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Prediction of emulsion particle sizes using a computational fluid dynamics approach

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Abstract

For many food products emulsification processes play an important role. Examples are ice cream, spreads, sauces, etc. As is well known, droplet break-up and coalescence phenomena are the local processes underlying the control of particle size in an emulsion process. Quite a number of studies have generated scaling laws which can be easily applied and which are useful in the design of a process. However, the prediction of particle sizes in an inhomogeneous flow, where the flow velocity is changing spatially in strength and direction and with time, is not yet well established. For one-phase flows computational fluid dynamics (CFD) methodologies are in use to predict details on the flow with quite some success. This methodology has been extended to capture the dispersed phase in an efficient way. The essence is that break-up and coalescence processes determine source terms in a transport equation for the moments of the particle size distribution, while velocity vectors as obtained in the one-phase CFD simulation determine the convective term. This method allows particle size prediction in any equipment. The approach is illustrated for the particle size evolution of an oil-in-water emulsion, for a phase-separated biopolymeric mixture (a so-called water-in-water emulsion) and for the escape of the included oil droplets from a double emulsion of the type oil-in-water-in-oil. In all cases experimental results are compared with simulation results, which match very well. This shows the strength of the method.

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1. Introduction

The prediction of the particle size in an emulsion is a difficult task. On the one hand, reliable models

are required for the prediction of the local phenomena such as droplet break-up and coalescence, and on the other hand, the flow has to be characterized as well. Under ideal conditions, the flow can be described in a simple way if simple geometries are used such as a Couette flow. In those cases, a population balance approach [1] can be used to fully analyze the evolution of the particle size with time. This approach results

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even in a particle size distribution. However, if the flow is inhomogeneous, viz. the local velocity vector is changing with time and direction for instance because of the impeller in the vessel in which emulsification takes place, a population balance approach can be used in principle, but it is not very practical. This problem is not specific for emulsions but is encountered in all multiphase flow processes.

For quite some time scientists investigate several approaches to come up with a reliable and computationally fast method. The ideal case is where the local phenomena are calculated at the same time as the local flow. This means that the particle sizes are affected by the flow and that on the other hand the local flow characteristics are affected by the presence of the particles. This goal has not been achieved yet, but will emerge soon. The approach which is taken here is where the flow in the vessel is calculated first in quite some detail by using computational fluid dynamics (CFD) which is followed by the analyses of evolution of the particle size while using the local flow properties as calculated in the first step. The last step allows taking into account break-up and coalescence and also emulsifier properties.

Below, we will explain the method in some detail. Subsequently, we will give three examples where we compare calculations with experimental results.

2. The population balance method

In this method, the particle size distribution is split up in classes, typically about 10–20. The population in each class is monitored in time, as the number will change by break-up and coalescence processes. The governing equation is [2]:

$$\frac{dn_i}{dt} = \sum_{j=1}^M N_{ji}^f K_j^{\text{br}} n_j - K_i^{\text{br}} n_i + \sum_{j=1}^M K_{jj-1}^c n_j n_{j-1} - \sum_{j=1}^M K_{ij}^c n_i n_j \quad (1)$$

The number of droplets in class i changes by break-up of large droplets into droplets of size i

and by the break-up of those in class i . Their number increases also by the coalescence of two smaller droplets such that one droplet of size i results; the number reduces by the coalescence of a droplet of size i with another droplet. If the rate constants K_i are known the equation can be solved with time for all the classes. This method is very powerful especially in well-defined homogeneous flows. However if the flow is inhomogeneous, as resulting from a CFD calculation for a complicated geometry, the population balance method seems to be too involved.

