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Is the Maxwell-Garnett Continuum Model Valid to Predict the Thermal Conductivity of Particle-Stabilized (Pickering) Emulsions?

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Abstract. An experimental heat transfer measurement apparatus is constructed to measure the thermal conductivity in two-phase systems using an internal standard. This apparatus is validated and used to obtain the thermal conductivity of glass bead-stabilized oil-in-water (o/w) emulsions. The experimentally obtained values are found to be in good agreement with the predictions from the Maxwell-Garnett continuum model, thus confirming that no preferential heat transfer route is formed through the glass beads in the emulsions.

Keywords: Emulsions, thermal conductivity, experimental validation, Maxwell-Garnett

1. Introduction

Pickering emulsions are emulsions stabilized by solid particles that have adsorbed at the interface between the two liquid phases (such as oil and water)[1]. Figure 1 shows a graphical representation of a solid-stabilized "Pickering" emulsion. Over the past few years, they have become the focus of several research groups, namely in biomedicine[2], food science[3], cosmetics[4] and the oil industry (tar sands treatment involve Pickering emulsions)[5, 6]. Thus far, the study and use of such emulsions has been limited to laboratory-scale experiments. If they are ever to be used on a larger scale, the physical properties of these emulsions must be characterized in greater detail. For example, given that solid particles are present at the interface between the two liquid phases, does this lead to the formation of a preferential route for heat transfer? While some work, dating as far back as the 1950s, has determined that the Maxwell-Garnett model for the thermal conductivity of two-phase systems is valid for liquid-liquid emulsions, no work has looked closely at the case of Pickering emulsion thermal conductivity[7, 8]. Through this work, we conduct an experimental protocol to determine if the 2-component Maxwell-Garnett continuum model can accurately predict the thermal conductivity of Pickering emulsions.
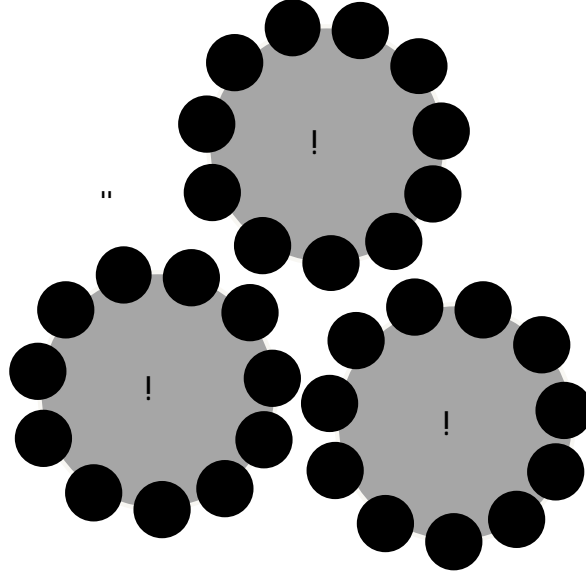
Figure 1: Schematic representation of a oil-in-water (o/w) solid-stabilized (Pickering) emulsion: white = water phase (W); grey = oil phase (O); black = solid particles.

2. Experimental method

2.1 Materials
For both the validation experiments and the tests on solid-stabilized emulsions, the same materials are used: light mineral oil (paraffin, Fisher Scientific) is used for the oil phase, de-ionized water (Milli-Q) is retained for the water phase and 35 m glass beads (Spheriglass-A 3000 modified with coupling agent CP-01, Potters Industries LLC) are used. The composition of coupling agent CP-01 is proprietary to the supplier; it acts by slightly reducing the hydrophilicity of the glass beads, thus facilitating the formation of oil-in-water emulsions.

