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SOME MATHEMATICAL PROBLEMS IN MODELLING THE DYNAMICS OF COAGULATION AND FRAGMENTATION

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CONTENT

- Introduction to the physics and mathematics of the problem
- State of the art and problems
- Our contribution

PROCESSES IN NATURE DESCRIBED IN TERMS OF PARTICLE SYSTEMS GOVERNED BY COAGULATION FRAGMENTATION INTERACTION

- **oil pipelining (oil/water or water/oil emulsions)**
- **food industry (suspensions, emulsions of various type)**
- **photography (emulsions involving chemical reactions)**
- **painting (suspensions with chemical additives)**
- **hematology (coagulation of cells)**
- **atmospheric physics (clouds and fog formation)**
- **polymers (break-up and recombination of long chains)**
- **astrophysics (simulation of star and galaxy formation)**
- **aerosol (liquid or solid particles suspended in a gas)**

MATHEMATICAL MODELS (DISCRETE AND CONTINUOUS) FOR CLUSTER DYNAMICS

— CHARACTERISTIC VARIABLE: **cluster size (or volume or number of particles) which may be either a positive real number (continuous models) or a positive integer (discrete models) depending on the physical context.**

— AIM OF THE THEORY: **to describe the particle size distribution as a function of time and space as the system undergoes changes due to various physical influences.**

— CHARACTERISTIC EVOLUTION EQUATION: **formally**

$$\partial_t f + \mathscr{A}(x,t,v) f = r(x,t,v,f), \qquad x \in \mathbb{R}^n, \quad t > 0$$
$$f(x,0,v) = f_0(x,v), \qquad x \in \mathbb{R}^n$$

- $\mathscr{A}$ **is a convection–diffusion operator,**
- r **describes the kinetic behaviour of the process,**
- f **is the particle–size distribution function,**
- v **is the volume (of the cluster).**

Moreover

- $f(x,t,v) \geq 0$ **(to be proved for every model for consistency)**
- $\int_X \int_{v_0}^{v_1} f(x,t,v)\,\mathrm{d}v\,\mathrm{d}x$ **is the total number of particles with volume belonging to the interval** $[v_0, v_1] \subset \mathbb{R}^+$ **and being at time** t **contained in the space region** $X \subset \mathbb{R}^n$**.**
- **The measure** $\mathrm{d}v$ **is either the Lebesgue on** $\mathbb{R}^+$ **(*continuous models*) or the counting measure on** $\dot{\mathbb{N}} := \{1,2,3,\ldots\}$ **(*discrete models*). In the latter case the integrals with respect to** $\mathrm{d}v$ **reduce to sums.**

THE DIFFUSIVE-CONVECTION TERM

$$\begin{aligned}\mathscr{A}(x,t,v)f \quad &:= -\operatorname{div}(\mathbf{A}(x,t,v)\operatorname{grad} f + \vec{a}(x,t,v)f) \\ &\quad +\vec{b}(x,t,v)\cdot\operatorname{grad} f + a_0(x,t,v)f\end{aligned}$$

- **$\mathbf{A}(x,t,v)$ —- diffusion matrix (depends in a known way by the temperature field $T(x,t)$ which may be unknown so it needs to be determined by coupling to the heat equation.)**
- **$\vec{a}$ —- describes the particle transport due to gravitational, electrical or thermal fields (determined by a set of pde coupled to the main reaction–diffusion system).**
- **$\vec{b}$ —- is the velocity of the fluid (if particles are being suspended in a flowing fluid). The whole systems needs to be also coupled to the Navier-Stokes equations.**
- **a_0 —- adsorption rate**

The whole system appears exceedingly complicated! However in many cases of physical interest T, $\vec{a}$, and $\vec{b}$ can be thought of as given.

For example if we assume that the suspended particles have no effect on the velocity distribution (as in low aerosol concentration) then we can solve the Navier–Stokes equation for $\vec{b}$ independently of the other equations.

Interesting problems

- **to prove the well–posedness of the initial value problem both in absence and in presence of diffusion**
- **to see if the continuous models are the limit (in some sense) of discrete ones**
- **to identify *the asymptotic size distribution function* via the steady state equation**
- **in case of instability of the asymptotic configuration, to have a model for *phase separation against gravity at rest* (when the final product is stored for long time) or against the combined action of gravity and shear**
- **TO CHECK THE PHYSICAL CONSISTENCY OF THE MODEL**

STATE OF THE ART

- **most of the mathematical research focuses on the discrete case (basically without diffusion) (many papers since von Smoluchowski [1917], Chandrasekhar[1943],…, Ball &Carr [1990], Bénilan & Wrzosek [1997]). The main system reduces to an *infinite system of ordinary integro–differential equations*. Works that take diffusion into account are very recent (Laurençot & Wrzosek [1998], Amann [2000]). In these papers $\mathscr{A}(x,t,v)f = -a(v)\nabla_2 f$ with $a(v)$ being non–negative constants for $v \in \dot{\mathbb{N}}$. Main interests are *existence, uniqueness, asymptotic behaviour under various functional hypotheses*.**

- **much less seems to be known for the case of continuous models (i.e. dv is the Lebesgue measure) without diffusion. Global existence and uniqueness proved by Melzak [1957] with kernels supposed to be symmetric, positive and bounded. Other results (with different methods) obtained by Aizenman & Bak [1979], McLaughlin, Lamb & McBride [1997–1998] Dubowski & Stewart [1996].**

- **ALL these papers allow v to run from 0 to $+\infty$ and claims that this — which is clearly a mathematical abstraction — is made for convenience and does not influence physical models since it can be always assumed that all the relevant kernels and coefficients vanish identically for sufficiently large or small values of v**
- **unbounded kernels and infinite domains of integration enhance the mathematical difficulties considerably**
- **In ALL these models — unless suitable ad–hoc assumptions are made on the kernels and the asymptotic decay of solutions — the conservation of volume may be violated, even for isolated systems (Simons [1983])!**
- **The failure of the volume conservation law does not occur if v is allowed to ran in a FINITE interval**

- **To keep v in a finite interval we should need some new physical mechanism able to control the growth of large particles. One could say (as Amann [2000]) that the coalescence kernel cuts off to zero at a critical upper bound or that the breakage kernel becomes singular there. However he former approach is quite unphysical, the latter destroys particles close to criticality but it doesn't affect at all the coalescence of small drops leading to droplets above criticality**

WHAT THE PHYSICS SAYS ABOUT THE TWO KEY PROCESSES

- **COALESCENCE**
  - **a) collision *does not imply* coalescence**
  - **b) usually *binary***
  - **c) evidence of a *critical size* $v_{\max}$ *for merging* droplets (droplets with $v > v_{\max}$ are *unstable* at any time)**
- **BREAKAGE**
  - **a) *several different mechanisms* (by elongation, pressure fluctuation, drop–eddy collision, erosion)**
  - **b) usually *multiple***
  - **c) experimental evidence of a *critical size* $v_{\min}$ *for breaking* droplets (droplets with $0 < v < v_{\min}$ are *stable* at any time)**

Coalescence modes in liquid–liquid dispersions:

- **by embedding and squeezing in one eddy,**
- **drops drawn together by asymmetric bombardment by small eddies,**
- **by shear coalescence (relatively slow motion)**

