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Drop breakage in liquid-liquid stirred dispersions - Modelling of single drop breakage

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Abstract

A new experimental approach has been set up for the identification of reasonable break-up mechanisms in stirred dispersions and of a physically-based model for the daughter drop size distribution. In the experiments, breakage of a single organic droplet and the subsequent fragments formation are analyzed by image processing techniques. The experimental data are then fitted by means of a daughter drop size distribution function written in terms of a probability density function (pdf). The mathematical approach that matches the theoretical requirements and that provides the best fit of the experimental data is the pdf proposed by Diemer and Olson (2002). This is a purely statistical model that does not contain any dependence on physical parameters, such as turbulence intensity and mother drop size. Based on the experimental results, an extension of the Diemer and Olson model is derived, in which dependence on the Weber number as well as on the mother drop diameter can be inserted. Other models appeared in the literature (Coulaloglou and Tavlarides, 1977; Konno et al., 1983; Martínez-Bazán et al., 1999) are also discussed and compared with experimental data. Out of them, the only model that approaches experimental data in a satisfactory way is the model by Martínez-Bazán et al. (1999).

Eventually the presence of the maximum break-up probability for symmetric breakage, in contrast with some theoretical models published in the literature, is explained and justified by means of energy considerations.

Keywords: drop; bubble; population balance; turbulence; suspension; stirred tank

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1. Introduction

Liquid-liquid dispersions play an important role in natural processes as well as in numerous industrial applications. The mass transfer rate between two phases which is fundamental to optimize the performance of reactors, absorbers and extraction columns is directly proportional to the interfacial area between the two phases. In order to calculate this area, the size distribution of the fluid particles must be determined, and this can be done by solving the *population balance equation*. Working under ideal mixing conditions, assuming that the number density function identifying the dispersed phase (i.e., fluid particles) is spatially homogeneous, and therefore neglecting spatial gradients, then the following formulation of the population balance equation in units [1/m^{3}s] is obtained (Gerstlauer, 1999; Hulburt and Katz, 1964):

$$\begin{aligned}
\frac{\partial f(\xi_p)}{\partial t} &= -g(\xi_p')f(\xi_p',t) + \\
&+ \int_{\xi_p}^{\xi_{p,\max}} \nu(\xi_p)b(\xi_p,\xi_p')g(\xi_p)f(\xi_p,t)\mathrm{d}\xi_p + \\
&- f(\xi_p,t)\int_0^{\xi_{p,\max}-\xi_p} F(\xi_p,\xi_p')f(\xi_p',t)\mathrm{d}\xi_p' + \\
&+ \frac{1}{2}\int_0^{\xi_p} F(\xi_p',\xi_p'')f(\xi_p',t)f(\xi_p'',t)\mathrm{d}\xi_p'
\end{aligned} \tag{1}$$

where $g(\xi_p)$ is the break-up frequency (or break-up kernel) of fluid particles of volume ξ_p, $\nu(\xi_p)$ indicates the number of fluid particles originating from the break-up of one mother particle having volume ξ_p, $b\left(\xi_p,\xi_p'\right)$ is the pdf that expresses the distribution of the daughters of a mother particle of volume ξ_p, and $F\left(\xi_p,\xi_p'\right)$ is the rate of coalescence (or coalescence kernel) of two particles of volume ξ_p and ξ_p' respectively.

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In the case of liquid-liquid dispersions, the four terms on the right hand side represent death (or disappearance) of droplets due to break-up, birth (or appearance) of droplets due to break-up, and death and birth of droplets due to coalescence, respectively. Applying elementary geometrical relations Eq. (1) can be rewritten using d_p, i.e. the diameter of the drops (treated as spherical objects), in place of the volume ξ_p, as the internal coordinate (Gerstlauer, 1999).

In order to determine the evolution of the droplet size distribution function $f(\xi_p;t)$, Eq. (1) must be solved numerically. To this aim, suitable and physically meaningful forms of the break-up kernel [$g(d_p)$ if expressed in terms of droplet size], the daughter pdf $b(d_p, d'_p)$, and the coalescence kernel $F(d_p, d'_p)$ are specified, with d_p and d'_p being the diameter of mother and daughter drops, respectively. In this case the daughter drop pdf has units [1/m].

The simulation of droplet breakage, by solving the population balance equation, requires the specification of both the breakage kernel and the daughter drop pdf. Although the distribution of the breakage products has been studied intensively from a theoretical point of view, experimental results on single fluid particles available in the literature are quite few. Hesketh et al. (1991) studied the break-up of bubbles in tubes, and used the experimental distribution of the daughter bubbles to develop a theoretical model. Their results show a minimum occurrence for breakage into two bubbles of equal size and a very high fraction of small fragments, indicating that for that particular system and under those operating conditions erosion was more likely to occur than a symmetric breakage mechanism. Kuriyama et al. (1995) restricted their investigation on the development of a relationship between the mean number of daughter drops formed per breakage event in a stirred vessel and physical parameters such as mother drop size, rotational speed of the impeller and viscosity. More recently, Galinat et al. (2005) have carried out single drop experiments in a turbulent pipe flow where injected droplets break-up due to a cross-sectional restriction in the pipe. The experimental distributions have been measured for different Weber numbers, $We = 2\rho_c \varepsilon^{2/3} d_p^{5/3} / \sigma$ (however always below We

= 100), and show a point of maximum frequency that shifts towards lower values of daughter drop diameters with increasing Weber numbers. The predictive model proposed by the authors is rather simple and consists essentially in a delta function.

Several approaches have appeared in the literature for modelling of the daughter drop pdf. In the following we are going to review some of them, with particular attention to the models proposed by Coulaloglou and Tavlarides (1977), Konno et al. (1983), Diemer and Olson (2002) and Martínez-Bazán et al. (1999). Coulaloglou and Tavlarides (1977) started from an early work of Valentas et al. (1966). The latter was based on the assumption that, given the random nature of droplet break-up, a purely statistical model in which the size of the daughter drops is normally distributed represents an appropriate description of the physical phenomenon. For example, if three droplets are originated [which according to Konno et al. (1983) is the most observed case in stirred tanks] then the Coulaglou and Tavlarides (1977) pdf in units [1/m] reads:

$$b(d_p, d'_p) = \frac{45 {d'_p}^2}{{d_p}^3 \sqrt{2\pi}} \exp\left\{ -\frac{25}{2} \left[3 \left(\frac{d'_p}{d_p} \right)^3 - 1 \right]^2 \right\}. \tag{2}$$