2.2 Experimental setup
In order to measure the thermal conductivity of liquids and of the solid-stabilized emulsions produced, the experimental apparatus illustrated in Figure 2 was constructed. It consists of a 1-liter beaker fitted with a 400 W disk heater (McMaster-Carr) at the top and sitting on an ice-water bath at the bottom. Using a Thermo Electrics temperature controller, it is possible to impose a temperature gradient from the top (typically 95 ¡C at steady state) to the bottom (0 ¡C) without any convective effects. Thus, it is possible to obtain almost perfect 1-D heat conduction conditions. Eight Type J thermocouples are used to monitor the temperature profile in the beaker; they are positioned at 0.0, 2.0, 2.9, 5.4, 6.5, 7.0, 8.7, 9.9 and 11.7 cm from the disk heater. Each experiment is conducted until the temperature variation at each thermocouple varies by no more than the known uncertainty of Type J thermocouples, 0.5 ¡C. Typical experiments last 3 hours. A minimum of three experiments is conducted at each condition to verify repeatability.
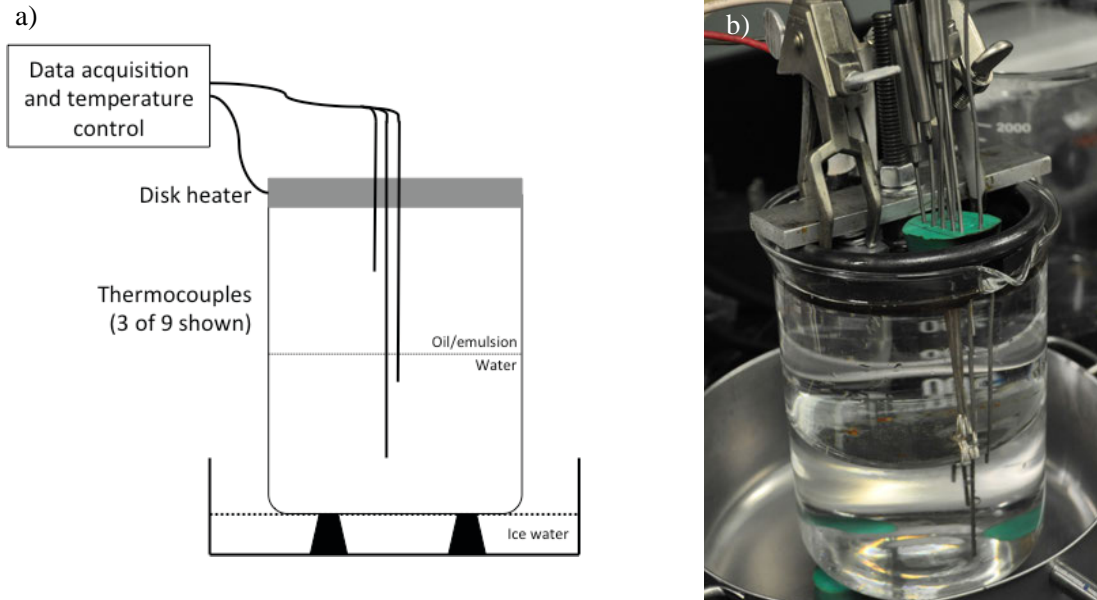
Figure 2: a) Schematic of the experimental setup constructed to measure the thermal conductivity of liquids, b) Picture of the experimental setup.

2.3 Preparation of solid-stabilized emulsions

The emulsions are prepared by combining 500 mL of mineral oil with 500 mL of water and varying quantities of 35 μm glass beads (40, 60, 80, 100 and 120 g). The mixture is agitated for 5 minutes using a hand-held blender until a stable emulsion is formed. The emulsion is allowed to cream. The volume of water below the creamed emulsion is recorded and is used for internal standard purposes, as described further (volume uncertainty is ±25 mL). For all emulsions, the aqueous phase remains turbid, even after several weeks of storage. Upon evaporation of the aqueous phase, no visible residue remains. Therefore the conductivity of the aqueous phased is deemed equal to that of pure water. The cause of the turbidity is the focus of on-going research.

