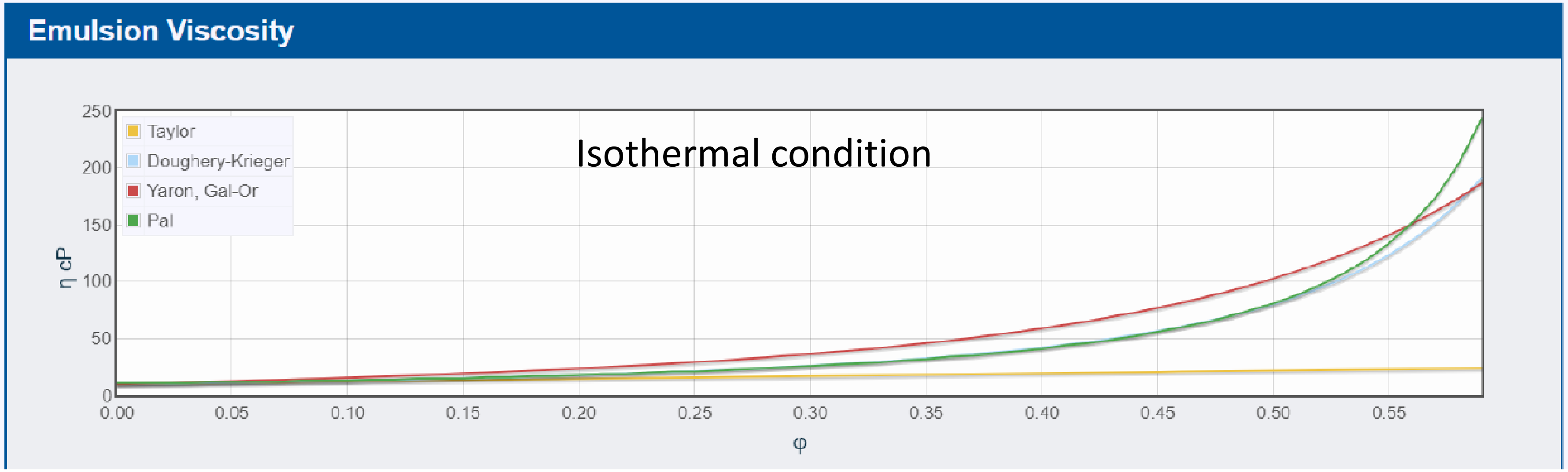
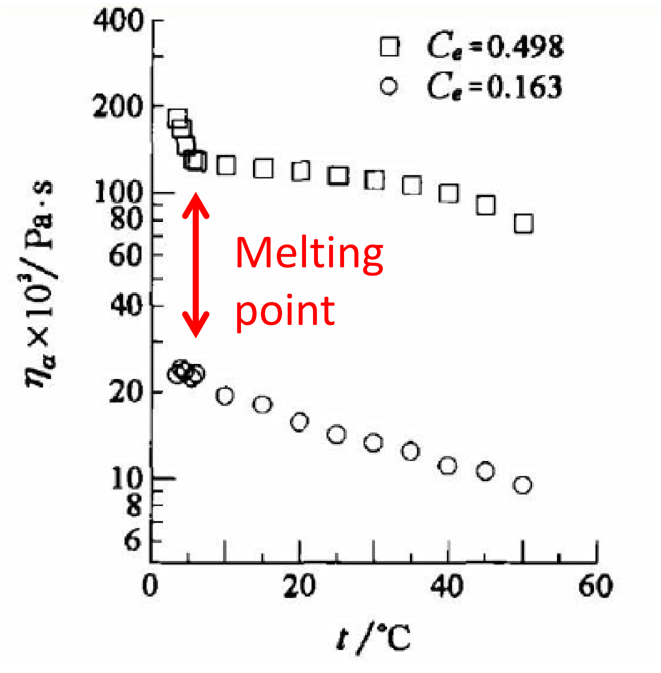