3. The S_γ method

A feasible alternative is offered under the assumption that the droplet size distribution has a certain predefined shape and that this shape is qualitatively retained during the process that is to be modeled. Under these conditions, the complete droplet size distribution can be represented by a limited number of parameters. Those are based on the so-called local intensity of dispersion, S_γ , which is conserved on a volumetric basis, and related to the moment M_γ of the distribution [3]:

$$S_\gamma = nM_\gamma = n \int_0^\infty d^\gamma P(d) dd \quad (2)$$

where n is the total number of the droplets and $P(d)$ the distribution. If $\gamma = 0$ then $S_0 = n$ (the number of droplets); if $\gamma = 3$, $S_3 = 6\varphi/\pi$, where φ is the volume fraction of dispersed phase. It can be shown that S_γ is related to the various mean diameters as:

$$d_{pq} = \left(\frac{S_p}{S_q} \right)^{1/(p-q)} \quad (3)$$

In this paper it will be assumed that the distribution is log-normal which is characterized by two parameters, a mean d_m and a width of the distribution σ . The choice for this distribution is made as it is often found in practice. For this case S_γ is:

$$S_\gamma = nd_m^\gamma \exp\left(\frac{1}{2}\gamma^2 \sigma^2\right) \quad (4)$$

For this distribution Eqs. (3) and (4) result in:

$$d_{pq} = d_m \exp(\frac{1}{2}\sigma^2(p + q)) \quad (5)$$

In principle, S_1 , S_2 and S_3 are sufficient to calculate d_m and σ .

The usefulness of the moments or the S_γ values in CFD calculations originates mainly from the fact that they satisfy the transport equation [4]:

$$\frac{\partial S_\gamma}{\partial t} + \vec{u} \cdot \nabla S_\gamma = s_\gamma \quad (6)$$

where s_γ denotes a source term that contains the kinetics of the processes that change the droplet size distribution such as break-up and coalescence. The local velocity vectors u result from the one-phase CFD calculation and is in fact the coupling between S_γ and the flow.

4. Source terms

The first contribution is the break-up of droplets. If droplets or the shear rates are large enough so that the capillary number is larger than a given criterion (the critical capillary number), the droplets will break. For binary break-up we apply the so-called Grace criteria [5] which depend on the viscosity ratio of the fluids involved. If the flow surpasses at least twice the critical capillary number the droplets break according to the capillary break-up mechanism. The source term can be written as (if $d > d_{cr}$) [9]:

$$s_{br} = \int_0^\infty \frac{d^\gamma}{\tau_{br}} (N_f^{(3-\gamma)/3}(d) - 1)nP(d) dd \quad (7)$$

where N_f is the number of fragments formed resulting from the break-up event and τ_{br} the break-up time-scale. Those parameters have to be modeled what will not be done explicitly here. If again a log-normal distribution is assumed for $P(d)$ a closed expression can be derived for s_{br} .

The coalescence source term s_c has to be modeled as well. In our calculations it is assumed that this process can be written as a product of collision and coalescence probability [6]. Still several choices have to be made with regard to the properties of the interface. If the interface is

covered with surfactant that will immobilize the interface the coalescence process can be described as a drainage between two solid spheres. This situation does not always occur. Depending on the local flow rates the droplets may deform what affects the film drainage rate considerably. Details can be found elsewhere [6]. The source term is given by:

$$s_c = (2^{\gamma/3} - 2) \left(\frac{6\phi}{\pi}\right)^2 k_{coll} u_{rel}(d) P_{coal}(d) d^{\gamma-4} \quad (8)$$

where $k_{coll} u_{rel}$ describes the Smoluchowski collision rate and P_{coal} the coalescence probability which is given by the ratio of the drainage time and the collision time during a coalescence event. Colloidal forces affect especially the drainage time.

The sum of s_{br} and s_c composes the source term in Eq. (6).

5. Simulations

The simulations have been carried out using the finite volume code STAR-CD, ex Computational Dynamics, Ltd. Pre- and post-processing were carried out in PROSTAR. Calculations were performed on a Silicon Graphics O2 workstation, equipped with an R10k processor and 256 MB of RAM, using IRIX 6.3 as a UNIX-based operating systems.