2.4 Methodology

Using the apparatus described in 2.2, the thermal conductivity of a given unknown phase can be determined by comparing its temperature profile to the temperature profile of another phase with a known thermal conductivity. For example, oil and water can be combined in the beaker to form two distinct phases (the oil will float on top of the water). Assuming that there are little to no heat losses, the heat flux (q) through the oil phase will be equal to the heat flux in the water phase at steady state:

$$q''_{oil} = q''_{water} \tag{1}$$

Assuming conduction is the only mechanism for heat transfer (given the 1-D geometry), using Fourier's law of heat conduction, the expression becomes:

$$-k_{oil} \frac{dT}{dx}_{oil} = -k_{water} \frac{dT}{dx}_{water} \tag{2}$$

Where k is the thermal conductivity of a given phase and dT/dx is the temperature gradient in that phase. It is thus possible to obtain the thermal conductivity of the oil phase given the temperature profile of the two-phase system and the thermal conductivity of water (in other words, water acts as an internal standard).

3

$$-_{"\#\$} \ \& \ \frac{1_{23456}\frac{78}{79}_{23456}}{\frac{78}{79}_{:\ ;<}} \tag{3}$$

The temperature gradients can be obtained from the experimentally obtained temperature profile by performing a linear regression on the data points in each phase.

3. Results and discussion

3.1 Validation experiments

In order to validate the experimental methodology, a first set of experiments is conducted with only mineral oil and water (500 mL of each). A picture of the oil and water two-phase system is shown in Figure 3a and the temperature profile obtained after reaching steady state is shown in Figure 4 (average of 5 experiments shown). The error bars shown in Figure 4 correspond to the larger of two values: the standard deviation for the measurement or the thermocouple measurement uncertainty (+/- 0.5 ¡C). The first four data points (0.0, 2.0, 2.9 and 5.4 cm) correspond to the oil phase, while the latter five (6.5, 7.0, 8.7, 9.9 and 11.7 cm) correspond to the water phase. Following linear regression on the average measurements, the gradient in the oil phase is found to be -1257 ¡C/m and -247 ¡C/m in the water phase. Knowing that the thermal conductivity of water is 0.58 W/m K[9] and using equation 3, the experimentally-determined thermal conductivity of the mineral oil is found to be 0.114 W/m K. By using the maximum and minimum slopes through the data points (taking into account the error bars), this value can range from 0.097 to 0.140 W/m K. The tabulated thermal conductivity of mineral oil is 0.130 W/m K[10], the experimental method is thus fairly accurate (error ranging from -26% to +7%) and our approach is deemed valid.

In order to further confirm the validity of the method, the thermal conductivity calculations are also conducted in reverse on the oil-water system: the same gradients are used to find the thermal conductivity of water measured by the experimental setup using the tabulated thermal conductivity of mineral oil. Using this reversed method, the thermal conductivity of water based on a linear regression of the average measurements is found to be 0.661 W/m K. By using the maximum and minimum slopes through the data points (taking into account the error bars), this value can range from 0.540 to 0.779 W/m K (error ranging from -7% to +34%). Using an average of the maximum errors, we deem our approach to be accurate within 30%.