Another statistical approach which is used very often consists of a beta pdf (Hsia and Tavlarides, 1983; Konno et al., 1983; Lee et al., 1987; Modes, 1999), mainly due to its flexibility in representing very different mechanisms (i.e., from symmetric breakage, to uniform distribution, and to erosion) only by changing a few parameters. Konno et al. (1983) demonstrated experimentally that the number of daughter drops generated in a stirred tank in the case of liquids of standard viscosity ranges between two and four, three being the most observed number of daughters. Focusing consequently on breakage into three droplets, they calculated the two free parameters of the canonical form of the beta pdf [see Abramowitz and Stegun (1965) for reference about beta pdf] by computing the probability associated with a certain combination of daughter droplets resorting to the Heisenberg spectrum. The final expression, in units [1/m], is a function of the droplet diameters only:

$$b(d_p, d'_p) = \frac{\Gamma(12)}{\Gamma(3)\Gamma(9)} \left(1 - \frac{d'_p}{d_p}\right)^2 \frac{{d'_p}^8}{{d_p}^9} \tag{3}$$

where Γ is the gamma function (Abramowitz and Stegun, 1965).

Diemer and Olson (2002) adjusted a previous model by Hill and Ng (1996) in such a way to identify a well defined class of beta pdfs where the two free parameters of the beta pdf are subject to a particular constraint that assures conservation of volume throughout the breakage event. In its final form, two parameters are present, one of them being the number of generated daughter droplets and the other one the shape parameter of the distribution. The Diemer-Olson pdf is analyzed and discussed in detail in Section 3 of this contribution.

Among the so-called phenomenological models (i.e. those derived from physical considerations and incorporating physical parameters in the pdf) one of the most cited was formulated by Luo and Svendsen (1996). These authors derived a breakage rate model based on analogies with the kinetic theory of gases, which gives the collision frequency between eddies and drops. Then, after multiplying this frequency by the probability of having daughter drops with a certain size, they expressed the overall break-up probability as a function of the increase in surface energy. The daughter drop pdf in this case is included in the break-up kernel and it can be extracted and isolated by proceeding to standard normalization. The model contains as unique free parameter the lower limit of integration on the eddy scale, namely the smallest length-scale of eddies that are able to result in effective droplet break-up, and although this is limited to only one parameter, it exerts a strong influence on the final prediction. This daughter drop pdf is valid for binary breakage and shows at low turbulent dissipation rates a typical U-shaped form, with a minimum corresponding to equal breakage and a probability approaching infinity for daughter to mother size ratio equal to zero and one. As anticipated, the

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shape of the pdf is a function of local turbulent conditions through the turbulent dissipation rate, and the curves flatten out by increasing this parameter. The probability of equal breakage increases very rapidly, but the dependency on this parameter seems to be highly non-monotonical and some authors (Lasheras et al., 2002) find that this behaviour does not describe the physical situation properly. Moreover, the fact that this function is not upper-bounded makes its implementation in commercial codes rather difficult.

A recent model that originates from the approach introduced by Luo and Svendsen (1996), is the one developed by Wang et al. (2003). The final shape of the daughter droplet pdf is upper-bounded and it predicts zero probability as the daughter-to-mother ratio equals zero and one and predicts minimum probability for equal size breakage. However, also for this approach, the implementation in numerical and simulation codes is made cumbersome by the mathematical complexity of its formulation that requires the solution of a three-dimensional integral. Much simpler is the daughter drop pdf proposed by Martínez-Bazán et al. (1999), on the base of pure mechanical principles. The pdf is derived by establishing a proportionality relationship between the probability of a pair of drops to be formed and the difference between turbulent kinetic energy and surface energy that would act on the two daughter drops. With some modifications, the original idea assuming binary breakage is then extended to ternary breakage as well. Unlike the phenomenological models previously discussed, the daughter drop pdf derived by Martínez-Bazán et al. (1999) shows a maximum for equal size breakage and, when expressed in terms of the daughter to mother drop diameter ratio ($D^* = d'_p / d_p$ with $0<D^*<1$), results in the following dimensionless form:

$$b(D^*) = \frac{[D^{*2/3} - \Lambda^{5/3}] \cdot \left[\left(\frac{1}{2}(1 - D^{*3}) \right)^{2/9} - \Lambda^{5/3} \right]^2}{\int_{D^*_{\min}}^{D^*_{\max}} \left[D^{*2/3} - \Lambda^{5/3} \right] \cdot \left[\left(\frac{1}{2}(1 - D^{*3}) \right)^{2/9} - \Lambda^{5/3} \right]^2 \mathrm{d}D^*} \qquad (4)$$

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where $\Lambda = d_c / d_p$, the maximum stable (critical) diameter being defined as $d_c = \left(12\sigma/(\beta\rho)\right)^{3/5} \varepsilon^{-2/5}$, and $D^*_{\min} = d_{p\min} / d_p$ where $d_{p\min} = \left(12\sigma/(\beta\rho)\right)^{3/2} \varepsilon^{-1}$ is the minimal daughter drop diameter. Furthermore, it is $D^*_{\max} = d_{p\max} / d_p$ since the maximal daughter drop diameter for three daughter droplets is $d_{p\max} = \left[d_p^{\,3} - 2\left(\frac{12\sigma}{\beta\ \rho\ d_p} \right)^{9/2} \varepsilon^{-3} \right]^{1/3}$. This model was derived under the assumption of homogeneous turbulence and cannot be applied to systems such as stirred tanks without some modifications, such as for example the recalculation of the Batchelor constant β by imposing experimentally measured values of the critical diameter.

A shortcoming present in many models, with the only exception of the Coulaloglou and Tavlarides (1977) pdf and the Luo and Svendsen (1996) model, is represented by the fact that the conservation of volume/mass is not always respected. Models that do not predict volume/mass conservation, once implemented in simulation codes for closed systems, lead to an evolution of the predicted volume fraction which is unstable and not meaningful from a physical point of view.

More recently, Rodríguez-Rodríguez et al. (2006) have simulated the break-up of droplets and bubbles numerically by imposing a straining hyperbolic flow at high Reynolds numbers. The computed evolution of droplets is in good agreement with the behaviour experimentally observed at high Reynolds numbers where binary break-up occurs due to stretching induced by the flow field. This results in daughter droplets of similar size and provides a second argument for the validity of the classical Hinze-Kolmogorov assumptions, which state that turbulent breakage is mainly due to the disruptive action of turbulent eddies (that are smaller in size than the drop diameter).