The calculations were done in 3D and took about half-a-day.

6. Break-up in an oil-in-water emulsion

Experiments have been done in a flat cylinder of 101 mm diameter and a volume of 146 ml, containing a pin as a stirrer of diameter of 89 mm and thickness of 6 mm. The water phase (containing a few percent CMC to increase its viscosity) was poured into the vessel first, followed by a known volume of sunflower oil. The turbidity was followed during the break-up of the oil droplets. As a CMC solution is shear thinning,

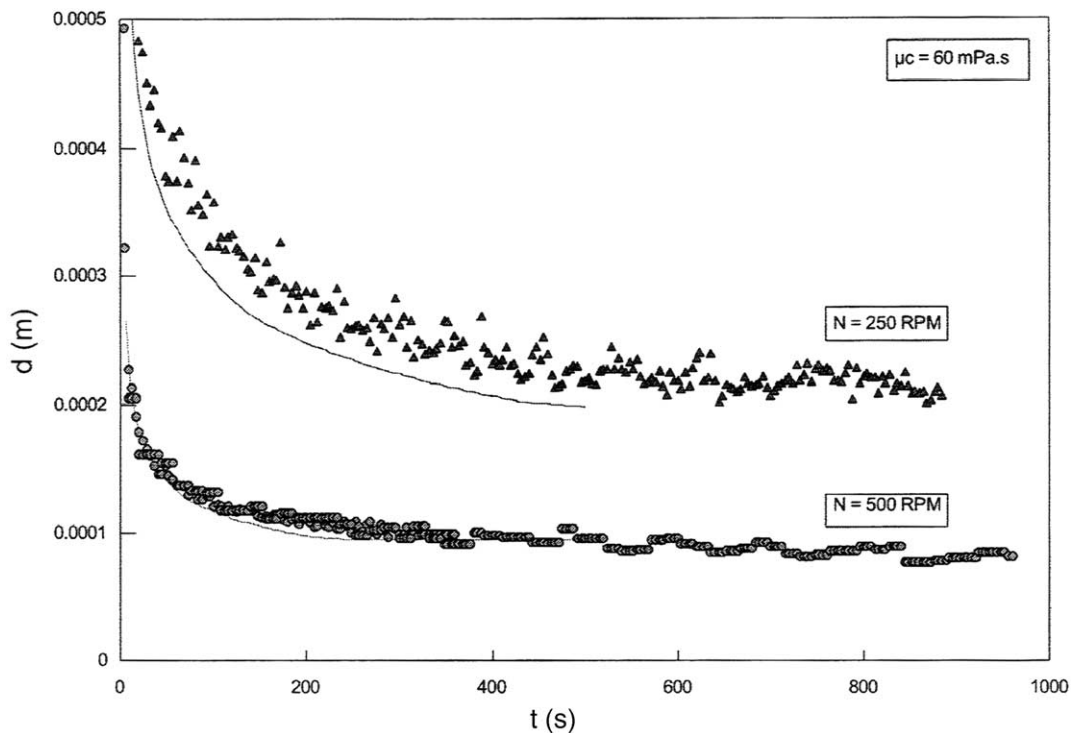


Fig. 1. Comparison between experiment and simulation for an oil-in-water emulsion at a viscosity ratio of 0.87, where the droplet size has been plotted as a function of time.

the local viscosity has to be taken into account in the simulations. In essence, this means that the break-up criteria change locally as the viscosity ratio is varying.

Fig. 1 displays the evolution of the droplet size as a function of time for two rotational speeds of the stirrer. The symbols are the experimental data, while the curves are the predictions by the simulations using the S_γ method. The comparison is very good. The time-scale of the break-up process is about 400 s.