3.2 Thermal conductivity of solid-stabilized emulsions

The emulsions prepared as per section 2.3 and pictured in Figure 3b-f are characterized using the same experimental apparatus. The temperature profile obtained for the emulsion prepared with 60 g of glass beads (Figure 3c) is given in Figure 5 (average of 3 experiments shown, error bars determined the same way as Figure 4). For that emulsion, 400 mL of water remained at the bottom of the beaker. As such, the first 5 data points correspond to the emulsion, while the last 4 are the internal standard (water). Following linear regression, the gradient in the emulsion is found to be -831 ¡C/m and -297 ¡C/m in the water phase. Using equation 3, the thermal conductivity of that emulsion is found to be 0.207 W/m K. By using the maximum and minimum slopes through the data points (taking into account the error bars), this value can range from 0.195 to 0.239 W/m K. The results for the other emulsions are summarized in table 1.
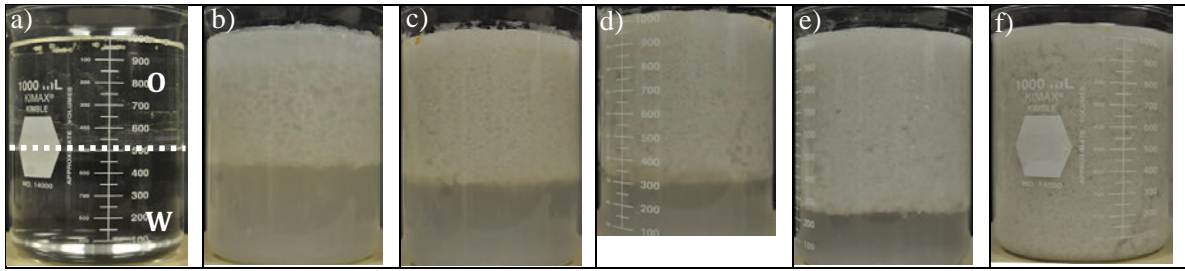
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Figure 3: Picture of the layered oil O (top) and water W (bottom) system used for the validation experiments (a). The dotted line indicates the position of the interface. Pictures of the oil-in-water (o/w) solid-stabilized emulsions formed for different quantities of glass beads: b) 40 g, c) 60 g, d) 80 g, e) 100 g, f) 120 g. Creaming of the emulsion is observed from 40 g to 100 g with residual water underneath. Note: all emulsions were formed in the same 1000-mL beaker.
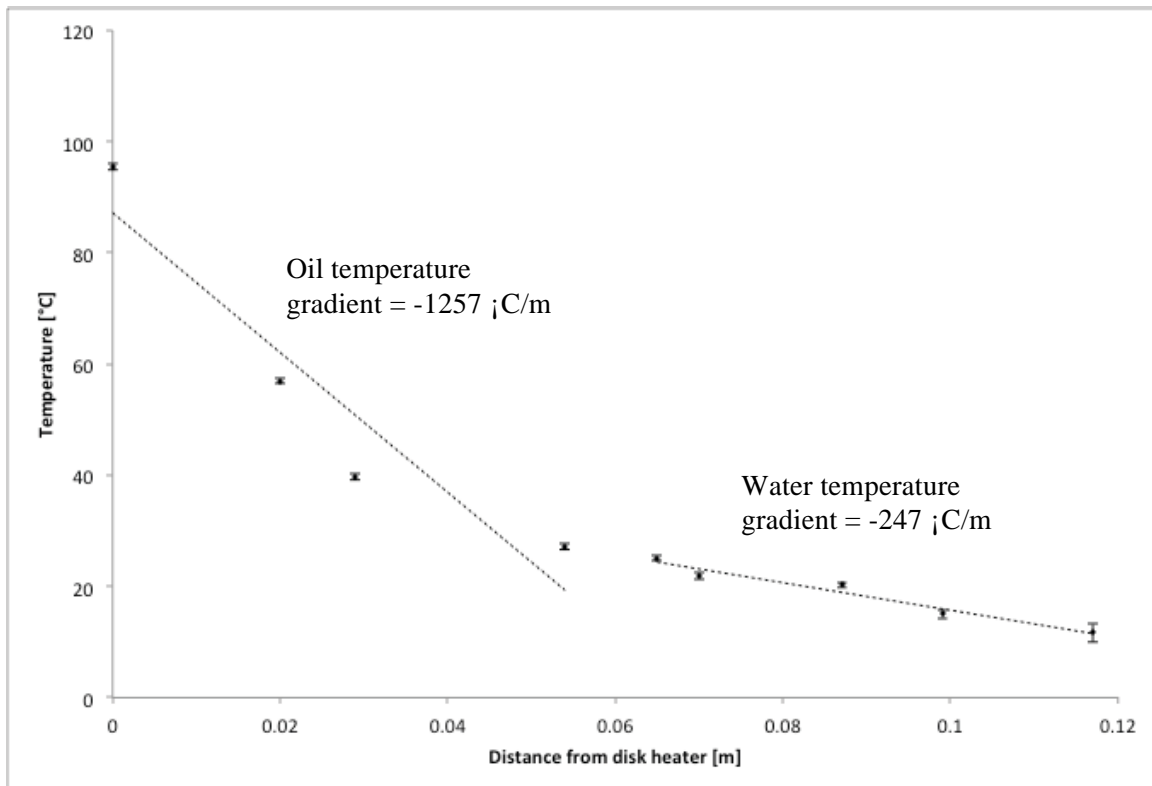