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2. Experimental setup and data analysis

The experimental setup used in this work was appositely designed to investigate breakage of single droplets, but representing the general fluid dynamics conditions of stirred tanks in the region around the impeller, where most of breakage occurs. For this reason, a section of a single blade of a Rushton turbine on a disk was fixed in a rectangular channel with an inner cross section of 30mm×30mm (Fig. 1). The geometry of the channel as well as the operating conditions was designed in order to reproduce the highest local velocity gradients inside the stirred tank. The correlation of the velocity at the stirrer tip u_{tip} and the average velocity of the fluid in the vicinity of the impeller, $\bar{u}$, reads (Laufhütte, 1986):

$$\frac{\bar{u}}{u_{tip}} = 0.18 Ne^{7/8} , \qquad (5)$$

where *Ne* is the Newton number defined as $Ne = \frac{P}{\rho n^3 d^5}$. The velocity gradients mainly responsible for droplet breakage in stirred tanks can be reproduced in the channel if a relative velocity of $u_{rel} = \dot{V}/A = u_{tip} - \bar{u} = 0.7 u_{tip}$ is maintained (Laufhütte, 1986), where $\dot{V}$ is the volumetric flow rate of the continuous liquid and A is the area of the channel's cross section. For a blade size of 19mm×17mm and a stirrer diameter *L*=0.08 m the fluid dynamic conditions equivalent to a stirrer speed of 550 rpm (*Ne*=3.8) in the corresponding stirred tank (with tank diameter *T*=0.25 m) can be achieved in the channel geometry used in this work ($\dot{V} = 9 \cdot 10^{-4}$ m³/s), resulting in a relative velocity of u_{rel}=1.5 m/s and in an average turbulent kinetic energy dissipation rate of about 0.34 m²/s³, namely 7.26 times higher in the region around the blades (Tsouris and Tavlarides, 1994).

The experimental procedure was as follows. A single droplet of petroleum was injected into the continuous phase flow by using a Hamilton dosing pump via a capillary made of glass. The droplet was then entrained by the continuous phase flow towards the blade behind of which breakage occurred. The daughter drops created at the blade were then photographed using a CMOS camera (Cam 1) with a flash energy of 2 J.

The reproducibility of droplet formation is ensured and experimental data for a mother droplet diameter of 1 mm and u_{rel}=1.5 m/s show a negligible deviation of diameter of about 6%.

The collected images (see Fig. 2) have been analyzed afterwards by using the commercial software ImageProPlus®. Initially, the images have been treated in order to eliminate the background by subtraction from a reference image without droplets. In a second step, the obtained image was transformed into a binary file by setting a threshold. The final picture contains only black droplets on a white background. These areas are analysed and associated with a diameter. For volume conserving reasons the sum of detected daughter drop volumes is related to the mother drop volume. If the deviation of the volumes is larger than 15% the break-up event is not taken into account.

The smallest diameter which can be detected with the applied system is 50μm. The significance of the measured data was investigated by statistical analysis. With increasing mother drop size the number of statistically required sample size is growing because the number of possible breakage events is increased (Kuriyama et al., 1995), and typical values of accomplished measurements for different mother droplet diameters are reported in Table 1.

Physicochemical properties of the dispersed phase used for the experiments (petroleum) are reported in Table 2.

The experimental data collected in this way are then labelled and sorted out by the number of daughter droplets (i.e., binary, ternary, quaternary breakage and so on) whose diameter falls in a certain size interval and then interpolated by means of Hermitian splines. Afterwards, each experimental value was divided by the area underlying the interpolating curve so that a normalized pdf was always obtained. It is clear that, when the number of measured drops is insufficient, the area of the interpolated curve is too small and the resulting normalized pdf is too narrow, giving probabilities that are too high at the point of maximum. On the other hand,

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if the number of measurements is close to the one required by statistical analysis, then the interpolated curve has a much more defined contour and the resulting pdf is more realistic.

3. Modelling and discussion

In the present work, a simple, empirical approach for the daughter drop pdf is developed and validated through comparison with experimental data. The approach is based on the statistical model originally proposed by Hill and Ng (1996) and successively modified and simplified by Diemer and Olson (2002). Results show that the model fits rather well single droplet breakage experiments and it is suitable to be further modified in order to include functional dependencies on physical parameters such as turbulence energy dissipation rate, in agreement with the phenomenological assumptions based on the Hinze-Kolmogorov theory (Hinze, 1955). Moreover, the model can be very easily implemented in simulation codes for particle dynamics such as PARSIVAL®, which has been successfully applied to the simulation of liquid-liquid systems in a previous work (Gäbler et al., 2006).

3.1 Fitting of experimental data and discussion

A daughter drop pdf must satisfy important requirements. Some of these requirements are due to mathematical considerations (e.g., the pdf must integrate to unity), some others are related to its ability of reasonably representing the physical process (e.g., the pdf must be mass-conserving), and some others are instead satisfied in order to guarantee an ease of implementation in population balance models (e.g., the pdf has no singularity points and it drops to zero as the ratio between the daughter and the mother drop diameters goes to zero and to one). Furthermore, the pdf must describe the effect of the relevant physical parameters such as turbulent kinetic energy dissipation rate and the mother drop diameter that should appear as pdf variables. In addition the pdf must be positive on the whole domain and upper-bounded.

As it has been already reported in this work, a newly conceived approach that satisfies all the requirements mentioned above was adopted and developed. The approach is based on the general statistical pdf proposed by Diemer and Olson (2002) that consists of a well specified class of beta pdfs in which the two free parameters are defined as functions of a shape parameter q and of the mean number of daughter drops resulting per breakage event, ν. This pdf was proposed by the authors as a simplification of the Hill-Ng equation (Hill and Ng, 1996). This latter one is a statistical daughter drop pdf that was derived by imposing the conservation of volume and the normalization condition. The model by Diemer and Olson (2002) is very flexible, since the shape parameter is suitable to be fitted to experimental data and modelled as a function of the underlying turbulence conditions as well as of the mother drop diameter. Furthermore, it satisfies all of the other requirements reported above, and it takes the following dimensionless form:

$$b(z)=\left(\frac{\Gamma(q\nu)}{\Gamma(q)\Gamma(q(\nu-1))}\right)z^{q-1}(1-z)^{q(\nu-1)-1}=\frac{z^{q-1}(1-z)^{r-1}}{B(q,r)}, \qquad r=q(\nu\text{-}1) \tag{6}$$

where q is the shape parameter, ν is the average number of daughter droplets per breakage event, z is the ratio between the daughter and the mother volumes, while $B(q,\nu)$ is a normalization factor (for the latter one, see Abramowitz and Stegun, 1965). Since the models that we are going to test and discuss, as well as simulation packages for particulate technology (like the aforementioned PARSIVAL®), make use of the droplet diameter as the internal coordinate, the relationship between the volume-based and the diameter-based daughter drop pdf in units [1/m] is used here (Gerstlauer, 1999):

$$b(d_p,d'_p)=3k_v d'^{2}_p b(d_p^{\,3},d'^{3}_p). \tag{7}$$

By applying $b(d_p^{\,3},d'^{3}_p)=\dfrac{b(z)}{k_v d_p^{\,3}}$ (Diemer and Olson, 2002) and assuming spherical geometry