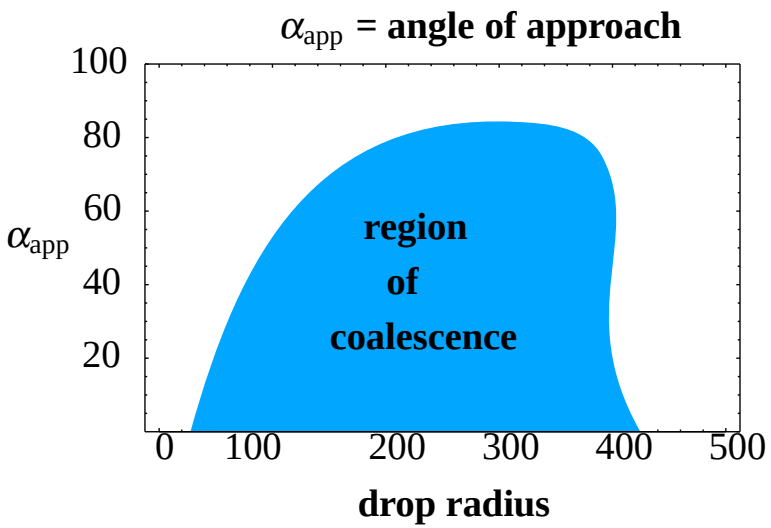

Figure 1. Coalescence region for drops of equal size (Kumar, Kumar, Ghandi [1993]). Very large and very small droplets do not coalesce regardless of the mutual angle of approach ($\alpha_{app} = 0^\circ$ means "head-on collision", $\alpha_{app} = 90^\circ$ means "grazing droplets")

PHYSICAL INTERPRETATION**: coalescence occurs by drainage and rupture of the interposed protective film.**

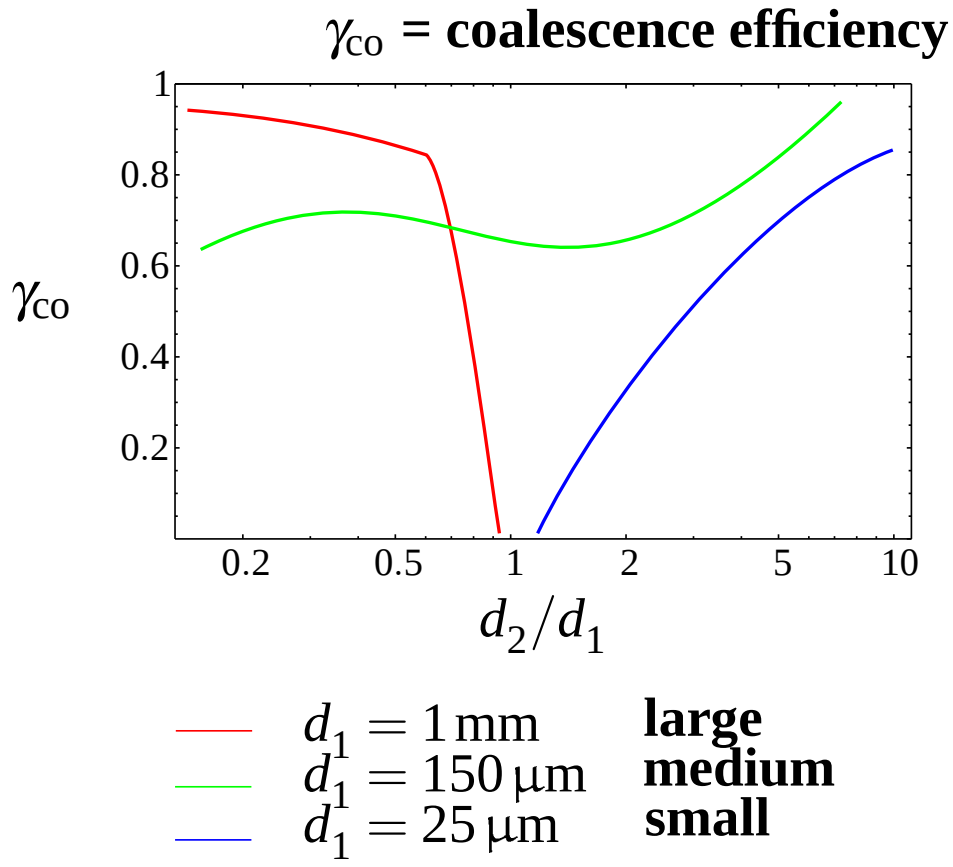

Figure 2. Coalescence efficiency *vs.* droplets ratio (Kumar, Kumar, Ghandi [1993])

(Tsouris and Tavlarides [1994])

Coalescence rate $= n_m n_j R(d_m, d_j)\lambda(d_m, d_j)$

$$
\begin{aligned}
R &= \text{collision frequency} \\
&= \kappa_1 \frac{\varepsilon^{1/3}}{1+\varphi}(d_m + d_j)^2 \left(d_m^{2/3} + d_j^{2/3}\right)^{1/2}
\end{aligned}
$$

$$
\begin{aligned}
\lambda &= \text{coalescence efficiency} \\
&= \exp\left[-\kappa_2 \frac{\mu_c \rho_c \varepsilon}{\sigma^2(1+\varphi)^3}\left(\frac{d_m d_j}{d_m + d_j}\right)^4\right]
\end{aligned}
$$

REMARK. **Even if** $\lambda \to 0$ **as** $\dfrac{d_m d_j}{d_m + d_j} \to +\infty$**, we can *fix* the product** $d_m d_j$ **letting** d_m **become *large* and** d_j **become *small* (large droplets can grow at the expense of small ones).**

SOME REMARKS ABOUT BREAKAGE

(Tsouris and Tavlarides [1994])

Possible breakage mechanisms:

- ELONGATION **in a shear flow field (Taylor [1934])**
- PRESSURE FLUCTUATIONS **in turbulence (Hinze [1955])**
- DROP–EDDY COLLISIONS **(Coulaloglou and Tavlarides [1977])**
- EROSIVE BREAKAGE **(stripping by turbulence)**

Breakage can be either *binary* or *multiple*. Erosive breakage generates a large number of very small droplets.

Breakage rate is always an *average*.

Some breakage rate formulas (independent of the breakage mode)

(Coulaloglou and Tavlarides 1977)

$$\textbf{break. rate} = \kappa_1 \frac{\varepsilon^{1/3}}{(1+\varphi_d)d^{2/3}} \exp\left[-\kappa_2 \frac{\sigma(1+\varphi)^2}{\rho_d \varepsilon^{2/3} d^{5/3}}\right]$$

- $d =$ **drop diameter**
- $\sigma =$ **inter-facial tension**
- $\rho_d =$ **density of dispersed phase**
- $\varepsilon =$ **energy dissipation rate**
- $\varphi_d =$ **volume fraction of dispersed phase (*hold–up*)**
- $\kappa_1, \kappa_2 =$ **constants**