Figure 4: Graph showing temperature as a function of distance from the disk heater in the thermal conductivity apparatus for a layered combination of oil and water. Error bars shown are the larger of two values: the thermocouple uncertainty (0.5 ¡C) or the standard deviation of the measurements.
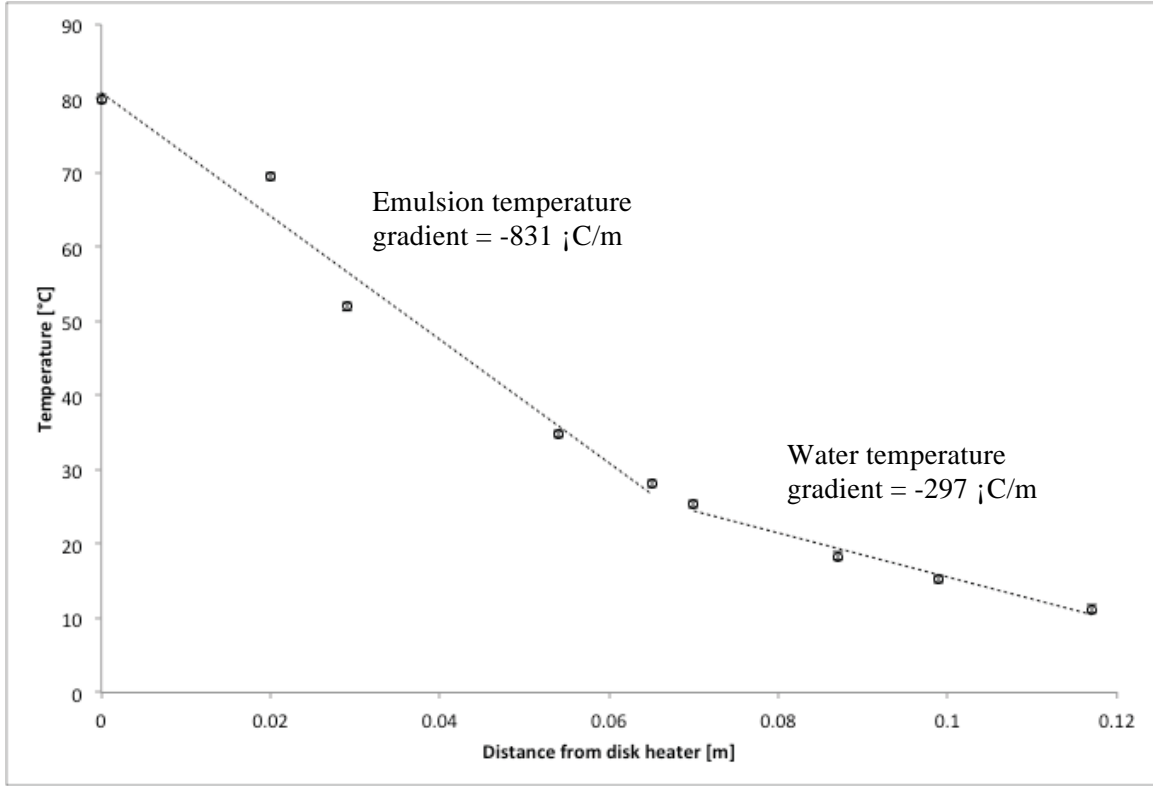
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Figure 5: Graph showing temperature as a function of distance from the disk heater in the thermal conductivity apparatus for the Pickering emulsion containing 60 g of glass beads (emulsion pictured in Figure 3c). Error bars shown are the larger of two values: the thermocouple uncertainty (0.5 ¡C) or the standard deviation of the measurements.