Fig. 2 shows the evolution of a few S_γ values (S_1 – S_4) with time during the simulation at two positions in the vessel where the rate of shear was highest and where it was lowest, respectively. The two top curves represent the evolution with time of d_{32} at the low rate of shear values as evaluated from (S_3/S_2) and $(S_4/S_1)^{1/3}$, respectively, both giving the same d_{32} as the plot shows. The two lower curves are at the position at the highest shear

rate. This plot shows the self-consistency of S_γ modeling.

7. Break-up and coalescence in emulsions at low interfacial tension

The fluid system considered here is a phase-separated biopolymeric system in water: the dispersed phase contains gelatin while dextran is dissolved in the continuous phase. This dispersion behaves as an emulsion, so it shows break-up and coalescence, but the interfacial tension is much lower; in this particular case it was 1.12×10^{-5} N/m. The concentration of gelatin was 0.32 wt.% and of dextran 8.4 wt.%. The mixture was held at 60 °C in order to prevent the gelatin from gelling. The mixture was mixed in a stirred vessel of volume 500 cm³, which was equipped with a helical impeller. The Reynolds number was about 100.

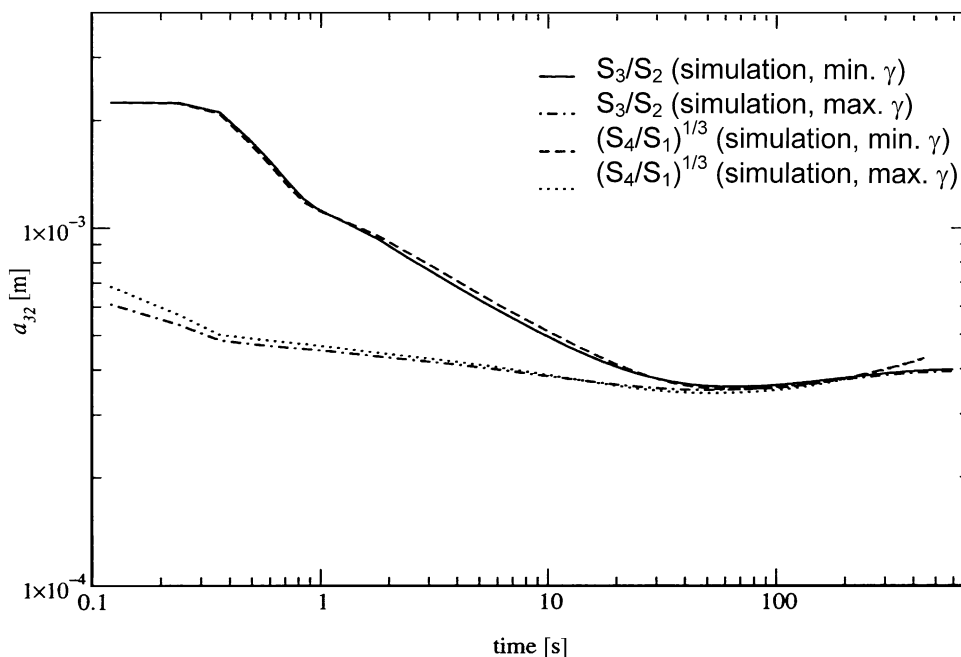


Fig. 2. Evolution of d_{32} in the course of the simulation at positions where the rate of shear is high and low, respectively.

Droplet sizes were measured close to the vessel wall at the University of Birmingham using a high-speed camera [7]. Digitized images from the camera were used to determine the drop size distribution based on approximately 300 droplets. The next graph (Fig. 3) summarizes the main results where the droplet size is given as a function of time for various impeller speeds.

The symbols are the experimental results while the curves are simulation results depicting d_{32} and d_{10} , respectively. Time here corresponds to the simulations. Both experimental results and simulations indicate that the droplet size gets smaller as the impeller speed is increased from 10 to 20, 40 and 60 rpm. The sizes get larger on decreasing the speed indicating that coalescence plays a role in these mixtures. The experimental data on d_{32} and d_{10} differ by 10–20% indicating that the distribution is rather narrow. The comparison in Fig. 3 is quite good indicating that the method developed is quite powerful at least at the low volume fractions considered. Some further discussions can be found in Ref. [7].