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($k_v = \pi/6$) one can get the diameter-based daughter drop pdf:

$$b(d_p, d'_p) = 3B^{-1}(q,r)\left[1-\left(\frac{d'_p}{d_p}\right)^3\right]^{r-1}\left(\frac{d'_p}{d_p}\right)^{3q-1}\frac{1}{d_p}\ . \quad (8)$$

Or, in terms of the dimensionless daughter-to-mother droplet diameter ratio D^*:

$$b(D^*) = b(d_p, d'_p)d_p = 3B^{-1}(q,r)\left[1-(D^*)^3\right]^{r-1}(D^*)^{3q-1}. \quad (9)$$

In Fig. 3, the comparison between experimental data and the Diemer-Olson pdf for a 2 mm diameter mother drop, in the case of binary, ternary and quaternary breakage respectively, is reported. The shape parameter q of the Diemer-Olson pdf has been used as fitting parameter in order to fit the model to the experiments by minimizing the residua between experimental data and theoretical values. Special attention has been paid in order to obtain a good agreement in the range where probability takes the highest values (i.e. near the maximum).

As one could expect, by passing from ternary breakage to binary breakage, the pdf becomes narrower and the maximum is shifted towards higher values of the diameter ratio.

In Fig. 4, the comparison between experimental data and model is reported for a mother droplet diameter of 1 mm. The same comparison for a mother droplet diameter of 0.6 mm is reported in Fig. 5. In this case we can observe a larger discrepancy between experimental data and the model in the range of smallest fragments, maybe due to erosive breakage phenomena which are not taken into account by the model. Furthermore, the maximum probability predicted by the model does not match the significantly lower values exhibited by the pdf measured experimentally. However, the measurement of the fragments originated in the latter case by means of the here employed technique is less accurate than for mother droplets having diameter larger than 1 mm.

According to the Hinze-Kolmogorov theory, the distribution of the breakage products becomes wider with increasing mother drop diameter, because, in this way, the spectrum of eddies smaller than the parent drop, which are able to induce break-up by collision (eddies that are larger merely transport the drop) becomes wider itself. This occurs when comparing the 0.6 mm with the 1 mm data. Similarly, it would have been expected that, with 1 mm droplets the pdf would have been narrower than with 2 mm droplets. This did not occur because the number of measured data, for the case of 2 mm drops, is too low and not sufficient to avoid overestimation during the normalization. A statistically significant number of measurements could not be obtained in this case (see Table 1) because of stability problems while injecting the mother droplet into the channel.

It is therefore necessary to collect a statistically meaningful number of data for different mother drop diameters in order to study the effect of the mother drop size on the distribution width and identify a relationship between the shape parameter q and the mother drop diameter. However, also in this case, it is seen how, with four daughter droplets, the distribution is wider than with two (the shape factor q decreases sensibly as well) and the point of maximum is significantly shifted toward lower values of the diameter ratio.

3.2 Comparison with other daughter drop pdf models

The Diemer-Olson equation is compared in Fig. 6 with other models which all predict a maximum probability for equal size breakage in the case of three daughter drops generated per breakage event, which, as mentioned previously, has been identified by Konno et al. (1983) as the most common situation for liquid dispersions in stirred tanks. However, in the case of highly viscous fluids (e.g. silicone oil) dispersed in water, as it was clarified by Kuriyama et al. (1995) and, more recently, by Eastwood et al. (2004), the number of fragments generated is higher and the breakage dynamics deviates from the description provided by the Hinze-Kolmogorov theory.

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The normal distribution in the form adjusted by Coulaloglou and Tavlarides (1977), exhibits a shape which is definitely too narrow in comparison with our experimental data and it predicts a likelihood for equal size breakage which is by far too high. The same shortcomings apply to the beta pdf proposed by Konno et al. (1983). In order to plot the model proposed by Martínez-Bazán et al. (1999), experimental values of the maximum stable (critical) diameter have been taken from a stirred vessel [see Gäbler et al. (2005) for description of tank geometry and operating conditions] instead of using the theoretical correlation valid for homogeneous turbulence used by Martínez-Bazán et al. (1999):

$$d_c = \left(\frac{12\sigma}{\rho\beta}\right)^{3/5} \varepsilon^{-2/5} \qquad (10)$$

The values refer to a toluene-water system at an impeller speed of N =550 rpm corresponding to the flow conditions of the single-drop experiment. The resulting pdf [i.e., the Martínez-Bazán pdf reported in Eq. (4) and depicted in Fig. 6], predicts a wider distribution which approaches the experimental data better than the ones discussed previously, including the Diemer-Olson pdf with q as fitting parameter.

In Fig. 7 the models that so far provided the best fit to the experimental data (i.e., the Diemer-Olson pdf and the Martínez-Bazán pdf) are compared for the case of generation of two daughter droplets. As it is seen the Diemer-Olson pdf matches the maximum of probability shown by measured data much better than the Martínez-Bazán pdf, which seems to fit better in the range of smallest fragments. Obviously, despite the large number of experimental observations for 1 mm mother droplets collected, an appreciable scatter of test data was to be expected since it is usual when dealing with phenomena governed by statistical laws (Hinze, 1955). We can also notice how this model underestimates the probability of being formed for small and very small droplets. This might be explained referring to the issue of satellite droplets, which are formed by erosive breakage. No model has faced this task yet and some authors explicitly neglect formation of satellite droplets arguing that the final drop size distribution is not affected at all by such phenomena and that the volume fraction contained in satellite drops is irrelevant (Martínez-Bazán et al., 1999).