Table 1: Thermal conductivity calculated for solid-stabilized emulsions with various glass bead contents.

Glass bead content	Water phase	Gradient in emulsion			Gradient in water			Thermal conductivity		
		[¡C/m]			[¡C/m]			[W/m K]		
[g]	[mL]	Min.	Avg.	Max.	Min.	Avg.	Max.	Min.	Avg.	Max.
40	450	-932	-982	-1004	-289	-313	-328	0.167	0.185	0.204
60	400	-783	-831	-832	-279	-297	-322	0.195	0.207	0.239
80	300	-802	-848	-849	-232	-265	-299	0.159	0.181	0.216
100	250	-786	-808	-814	-205	-271	-341	0.146	0.194	0.252
120	0	-594	-599	-773	-	-	-	0.161	0.262[a]	0.292

[a]Given that no creaming is observed for the 120 g emulsion (no remaining water phase at the bottom), the water temperature gradient used for the calculations of the thermal conductivities is the temperature gradient from the 100 g emulsion.

3.3 Comparison to the Maxwell-Garnett model

In order to validate the hypothesis, it is necessary to compare the calculated thermal conductivities to the values predicted using the 2-component Maxwell-Garnett effective medium model[11]:

$$- \& - = \left[\frac{1_>? @1_A B @C_> DI_A B 1_> E}{1_>? @1_A ? C_> DI_A B 1_> E} \right] \tag{4}$$

6

where k_1 is the thermal conductivity of the continuous phase (water – 0.58 W/m K), k_2 is the conductivity of the dispersed phase (oil – 0.13 W/m K), k is the effective thermal conductivity and V_2 is the volume fraction of the dispersed fluid. For the emulsions formed in these experiments, the water is the continuous phase (in other words, the droplets are made of oil). The volume fraction V_2 is calculated by dividing the oil found in the emulsion by the total volume of the emulsion. The contribution of the third component in the emulsion, the glass particles, to the emulsion thermal conductivity is not considered, given that their overall volume fraction is relatively low (less than 5%). The predictions for the various emulsion prepared are tabulated in table 2.

Table 2: Predicted thermal conductivity values for the solid-stabilized emulsions formed

Glass bead content	Total emulsion volume	Uncertainty on emulsion volume	Volume fraction of oil in emulsion	Predicted thermal conductivity [W/m K]		
[g]	[mL]	[mL]	[-]	Min.	Avg.	Max.
40	550	+/- 25	0.91 $\pm$ 0.04	0.146	0.161	0.175
60	600	+/- 25	0.83 $\pm$ 0.04	0.175	0.188	0.200
80	700	+/- 25	0.71 $\pm$ 0.03	0.223	0.233	0.243
100	750	+/- 25	0.66 $\pm$ 0.02	0.243	0.252	0.260
120	1000	- 25	0.50 - 0.01	0.316	0.322	0.322

A visual comparison of the predicted versus experimentally obtained thermal conductivities is given in Figure 6. The error bars on the Maxwell-Garnett predictions represent the minimum and maximum predicted thermal conductivities, resulting from the uncertainty in the emulsion volume measurement. The error bars on the experimental data represent the larger of two values: the minimum and maximum thermal conductivities calculated (see Table 1) or the 30% accuracy of the measurement. In all cases, there is agreement between the data and the predictions (error bars overlap).