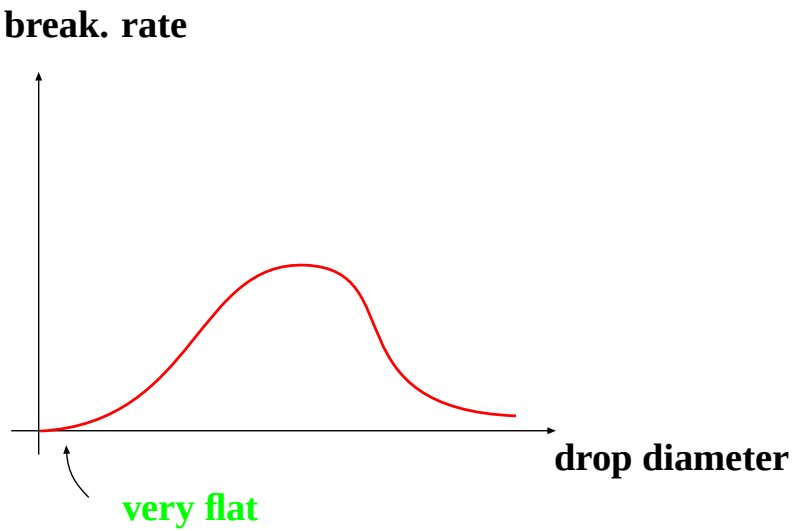

Figure 3. Breakage rate *vs.* drop size according Coulaloglou and Tavlarides

Disadvantages: existence of a maximum, positive for all *d* (even very small drops could break against experimental evidence)

(Narsimhan *et al.* (1980,1984))

$$\textbf{break. rate} = 5.75 \left(\frac{\sigma}{\rho v} \right)^{1/2} \mathrm{We}^{3.2} \left(\frac{v}{D_i^3} \right)^{1.78}$$

— $v =$ **drop volume**

— $D_i =$ **impeller diameter**

— $\mathrm{We} = \Theta^2 \rho D_i^3 \sigma^{-1}$ **Weber number**

— $\Theta =$ **agitation speed**

Disadvantage: not easy to define the size of the largest stable drop (that we called $v_{\min}$)

Diameter of the largest stable drop (Shinnar [1961])

$$d_{\text{stable}} = c\text{We}^{-0.6} D_i \frac{\mu^*}{\mu_c}$$

where $\mu^* = \mu_c \left[1 + 2.5\varphi \left(\frac{\mu_d + 0.4\mu_c}{\mu_d + \mu_c} \right) \right]$ **(Taylor [1932])**

($\bullet_c$ =*continuous phase*, $\bullet_d$ =*dispersed phase* $\bullet^*$ =*dispersion*

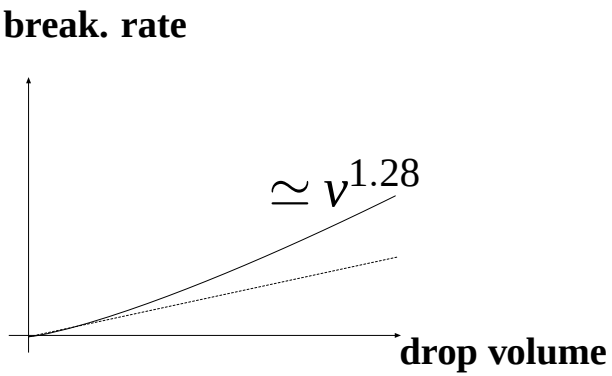

Figure 4. Breakage rate *vs.* drop size according to Narsimhan *et al.* [1980,1984]

Breakage by eddy–drop collision

- **(Prince and Blanch, [1990])**

$$\textbf{break. rate} = h(d)B$$

$h =$***eddy–drop collision frequency***, $B =$***breakage efficiency***.

- **(Tsouris and Tavlarides, [1994])**

$$h(d) = \kappa_1 \chi(\varphi)\varepsilon^{1/3} \int_{2/d}^{2/d_{e,\min}} \left(\frac{2}{\kappa} + d\right)^2$$

$$\times n_d \left(8.2\kappa^{-2/3} + 1.07 d^{2/3}\right)^{1/2} \kappa^2 \, \mathrm{d}\kappa$$

where

— κ_1 **constant**

— $\chi(\varphi)$ **damping factor**

— $d_{e,\min}$ **diameter of the smallest eddy**

— κ **eddy wave number (**$= 1/r_e$**)**

— n_d **number of drops**

— $B = \exp\left(-\dfrac{E_c}{c_1 e}\right)$

— E_c **energy for (binary) breakage**

— $c = O(1)$

— $E_c = \dfrac{1}{2}\left\{2\pi\sigma\left(\dfrac{d}{2^{1/3}}\right)^2 + \pi\sigma d_{\max}^2 + \pi\sigma d_{\min}^2 - 2\pi\sigma d^2\right\}$

In any case we have to answer the question:

what is the maximum size of the drops in a dispersion?

Experimental evidence: there is a maximum size depending on the agitation speed

Not much attention has been devoted to explaining the maximum size (the practical relevant quantity is d_{stable}, that is the size of unbreakable drops).

Conjecture: reduced coalescence efficiency for large drops is not enough to account for the existence of a maximum drop size.

Thus we need one more mechanism (in addition to coalescence and breakage). This leads naturally to a new mechanism that we called volume scattering (Fasano & Rosso [1998,2000,2001,2002], Mancini & Rosso (num. simulations) [2002], Borsi (generalizes our model [2000], Walker (generalizes our model [2001])

MATHEMATICAL DETAILS: THE KINETIC TERM ACCORDING WITH THE CLASSICAL THEORY

We neglect — for simplicity — diffusion and refer directly to continuous models for liquid–liquid dispersions in a batch reactor so the basic reactions (classically) are “coalescence” and “breakage”

We assume

— **droplets uniformly distributed in the reactor (thus $f(v,t)$ does not depend on spatial coordinates) (thus no diffusion!).**

— **whole system isolated (thus no heat or mass exchange!).**

Classical model for the distribution function $f(v,t)$ (*per unit volume*), with no diffusion and mass or heat exchange

$$\frac{\partial f}{\partial t} = L_{\text{coal}} f + L_{\text{break}} f \tag{1}$$

where

— **coagulation (or coalescence) operator**

$$L_{\text{coal}} f := \underbrace{\frac{1}{2}\int_0^{v} \tau_{\text{c}}(t,w,v-w)\, f(w,t)\, f(v-w,t)\, \mathrm{d}w}_{\text{gain}}$$

$$\underbrace{- f(v,t)\int_0^{+\infty} \tau_{\text{c}}(t,v,w)\, f(w,t)\, \mathrm{d}w}_{\text{loss}}$$

(τ_{c} coal. kernel, symmetric: $\tau_{\text{c}}(\cdot,a,b) = \tau_{\text{c}}(\cdot,b,a)$)

— **fragmentation (or breakage) operator**

$$L_{\text{break}} f := \underbrace{\int_v^{+\infty} \alpha(t,w)\beta(t,w,v) f(w,t)\, \mathrm{d}w}_{\text{gain}} - \underbrace{\alpha(t,v) f(v,t)}_{\text{loss}}$$

(α breakage frequency, β probability density of splitting $w \longrightarrow (v, w-v)$**)**

— **notice:** $v \in [0, +\infty)$ **!**

DRAWBACKS OF THE CLASSICAL MODEL

—> **In a practical experiment we deal with systems of finite volume. Thus drops with arbitrarily large size are physically meaningless!**