8. Stability of a double emulsion in a flow

Often in a phase inversion process double emulsions are formed before inversion takes place. Those emulsions contain droplets of the continuous phase dispersed in the dispersed phase; for instance an oil-in-water-in-oil emulsion. The kinetics of the inversion process is to quite some extent determined by the stability of the double emulsion. If the double emulsion is highly unstable inversion can only be brought about by an increase of the volume fraction of the dispersed phase so that coalescence becomes faster. A stable double emulsion increases the effective volume fraction of the dispersed phase and increases the rate of coalescence in this way promoting inversion.

The instability of a double emulsion is governed by the external flow, which generates a flow in the emulsion droplet by which an inclusion is pushed against the interface of the emulsion droplet. This results in a fluid film that starts to drain as in a traditional coalescence process. If the drainage is fast enough the inclusion will coalesce with the

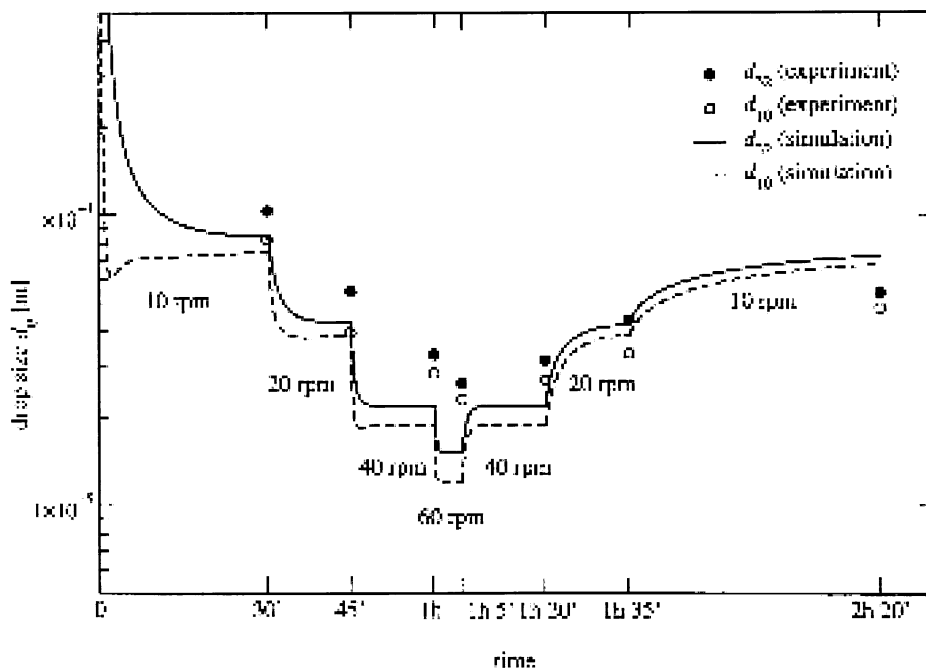


Fig. 3. Water –in water emulsion: comparison of experimental results and simulations on variations of the impeller speed in a stirred vessel.

continuous phase. This process is called ‘escape’. As the streamlines in the emulsion droplet are closed, there will be hardly any mixing in the droplet. The consequence is that only the droplets close to the outer interface of the emulsion droplet will escape and that the volume from which escape will take place is related to the inclusion diameter.

It can be argued that the escape process is given by the following equation:

$$\frac{d\varphi_i}{dt} = \frac{-2P}{t_c \alpha_{cr}} (\varphi_i - (1 - \alpha_{cr})\varphi_{i0}) \quad (9)$$

where φ_i is the volume fraction on the inclusions, P the probability of coalescence, t_c the circulation time of an inclusion in the emulsion droplet, α_{cr} the fraction of the volume of the droplet from which escape occurs and φ_{i0} the volume fraction of inclusions at $t = 0$. The parameters P , t_c and α_{cr} have to be modeled. A full account has been given in Ref. [8] and will not be repeated here.