4. Conclusions

By using a one-dimension heat transfer measurement rig, we have measured the thermal conductivity of various mineral oil-glass beads-water solid-stabilized Pickering emulsions. We have demonstrated that the Maxwell-Garnett model is valid, within an acceptable margin, to predict the resulting thermal conductivity. As such, we can conclude that, under the conditions verified experimentally, no preferential route for heat transfer is formed in such emulsions (i.e. the glass beads do not promote heat transfer in any significant manner).
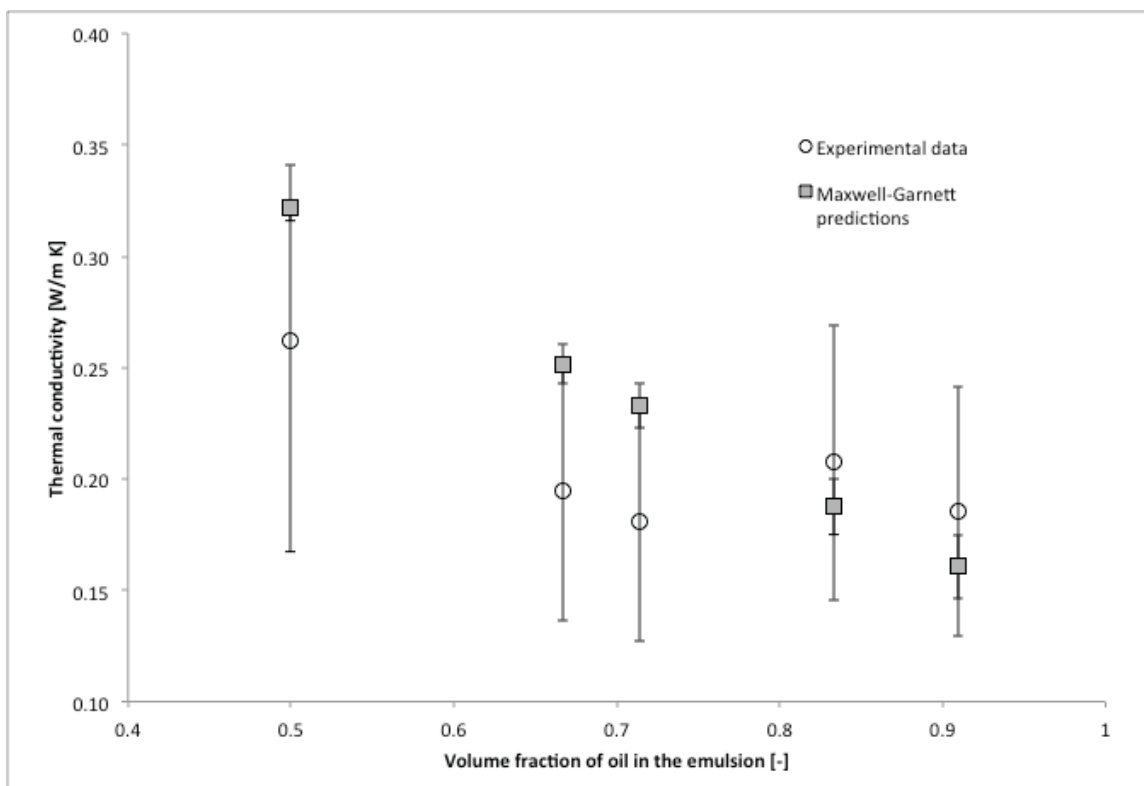
Acknowledgements

Figure 6: Comparison of the experimentally measured thermal conductivity of Pickering emulsions and the corresponding expected value calculated from the Maxwell-Garnett continuum model as a function of the volume fraction of mineral oil in the emulsion.

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Figure captions

Figure 1: Schematic representation of a oil-in-water (o/w) solid-stabilized (Pickering) emulsion: white = water phase (W); grey = oil phase (O); black = solid particles.

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