As we have seen, the shape parameter of the Diemer-Olson pdf (Diemer and Olson, 2002), seems to be able to reflect the underlying physical aspects of the turbulent drop breakage. In conclusion, an empirical model can thus be thought of, where the daughter drop pdf in the statistical form presented by Diemer and Olson (2002) is related, through the shape parameter q, to the Weber number. By scaling also with the ratio between diameter of the mother drop and critical diameter of the turbulent suspension, we obtain the following relation:

$$q = \alpha \, We^{\gamma} \left(\frac{d_c}{d_p} \right)^{\delta} \tag{11}$$

where α is a proportionality constant to be found by interpolation, while γ and δ are exponents to be determined empirically. The critical diameter is defined as the maximum stable diameter according to the assumptions of the Hinze-Kolmogorov theory (Hinze, 1955).

3.3 Probability of equal-size breakage

Comparing the various models that have been proposed in the literature, some obvious discrepancies between different models appear. One of the most evident is that some pdfs predict a minimum probability for symmetric break-up (Nambiar et al., 1992; Tsouris and Tavlarides, 1984; Luo and Svendsen, 1996; Wang et al., 2003) whereas other ones show a maximum (Valentas et al., 1966; Konno et al., 1983; Lee et al., 1987). This point has been treated with particular attention in a recent work (Wang et al., 2003) where it has been stated that the existence of a minimum break-up probability for symmetric break-up is justified by the fact that more energy is required for binary symmetric break-up. In fact, the change in surface energy related to the formation of two fragments is maximal if the daughter droplets have the

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same size. However, this change in interfacial area, that can be thought of as a sort of potential barrier, is generally small compared to the other energies involved in a break-up event. Therefore, a rigorous energy balance must include this remaining energy absorbed by the daughter droplets in other forms, such as kinetic and oscillatory and the role of configuration entropy should also be accounted for (Cohen, 1991). Simple calculations, however, show that for a model system consisting of a 1 mm parental drop of toluene in water the maximum change in surface energy in the case of symmetric breakage is:

$$e_{surf} = \pi\sigma\, d_p^{\,2}\left[2^{1/3}-1\right] = 2.8\cdot 10^{-8}\,J\,, \tag{12}$$

whereas the typical energy during eddies impact on the droplet can be evaluated by applying the following relationship (Martínez-Bazán et al., 1999):

$$e_{turb} = \frac{1}{2}\rho\beta^{*}(\varepsilon\, d_p)^{2/3}\frac{1}{6}\pi\, d_p^{\,3} = 5.23\cdot 10^{-7}\,J\,. \tag{13}$$

In Eq. (13) β^{*}, as already explained, is a value calculated by fitting the expression of the maximum stable (critical) diameter [Eq. (10)] to experimental values obtained in a stirred tank for the system studied here, since, in an inhomogeneous turbulent system Batchelor's constant β takes higher values than value 8.2 obtained by Batchelor under the hypothesis of homogeneous turbulence (Batchelor, 1956). By identifying the remaining energy with the turbulent kinetic energy absorbed by the daughter droplets only, we can calculate it as the sum of all turbulent kinetic energy terms owned by the daughter droplets for the same system, and obtain:

$$e_r = \sum_{i=1}^{\nu}\frac{1}{2}\rho\,\beta^{*} N_i(\varepsilon\, d'_{p,i})^{2/3} = 4.95\cdot 10^{-7}\,J \tag{14}$$

where in the case of binary breakage $\nu = 2$. Comparison of these quantities show that only 5 % of the total energy absorbed by the daughter droplets is converted into surface energy, and it is therefore possible to conclude that the energy associated with the surface increment, compared to the other energy terms involved during breakage, does not constitute a determining factor, and therefore this argument cannot be used to demonstrate the existence of a minimum in the daughter drop pdf for symmetric breakage.

4. Concluding remarks

A simple approach for describing the daughter drop pdf suitable for population balance modeling has been presented and compared with experimental data. The mathematical background for the model is offered by the general statistical pdf approach formulated by Diemer and Olson (2002). Within the present work, this general model has been applied to breakup of organic droplets in water within a stirred tank. Experimental data of daughter droplets originated by single mother droplets undergoing breakup have been obtained in a channel device where operating conditions are created in order to reproduce those existing in a stirred tank. The diameter of the daughter droplets is determined by image processing. The agreement of the model with these experimental data is satisfactory when a sufficient amount of data is available, and particularly when the number of daughter droplets equals three, which is the most frequent case in stirred tank dispersions. When the size of the mother drop undergoing breakage is small (0.6 mm) the agreement with experimental data is much less satisfactory, and the experimental pdf shows a sensibly different trend.

Out of the two free parameters present in the Diemer - Olson pdf (Diemer and Olson, 2002) used for the fitting of the experimental data, one, as suggested by the authors, is fixed equal to the number of daughter droplets originated per breakup event (ranging from 2 to 4 in the considered system according to Konno et al., 1983). The other one, q, is suitable to be modeled as an empirical function of the underlying physical situation. A model formulated in this way satisfies various requirements both in terms of accuracy in reflecting the physics of the system as well as in terms of ease of implementation for simulations within the population balance framework.

In forthcoming work, the empirical parameters in the empirical relation for q [see Eq. (11)] are going to be identified based on experiments which are in progress.

Finally, the questionable argument that turbulent breakage resulting in equal size daughter drops is not likely to take place only because of considerations related to surface energy, is discussed and confuted by a simple energy balance approach.

Notation

A	cross section of the breakage channel, m^2
$b\left(\xi_p, \xi'_p\right)$	daughter drop probability density function, $1/m^3$
$b(d_p, d'_p)$	daughter drop probability density function, 1/m
$b(z)$	volume-based dimensionless daughter drop probability density function
$b(D^*)$	diameter-based dimensionless daughter drop probability density function
B	normalization factor of the beta function
d	drop diameter, m
D^*	ratio between daughter drop and mother drop diameter
e	energy, J
f	drop size number density function, $1/m^3$
F	coalescence kernel, 1/s
g	breakage rate kernel, 1/s
k	particle shape coefficient
L	diameter of the stirrer, m
N	stirring speed, rpm
Ne	Newton number
P	power of the imperller, J/s
q	extended Hill–Ng daughter distribution parameter
r	$q(p\text{-}1)$, extended Hill–Ng parameter
T	diameter of the stirred tank, m

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u	velocity of the liquid suspension, m/s
We	Weber number
$\dot{V}$	volumetric flow rate of the suspension in the breakage channel, m^3/s
z	ratio between daughter drop and mother drop volume

Greek letters

α	constant
β	pre-factor of the Batchelor formula for the turbulent velocity fluctuations
γ	empirical exponent
Γ	the gamma function
δ	empirical exponent
ε	average turbulent energy dissipation rate, m^3/s^2
ξ	drop volume, m^3
Λ	ratio between critical diameter and mother drop diameter
μ	viscosity of the dispersed fluid, mPa·s
ν	number of daughter drops generated per breakage event
π	the irrational number pi
ρ	density of the dispersion, kg/m^3
ρ_c	density of the continuous phase, kg/m^3
σ	surface tension mN/m

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Figure Captions

Table 1. Sizes of mother droplets used for the experiment and corresponding number of measurements accomplished (first column) and required by statistical analysis (second column).