—> **THUS WHY $v \in [0, +\infty)$? Simply because the total volume of the dispersed phase is so much greater that the average size of droplets that the definition of f is usually extended to the whole $\mathbb{R}^+$ since it is expected that even if the support of f — as predicted by the main balance equation equation — is not bounded, *the contribution of f for large values of v will be totally negligible*.**

—> **This point of view looks reasonable within the mathematical community and commonly accepted.**

—> **However the above picture misses one fundamental feature of the process: EXPERIMENTS show there exists a *small* upper bound $\nu_{\max}$ for ν (depending on the agitation speed) beyond which no drop is observed!**

—> **THUS WHAT HAVE WE TO DO?**

—> **For example we can allow the breakage kernel to become singular at a given critical volume.**

—> **BUT THIS DOES NOT SOLVE THE PROBLEM!**

—> **WHY? Because it is unphysical, it is only a "mathematical trick" and finally – *more significantly* – because the coalescence kernel is not touched by this procedure and *droplets are not smart enough to stop their coalescence if the resulting drop would turn out to be above the admissible volume*.**

—> **Also recall that Simons' counterexample works only if $v \in [0, +\infty)$ and if this is the case also the steady–state equations leads to unacceptable conclusions!**

OUR SUGGESTION: **It seems more physical to admit that when two droplets coalesce to form a drop above the critical size, the result is a *virtual drop* that is totally unstable and breaks immediately into two or more daughters, each with volume within the admissible range. The stabilizing interaction must be a *combination* of the two well established mechanisms (coalescence+breakage). By analogy with kinetic theory we called this phenomenon *volume scattering*. This is meant as a *third mechanism* regulating the evolution of** f

$$\frac{\partial}{\partial t} f = L_{coal} f + L_{break} f + L_{scatt} f \qquad (2)$$

where $L_{scatt} f$ **also consists of one production and one loss term.**

Consistently with this picture in equation (2) v **varies in a *bounded interval*.**

BEFORE FURTHER DETAILS, A GENERAL COMMENT:

The many models proposed (all based on (1) but with different choices of breakage and coalescence kernels) have all been claimed to be consistent with experimental data.

SO WHAT IS THE NEED OF ONE MORE MODEL?

The answer is simple: $L_{\text{coal}}, L_{\text{break}}$ **contain so many parameters that it is not surprising that one can manage to fit experimental data.**

However equation (2) including volume scattering is much closer to physics and can fit the data too. Moreover – as we shall see – this new model *DOES NOT INTRODUCE ANY NEW PARAMETER*. Indeed *the scattering operator is formed with a suitable combination of coalescence and breakage, just following its physical interpretation*.

VOLUME SCATTERING (A NECESSARY INTERACTION!)

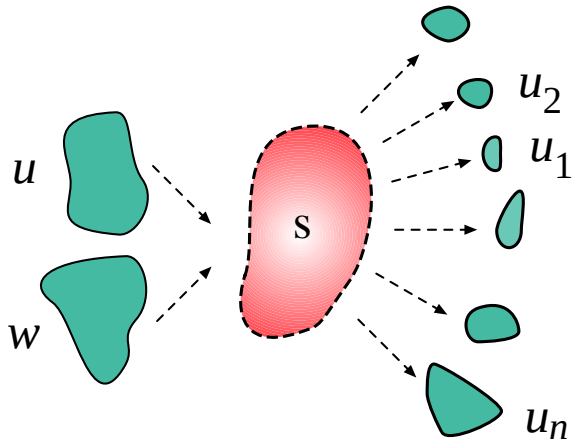

Figure 5. Scattering mechanism: droplet $s = u + w > v_{\max}$ (resulting from coalescence of u and w) is unstable and decays immediately into n "daughters" with volume $< v_{\max}$.

WITHOUT VOLUME SCATTERING THERE IS NO NATURAL MECHANISM IN THE CLASSICAL MODEL TO PREVENT THE APPEARANCE OF "LARGE DROPLETS"!

OUR MODEL (for binary breakage, but we recently extended that to include multiple breakage) with an "efficiency" factor

— **balance population equation:**

$$\frac{\partial}{\partial t} f = \varphi(t) \left(L_{coal} f + L_{break} f + L_{scatt} f \right)$$

$$\varphi(t) = \varphi\left[\mathfrak{N}(t), \mathfrak{S}(t)\right], \qquad (\textbf{ efficiency factor})$$

$$\mathfrak{N}(t) = \int_0^{v_{\max}} f(v,t)\, \mathrm{d}v, \qquad (\textbf{\# of drops p.u.v.})$$

$$\mathfrak{S}(t) = \int_0^{v_{\max}} v^{(2/3)} f(v,t)\, \mathrm{d}v, \qquad (\textbf{interfacial area p.u.v.})$$

— **coalescence operator**

$$L_{coal}\, f := \int_0^{v/2} \tau_c(w, v-w)\, f(w,t)\, f(v-w,t)\, \mathrm{d}w$$

$$- f(v,t) \int_0^{v_{\max}-v} \tau_c(v,w)\, f(w,t)\, \mathrm{d}w$$

— **breakage operator**

$$L_{break}\, f := \int_v^{v_{\max}} \alpha(w)\beta(w,v)\, f(w,t)\, \mathrm{d}w - \alpha(v)\, f(v,t)$$

— **scattering operator**

$$L_{scatt}\, f := \int_{v_{\max}-v}^{v_{\max}} \mathrm{d}w \int_{v+w-v_{\max}}^{(v+w)/2} \tau_{\mathrm{c}}(u, v+w-u)\beta(v+w, v)\, f(u,t)$$

$$\times f(v+w-u,t)\,\mathrm{d}u - f(v,t)\int_{v_{\max}-v}^{v_{\max}} \tau_{\mathrm{c}}(v,w)\, f(w,t)\,\mathrm{d}w \quad .$$

gain scatt. kernel

$$(u, v+w-u) \longrightarrow \boxed{w+v} \longrightarrow (v,w) \qquad \tau_{\mathrm{s,gain}} := \tau_{\mathrm{c}}(u, v+w-u)\beta(v+w, v)$$

loss scatt. kernel

$$(v,w) \longrightarrow \boxed{w+v} \longrightarrow (u, v+w-u) \qquad \tau_{\mathrm{s,loss}} := \tau_{\mathrm{c}}(v,w)\beta(v+w, u)$$

— NOTICE: IN THIS MODEL $v \in [0, v_{\max}]$ (PHYSICALLY MEANINGFUL).
A LOWER CRITICAL SIZE $v_{\min}$ CAN BE EASILY INCLUDED

MULTIPLE BREAKAGE (TERNARY MODE)

Ternary breakage of a droplet of volume $w \leq v_{\max}$ produces three droplets *with preservation of volume*.

The main difficulty is to describe correctly the integration domain. The trick is to select the volumes u_1, u_2 as *ordered* independent variables ($u_1 \leq u_2$) and distinguish *three cases* depending on the size of the third droplet $\widetilde{u} = w - u_1 - u_2$ compared to u_1, u_2.