This process can also be described by the S_y formalism, where we have to analyze for two S_y values: one for the volume fraction of the inclu-

sions that change with time, which is given by the previous equation and one for the number of droplets, S_0 , which changes because of break-up.

Here, we will compare experimental results with simulations for the case of an oil-in-water-in-oil double emulsion. First, an oil-in-water pre-emulsion is made in a stirred Rushton vessel, which was stabilized with 2% Tween (ex Merck). After steady state was reached, 0.5 ml of this fine emulsion was added with a micropipette to oil in the flat cylinder, which was also used in the experiment on the break-up of emulsions described above. This procedure led to a double emulsion which particle size reduced during stirring while escape of the inclusions (the oil droplets made in the pre-emulsion) took place as well. The way in which these processes were measured was as follows. First, the particle size evolution was measured by turbidimetry. Secondly, the pre-emulsion droplet phase was dyed with chlorophyll which dissolved in the continuous phase via the escape process. As long as escape did not occur, the chlorophyll was not detectable by the red laser light in the turbidity

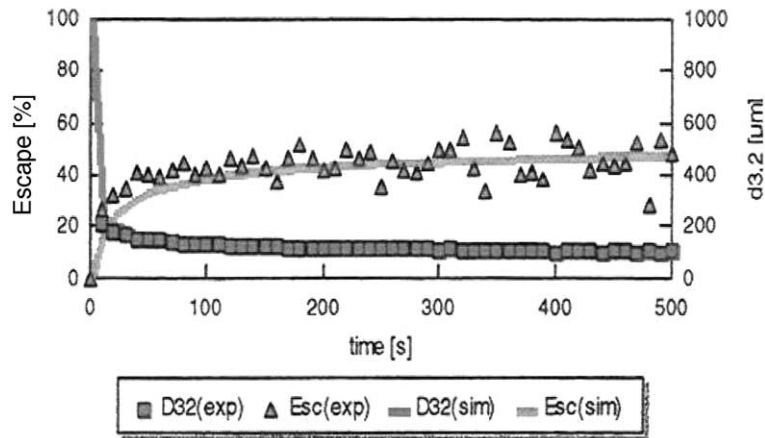


Fig. 4. Comparison of experimental data (symbols) to simulation results (full lines) for inclusions of $d_{3,2} = 30 \mu\text{m}$ at a pin stirrer speed of 250 rpm.

measurement. From the difference of the two signals of the two measurements the amount of escape was extracted.

Fig. 4 depicts the escape as a function of time defined as $E = 1 - (\varphi_t/\varphi_{t0})$.

As can be seen, the simulation follows the experimental data very well both for the time-scale of the escape process as well as for the absolute degree of escape.

Experiments in which the diameter of the pre-emulsion has been changed and also the pin stirrer speed have been simulated satisfactorily as well.

9. Discussion

Above three different examples have been given where it has been shown that good comparison between experiments and simulations has been reached. The simulation method is a hybrid approach: first the velocity field is calculated using CFD and subsequently that field is used in the calculation of S_j using a transport equation. This approach appeared to be simple and powerful. It has to be realized that this method can only be applied if the volume fraction is low, as it is implicitly assumed that there is no consequence of the presence of the particles for the properties of the flow. Of course at high volume fractions this assumption is not justified.

A drawback of this approach is that the source terms have to be modeled explicitly and that they should be preferably expressed in analytical form. For two-phase flow problems this can be done; however, for three-phase flow processes, as often encountered in industry, the modeling of the source terms will be a tremendous task. It is likely that another approach has to be taken for those cases.

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