Table 2. Physicochemical properties of the dispersed phase.

Fig. 1. Sketch of the single drop breakage cell.

Fig. 2. Pictures of drops in the breakage channel. The picture with drops is subtracted from a reference one without drops. The final picture shows black drops only.

Fig. 3. Comparisons between the measured (bars) and calculated values (curves) of the daughter drop pdf for mother drops of diameter equal to 2 mm; (a) generation of two daughter drops; (b) generation of three daughter drops; (c) generation of four daughter drops.

Fig. 4. Comparisons between the measured (bars) and calculated values (curves) of the daughter drop pdf for mother drops of diameter equal to 1mm; (a) generation of two daughter drops; (b) generation of three daughter drops; (c) generation of four daughter drops.

Fig. 5. Comparisons between the measured (bars) and calculated values (curves) of the daughter drop pdf for mother drops of diameter equal to 0.6 mm; (a) generation of two daughter drops; (b) generation of three daughter drops; (c) generation of four daughter drops.

Fig. 6. Comparisons between the measured values (bars) and values calculated through various models [Martínez-Bazán et al. (1999): dashed curve; Coulaloglou and Tavlarides (1977): dots; Konno et al. (1983): dashed-dots; Diemer and Olson (2002) fitted to experimental data: continuous curve] of the daughter drop pdf for mother drops of diameter equal to 1mm. Figure refers to generation of three daughter drops.

Fig. 7. Comparisons between the measured values (bars) of the daughter drop pdf for mother drops of diameter equal to 1mm and pdfs calculated with the model of Martínez-Bazán et al.

(1999) (dashed line) and the model of Diemer and Olson fitted to experimental data (solid line). Figure refers to generation of two daughter drops.

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Table 1

Diameter of mother droplet [mm]	Existing sample size [number]	Necessary sample size [number]
0.56	284	234
1.00	503	154
2.00	184	622

Table 1. Sizes of mother droplets used for the experiment and corresponding number of measurements accomplished (first column) and required by statistical analysis (second column).

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Table 2

ρ	μ	σ (relative to water)	σ (relative to Sudan-black coloured water)
[kg/m^3]	[mPa · s]	[mN/m]	[mN/m]
760	1,9	42	28

Table 2. Physicochemical properties of the dispersed phase.

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Fig.1

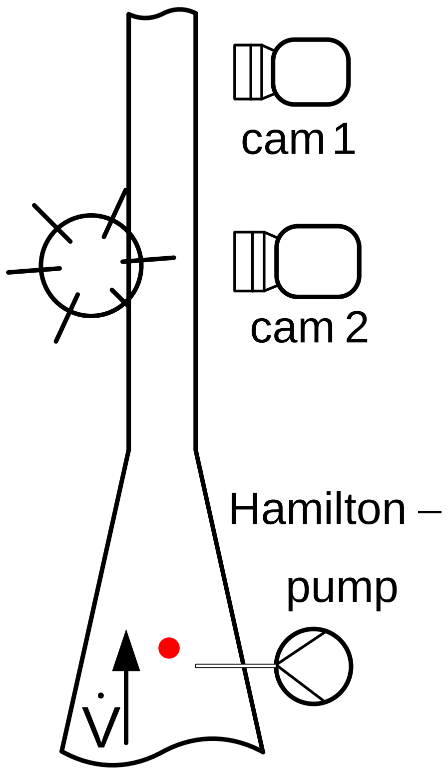

Fig. 1. Sketch of the single drop breakage cell.