(The subscript "3" means *ternary mode*)

(b_1) $u_1 \leq u_2 \leq \widetilde{u} \leq v_{\max} \Rightarrow u_1 \in (0, w/3)$ **and** $u_2 \in \left(u_1, \left(w-u_1\right)/2\right)$**, defining region** $T_{3,1}(w) \subset \mathbb{R}^2$

(b_2) $u_1 \leq \widetilde{u} \leq u_2 \leq v_{\max} \Rightarrow u_1 \in (0, w/3)$ **and** $u_2 \in \left(\left(w-u_1\right)/2, w-2u_1\right)$ **defining region** $T_{3,2}(w) \subset \mathbb{R}^2$

(b_3) $0 < \widetilde{u} \leq u_1 \leq u_2 \leq v_{\max} \Rightarrow u_2 \in \left(w-2u_1, w-u_1\right)$ **if** $u_1 \in (0, w/3)$ **while** $u_2 \in \left(u_1, w-u_1\right)$ **if** $u_1 \in (w/3, w/2)$**. Thus** $T_{3,3}(w)$ **is the union of two disjoint subregions in the plane.**

CHARACTERISTIC DOMAINS FOR BREAKAGE

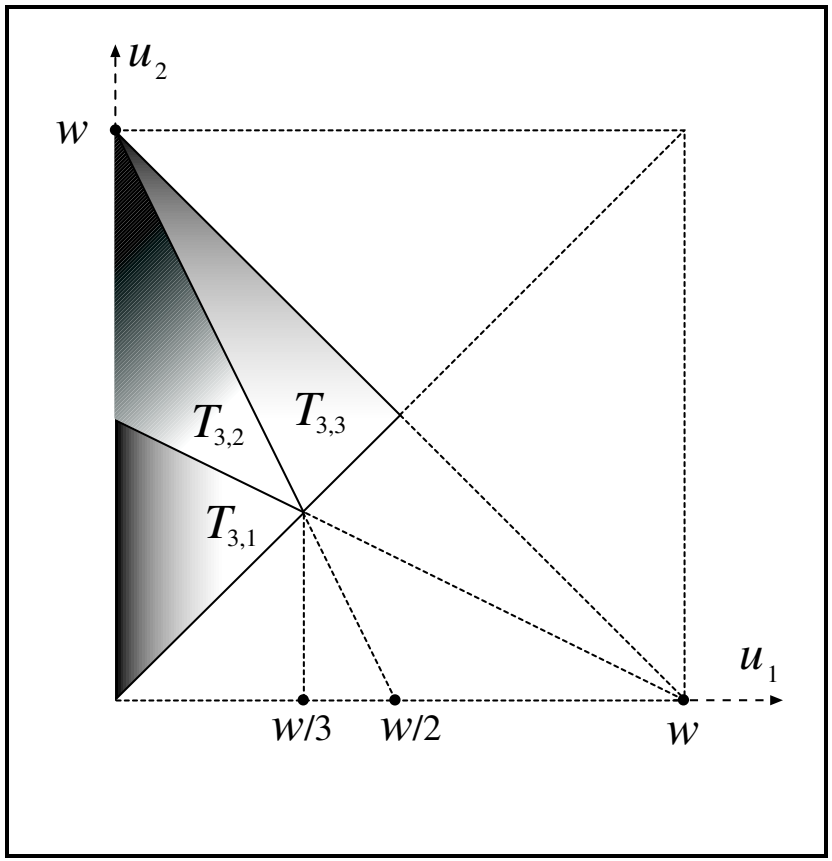

Figure 6: Triangular regions $T_{3,i}$ where β is defined. The three triangles have the same area

HOW TO DEAL WITH PROBABILITY

Mathematical strategy

— $\beta_3(w,u_1,u_2)\,\mathrm{d}u_1\,\mathrm{d}u_2$ **be the probability that two, among the daughters, have volumes in the intervals** (u_1,u_1+du_1)**,** (u_2,u_2+du_2)**.**

— **Natural normalization** $\displaystyle\int_{T_{3,1}(w)} \beta_3\left(w,u_1,u_2\right)\,\mathrm{d}u_1\,\mathrm{d}u_2 = 1.$

— **The probability density** β_3 **is then extended over the other two regions.**

CONSEQUENCE ***The probability remains the same regardless of*** $\widetilde{u}$ ***being the largest droplet, the middle or the smallest one***

OTHER CONSEQUENCES: **The *gain part* of the breakage operator writes as follows ($\widetilde{u}$ playing the role of v)**

$$L^{(3)}_{\text{b,gain}} f(v,t) = \int_v^{v_{\max}} \mathrm{d}w \int_0^{(w-v)/2} \alpha_3(w)\beta_3(w,u_1,w-v-u_1) f(w,t)\, \mathrm{d}u_1.$$

The normalization property implies that *overall production rate due to ternary breakage* is

$$\int_0^{v_{\max}} L^{(3)}_{\text{b,gain}} f(v,t)\, \mathrm{d}v \quad = \ldots = 3 \int_0^{v_{\max}} \alpha_3(w) f(w,t)\, \mathrm{d}w,$$

The *loss part* of the breakage operator is $L^{(3)}_{\text{b,loss}} f(v,t) = \alpha_3(v) f(v,t)$, the *net production* amounts to $2 \int_0^{v_{\max}} \alpha_3(w) f(w,t) dw$.

THEOREM — ***The breakage operator is volume preserving.*** **(The model is consistent!)**

SCATTERING (TERNARY MODE) **Parent droplet s now belongs to $(v_{\max}, 2v_{\max}]$. As before fix s and v and distinguish *three cases* according to the size of $\widetilde{u}$.**

(s_1) $u_1 \le u_2 \le \widetilde{u} \le v_{\max} \Rightarrow u_1 \in (0, s/3)$, $u_2 \in \left(u_1, s-u_1-u_2\right)$ **and** $s-u_1-u_2 < v_{\max}$. **This defines region** $T^*_{3,1} \subset \mathbb{R}^2$ **(notice:** $T^*_{3,1} \neq \varnothing$ **since, for** $s \in (v_{\max}, 2v_{\max})$**, the straight line** $u_1+u_2 = s-v_{\max}$ **remains always below the line** $u_1+u_2 = 2s/3$**).**

(s_2) $u_1 \le \widetilde{u} \le u_2 \le v_{\max} \Rightarrow u_1 \in (0, s/3)$ **and** $u_2 \in \left(\left(s-u_1\right)/2, s-2u_1\right)$. **This defines region** $T^*_{3,2} \subset \mathbb{R}^2$ **(notice:** $T^*_{3,1} \neq \varnothing$ **since, for** $s \in (v_{\max}, 2v_{\max})$**, the horizontal line** $u_2 = v_{\max}$ **is always above the line** $u_2 = s/3$**).**

(s_3) $0 < \widetilde{u} \le u_1 \le u_2 \le v_{\max} \Rightarrow u_1 \in (0, s/3)$ **it must be** $u_2 \in \left(s-2u_1, s-u_1\right)$ **while, if** $u_1 \in (s/3, s/2)$**, the correct bounds are** $u_2 \in \left(u_1, s-u_1\right)$. **This defines region** $T^*_{3,3}(s) \subset \mathbb{R}^2$