Isothermal condition

Phase change of PCM particles – Effect on emulsion viscosity



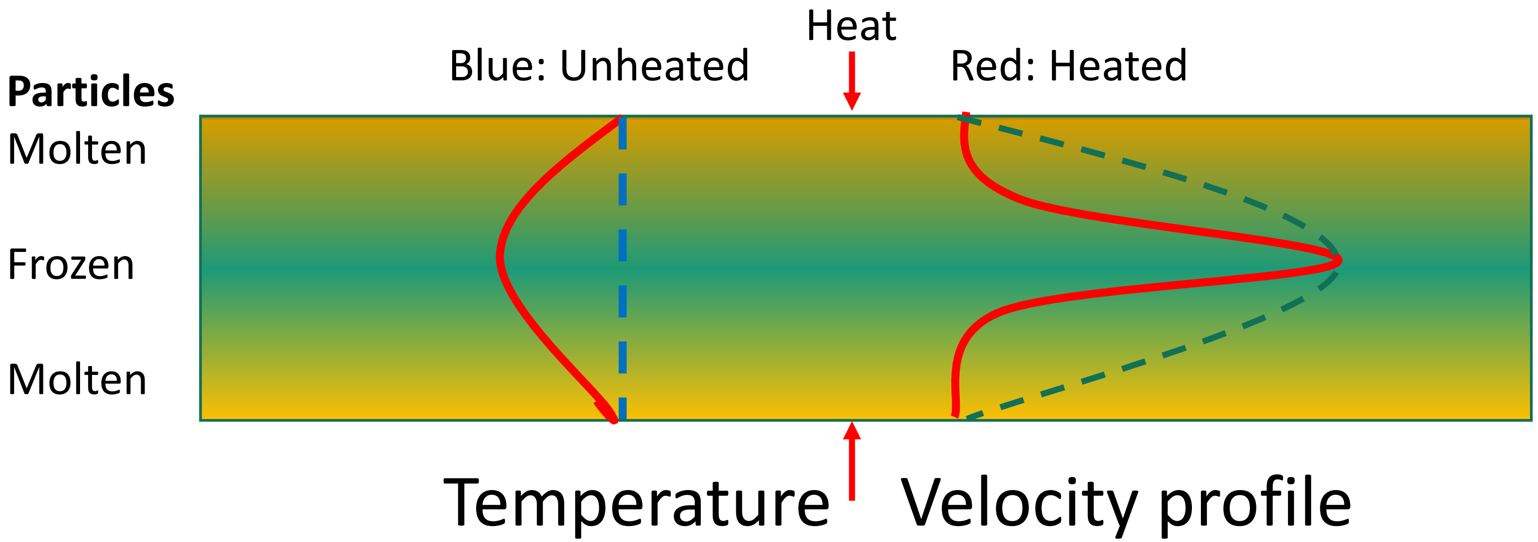
Melting point

Figure 19: Viscosity against temperature phase change emulsions [9]

Prediction of viscosity variation with temperature and phase change

Radial variations of temperature and viscosity

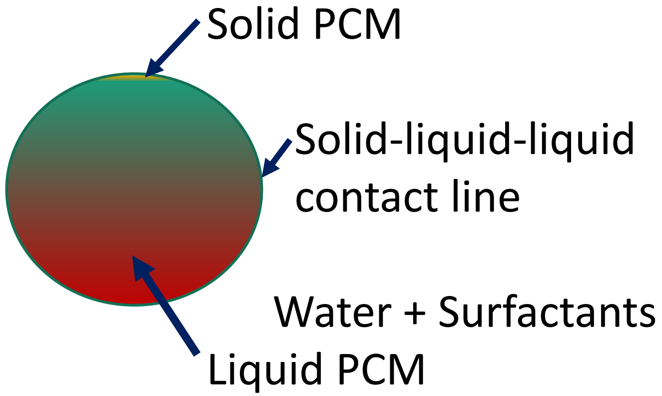
- High viscosity near the heated tube wall and low viscosity in the core.



Viscosity

- 73 cP above 62 °C
- 23 cP at 60 °C
- 73 cP above 62 °C

- Also, partial melting of the solid particle surface would lead to a three-phase contact line on the particle surface, affecting the particle-to-particle interactions and particle behavior.



MD Simulation of PCM nanoemulsion

Surfactant behavior at the interface of a PCM particle upon phase change in a carrier fluid, e.g., water.