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Fig. 2

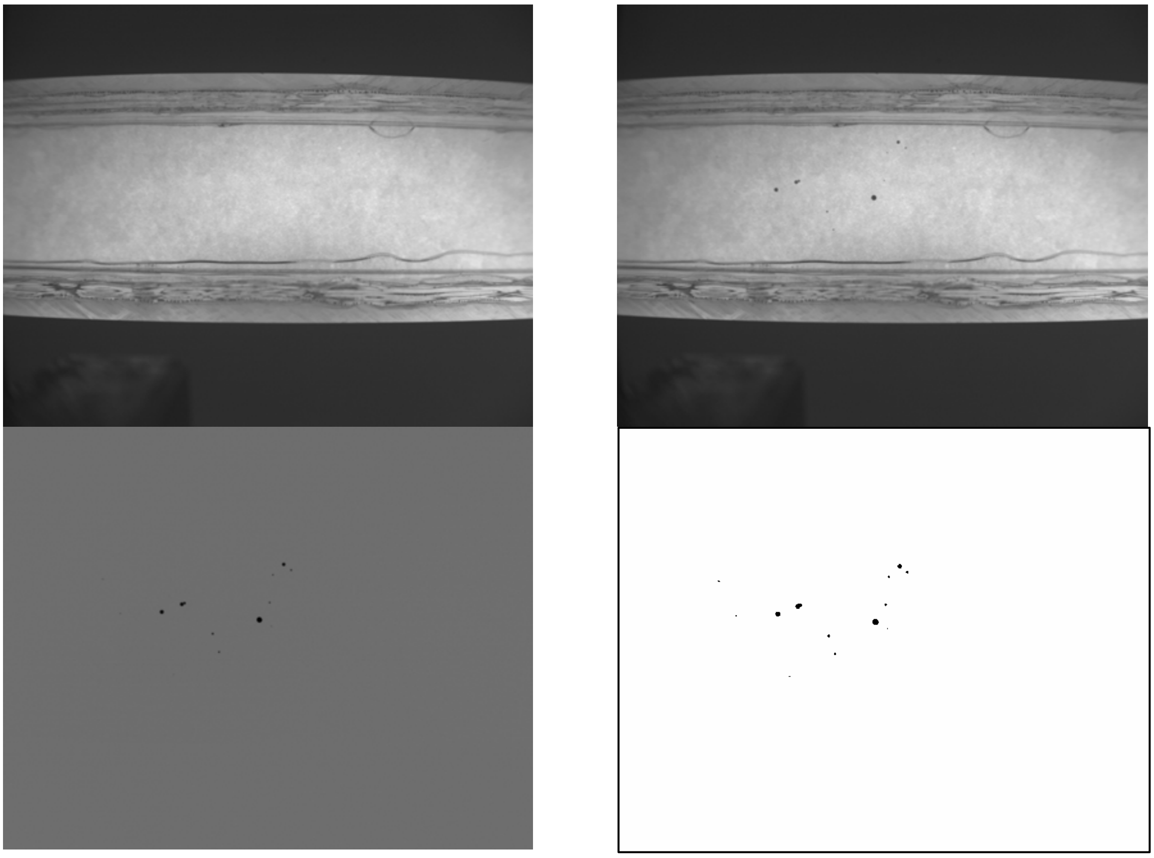

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Fig. 3

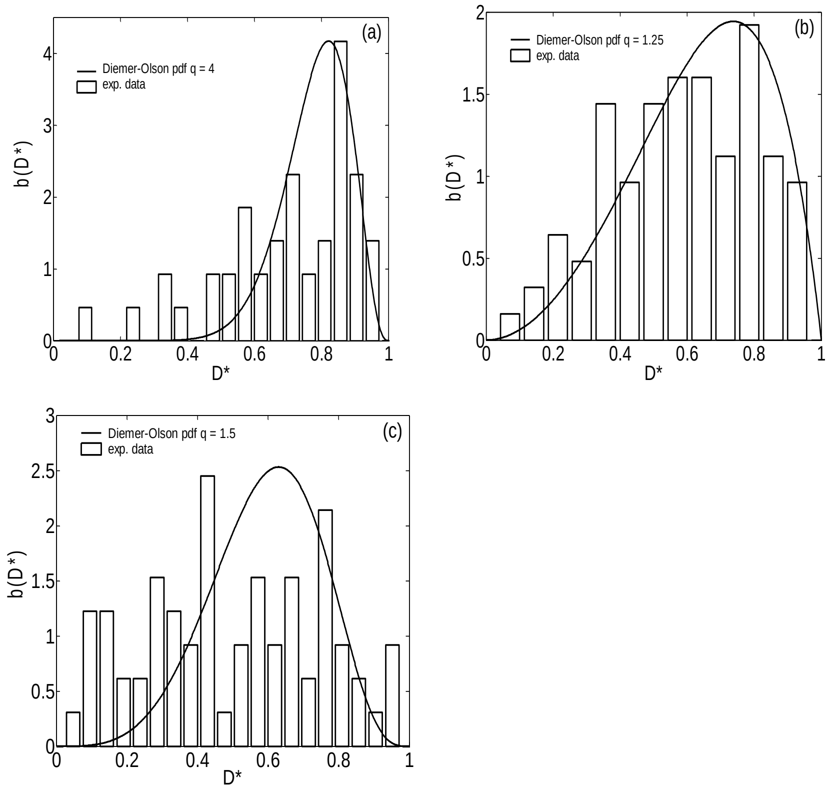

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Fig. 4

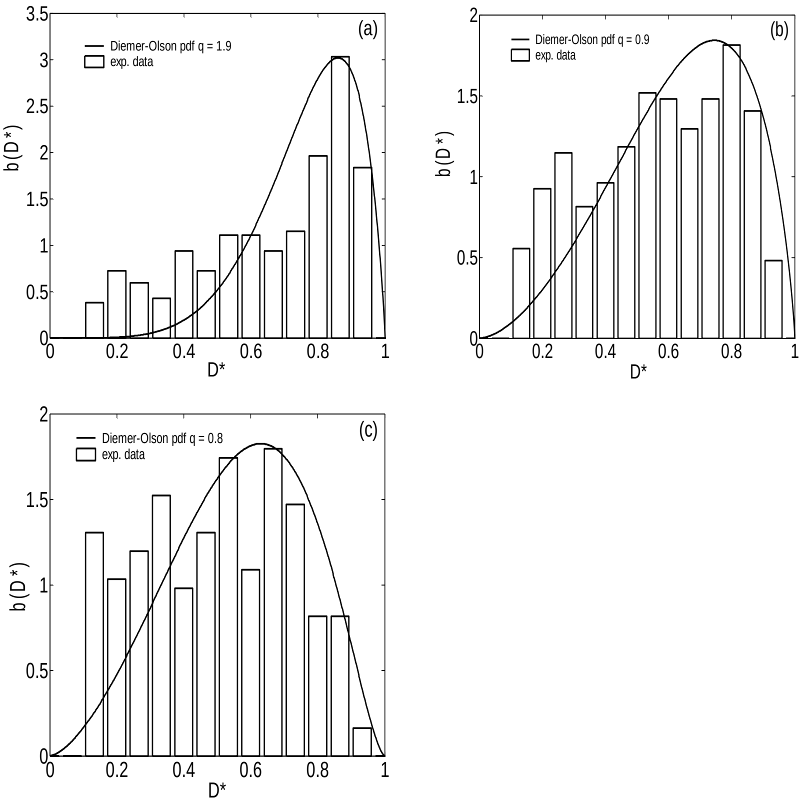

Fig. 4. Comparisons between the measured (bars) and calculated values (curves) of the daughter drop pdf for mother drops of diameter equal to 1mm; (a) generation of two daughter drops; (b) generation of three daughter drops; (c) generation of four daughter drops.