CHARACTERISTIC REGIONS FOR SCATTERING

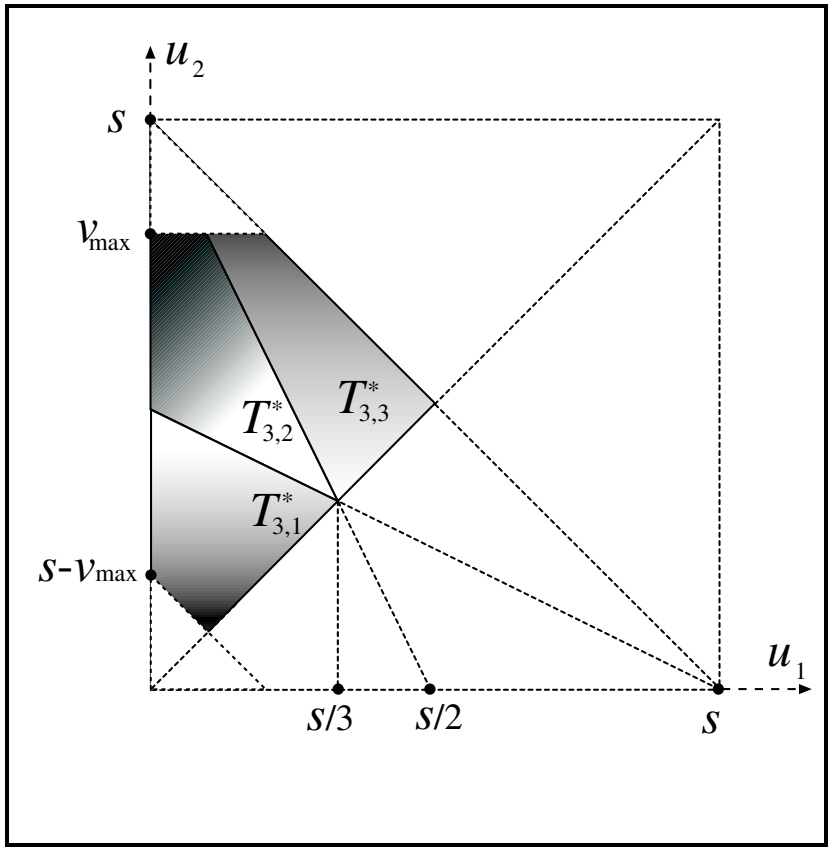

Figure 7: Triangular regions $T^*_{3,i}$ where β is defined. The three triangles have the same area

The same argument developed for the breakage case still applies: β_3 is extended for $s \in (\nu_{\max}, 2\nu_{\max})$ in such a way that

$$\int_{T^*_{3,1}(s)} \beta_3 \left(s, u_1, u_2\right) du_1 du_2 = 1.$$

A suitable plane transformation shows that

$$\int_{T^*_{3,1}(s)} \beta_3 \left(s, u_1, u_2\right) du_1 du_2 = 1$$

$$= \int_{T^*_{3,2}(s)} \beta_3 \left(s, u_1, u_2\right) du_1 du_2 \qquad (3)$$

$$= \int_{T^*_{3,3}(s)} \beta_3 \left(s, u_1, u_2\right) du_1 du_2.$$

SCATTERING OPERATOR

Put $L_s = L_{\text{s,gain}} - L_{\text{s,loss}}$; then

$$L_{\text{s,gain}} f(v,t) = \int_{\Omega(v)} S_g(s,u,u_1,u_2 \mid v = s-u_1-u_2)\, \mathrm{d}\omega$$

$$L_{\text{s,loss}} f(v,t) = \int_{\Lambda(v)} S_\ell(s,v,u_1,u_2)\, \mathrm{d}\lambda$$

where

$$S_g = \tau_c(u,s-u)\beta_3(s,u_1,u_2) f(u,t) f(s-u,t),$$
$$S_\ell = f(v,t) f(s-v,t) \tau_c(v,s-v)\beta_3(s,u_1,u_2)$$

and

$$\int_{\Omega(v)} \mathrm{d}\omega \quad = \int_{v_{\max}}^{v_{\max}+v} \mathrm{d}s \int_{s-v_{\max}}^{s/2} \mathrm{d}u \int_{0}^{(s-v)/2} \mathrm{d}u_1$$

$$+ \int_{v_{\max}+v}^{2v_{\max}} \mathrm{d}s \int_{s-v_{\max}}^{s/2} \mathrm{d}u \int_{s-v-v_{\max}}^{(s-v)/2} \mathrm{d}u_1,$$

$$\int_{\Lambda(v)} \mathrm{d}\lambda \quad = \int_{v_{\max}}^{v_{\max}+v} \mathrm{d}s \iint_{T_3^*(s)} \mathrm{d}u_1 \, \mathrm{d}u_2.$$

The normalization condition for β in the scattering region implies

$$\int_{\Lambda(v)} S_\ell(s,v,u_1,u_2) \, \mathrm{d}\lambda \; = 3 f(v,t) \int_{v_{\max}}^{v_{\max}+v} f(s-v,t) \tau_c(v,s-v) \, \mathrm{d}s.$$

THEOREM — ***The scattering operator is volume preserving*** **(The model is consistent!)**

Assume reasonable regularity conditions on β, α, τ_c (such as continuity, boundedness,...).

MAIN THEOREM — ***Let f_0 be a Lipschitz continuous initial size distribution on $[0, v_{\max}]$. Then the Cauchy problem for the mathematical model***

$$\frac{\partial}{\partial t} f = \varphi(t) \left(L_{coal} f + L_{break} f + L_{scatt} f \right)$$

(with both binary and multiple modes) is well posed. The unique solution f is non–negative, exists for all times, continuously differentiable with respect to time and Lipschitz continuous with respect to v

Notice: the extension to *higher order modes* is only a matter of increasing mathematical complication but the strategy remains the same.

EXISTENCE and UNIQUENESS: sketch of the proof

NUMERICAL SIMULATIONS

PRELIMINARY REMARKS

— **Simulations consider the binary mode only (the addition of the sole ternary mode increases considerably the computational time!)**

— **Our model applies to any kind of fluid–fluid dispersion (with no chemical reactions) since it is just based on the *mechanics* of breakage and coalescence. However the selection of the parameters of the model (the *coalescence kernel* τ_c, the *breakage-frequency* α and the probability distribution β), able to fit the effective behavior of a real dispersion, is really a hard problem.**

— **We used the simplest possible equations for the kernels based just on geometrical and mechanical considerations (with an eye also towards technical papers. . . !)**

REMARKS ABOUT THE INTEGRATION DOMAIN

— **Mathematically $v_{\max}$ is a *fixed* upper bound for the volume size of droplets independent of time.**

— **In practice characteristic length scales for f_{o} and $f(v,\infty)$ may differ even by two or three orders of magnitude. Define**

$$v^{\star}(t) = \sup \operatorname{supp} f(v,t);$$

clearly $v^{\star}$ depends, besides t, on the rotational speed Θ, the geometry of the container and impeller, the hold-up λ, the temperature and many other rheological parameters

— **Mathematically we put the lower bound for the volume of breakable drops $v_{\min} = 0$ in all simulations.**

— **In practice $v_{\min}$ is given by (Weber relation)**

$$v_{\min} = 10^{-4}\pi D^3 We^{-1.8}, \qquad \left(We := \frac{\Theta D^3 \rho_c}{\sigma}\right)$$

where σ, ρ_c and D are the surface tension, the density of the dispersed phase and the impeller diameter respectively.

EXAMPLE**: for** $\sigma = 29$ **dyne/cm,** $\rho \simeq 1\ \mathrm{gr}/\mathrm{cm}^3$ **and** $D = 15$ **cm**

Θ **(in r.p.m.)**	$v_{\min}$ **(in cm^3)**
1000	$8.094\,10^{-9}$
2000	$6.675\,10^{-10}$
3000	$1.550\,10^{-10}$
4000	$5.505\,10^{-11}$
5000	$2.465\,10^{-11}$
6000	$1.278\,10^{-11}$
7000	$7.342\,10^{-12}$
8000	$4.540\,10^{-12}$

CONSEQUENCE:

$v^\star(\infty)/v_{\min} \simeq 10^4$ **for** $\Theta \simeq 4000 \div 6000$ **r.p.m. (which is a rather standard rotational speed in industrial applications). This means that only with a very large sampling in the** v **axis (something like** 10^5 **or more nodes in the** v **direction) the numerical code is able to appreciate the effect of** $v_{\min} \neq 0$**. Being all the simulations done with nodes on the** v **axis spaced not less than** $.01$ **units, we consistently set** $v_{\min} = 0$**.**

EXAMPLE: **for a water–in–oil dispersion, temperature** $\simeq 60\ ^{\circ}C$**, high rotational speeds (**$\simeq 4000 - -6000$ **r.p.m.), hold-up** $\simeq 60\%$**, and an agitation time of about** 15 **minutes, the top size diameter is** $\simeq 60 \div 70$ μm**. This can be identified with the asymptotic value since there is practically no change for** $t > 15$ **minutes. This means, for this case, that we can set** $v^{\star}(\infty) \simeq 10^{-7}\,\mathrm{cm}^3$**; since typical values of the maximum diameter at the very early stages of agitation is about ten times larger than the initial ones, we have**

$$\frac{v^{\star}(\infty)}{v^{\star}(0)} \simeq 10^{-3}.$$

CONSEQUENCE:

Thus, in cases like the above, it is quite difficult to show graphically the evolution of f from f_o using the same length scale v_{max}. In these cases we did not use the effective initial data but rather an intermediate configuration with a characteristic length much closer to that of the expected asymptotic distribution. Physically this corresponds to a *pre–mixing* period before examining the evolution.

Choice of the initial distribution and kernels

Initial distributions $f_o(v)$ we considered:

- **a *a Gaussian distribution function* centered somewhere about the middle of the normalized droplet size interval**

$$f_o(v) = k\exp(-(v-\mu)^2/2\sigma^2)$$

- **a *piecewise constant function***

$$f_o(v) = \begin{cases} k & \textbf{if} \quad v \in [0.2, 0.6], \\ 0 & \textbf{otherwise}, \end{cases}$$

$$\lambda = \int_0^1 v f_o(v)\, \mathrm{d}v \in (0,1) \qquad (\textit{given hold-up})$$

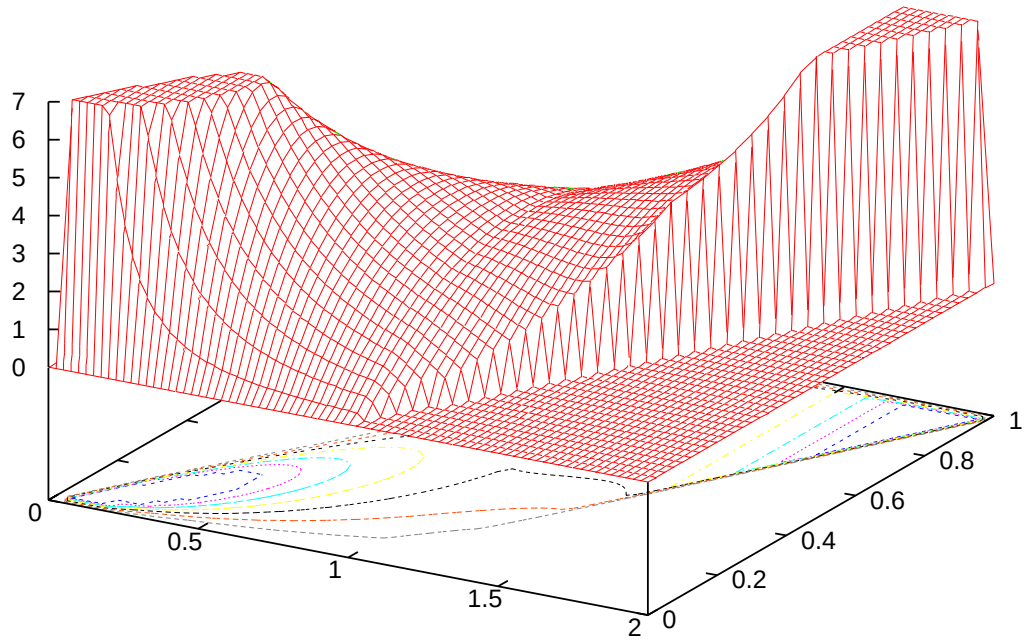

Figure 8. Probability distribution density β

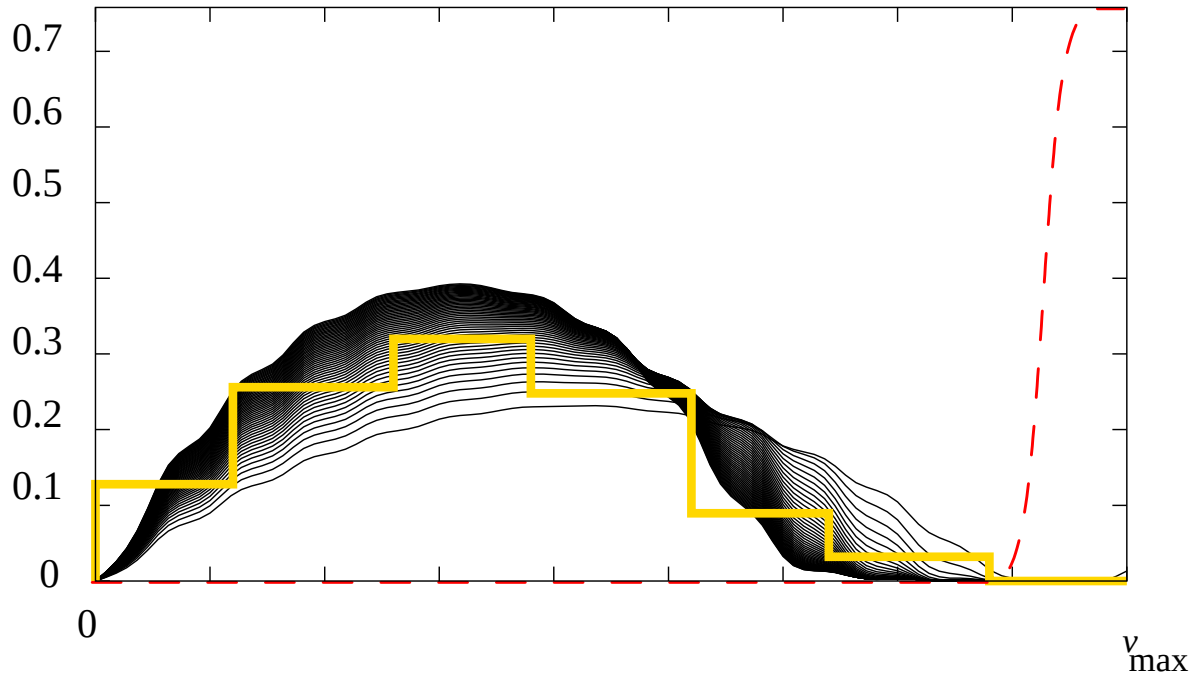

Figure 9. Evolution from a stepwise initial data (dashed) towards a final distribution (solid lines). The asymptotic shape fits one of the experimental curves (histogram) and obtained with a high-speed rotational impeller (ultra-Turrax at 8000 r.p.m.); v_{max} **is about** 70 μm