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Fig. 5

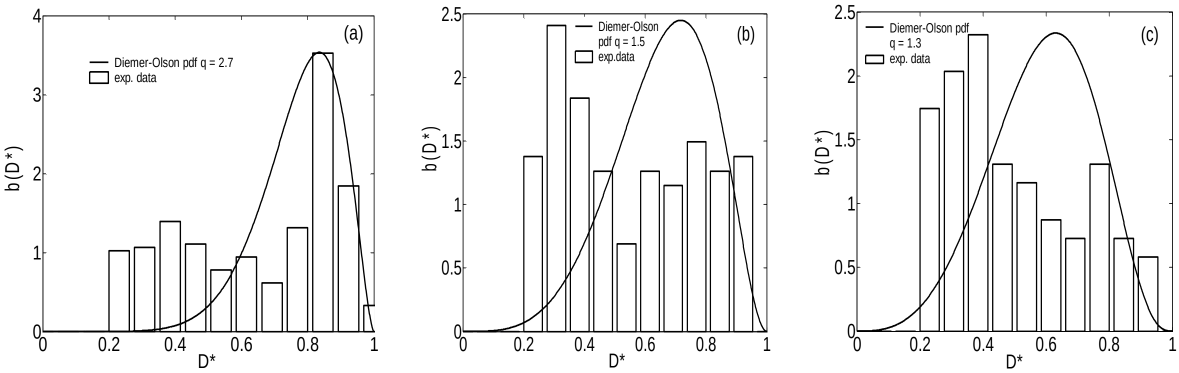

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Fig. 6

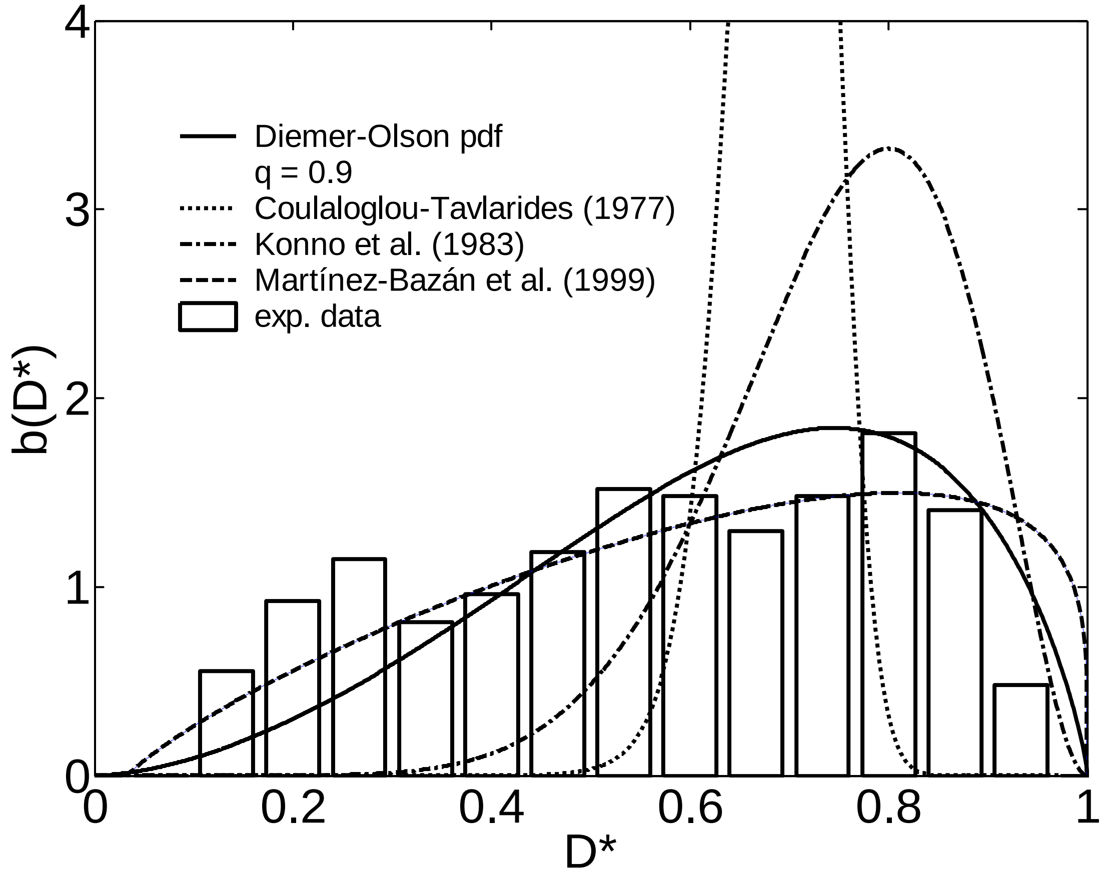

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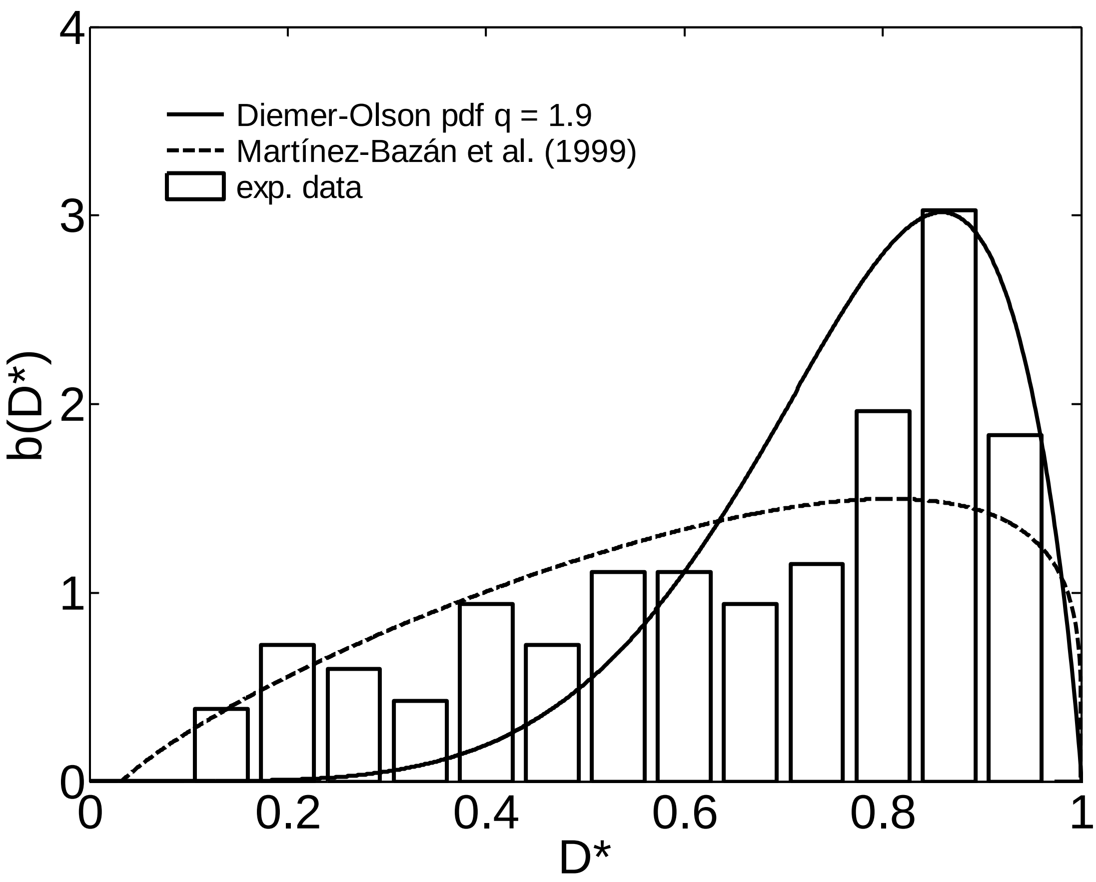
Fig. 7



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