Breakage frequency:

$$\alpha(w) = A_{\min} w^q, \qquad q > 0, \tag{4}$$

Coalescence kernel:

$$\tau_c(v,w) \quad = A_c \left(v^{\frac{1}{3}} + w^{\frac{1}{3}} \right)^2 \exp\left[- \left(\frac{v^{1/3}+w^{1/3}}{v^{1/3} w^{1/3}} \right)^4 \right], \tag{5}$$

Proportionality factors depend on the rotational speed: we set $A_{\min}(\Theta) = \overline{A}_{\min}\Theta$, $A_c(\Theta) = \overline{A}_c(\overline{\Theta} - \Theta)\Theta$, where $\overline{A}_{\min}$, $\overline{A}_c$, $\overline{\Theta}$ are constants which typically depend on the rheology, geometry and the hold-up λ.

The expression for A_c is suggested by the fact that in most cases the coalescence efficiency increases with Θ up to a maximum and then reduces drastically for high rotational speeds.

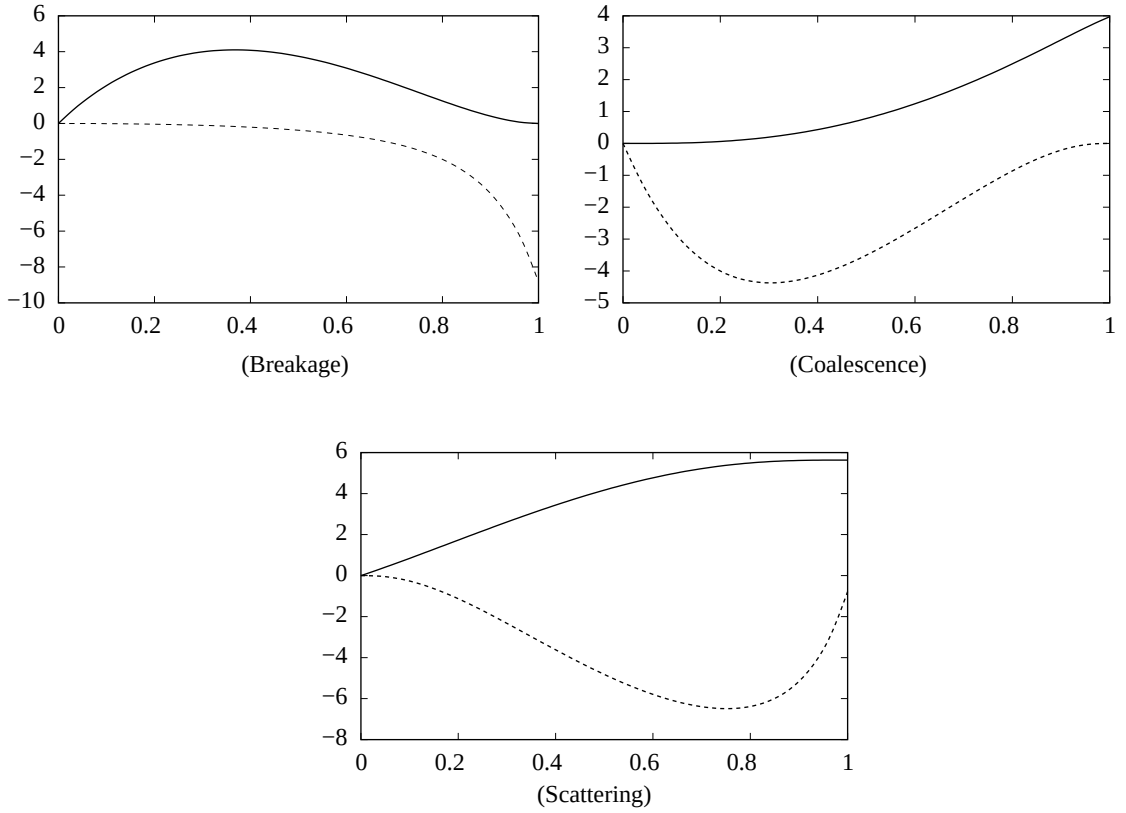

Figure 10. Mutual importance at equilibrium (large t) of breakage, coalescence and scattering terms at low rotational speed; the dashed line represents the loss term, the solid one the gain term

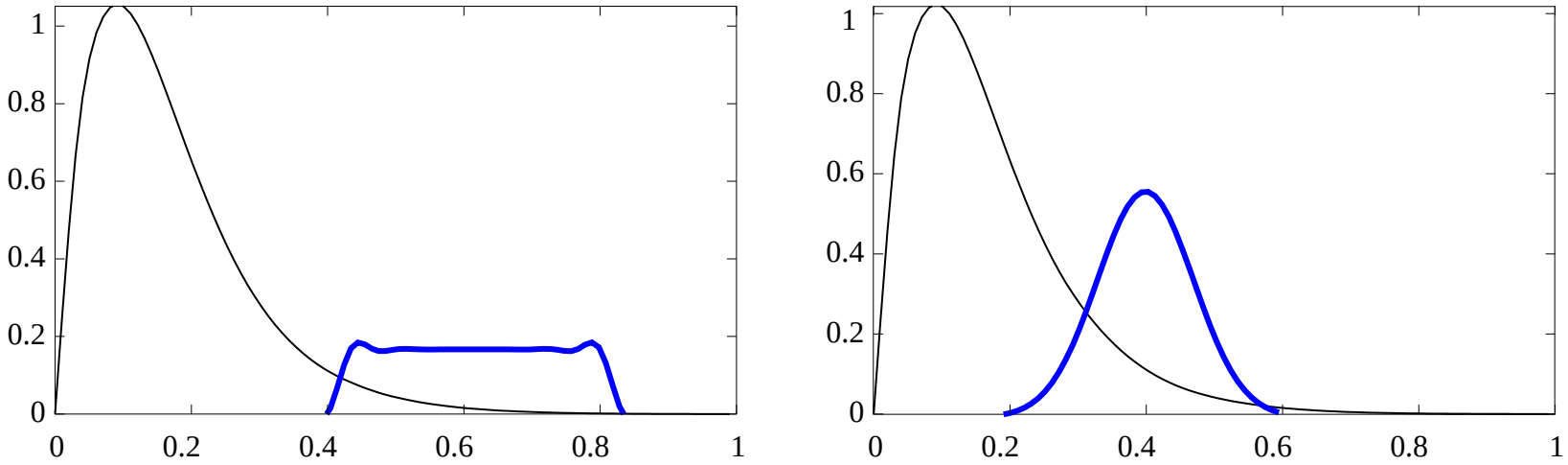

Figure 11. Invariance of the asymptotic configuration with respect to $f_{\mathrm{o}}(v)$: in the two cases considered the volume of dispersed phase (*hold–up)*) is the same but the shape of the initial distribution is totally different