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The “Volume Scattering” Effect in The Dynamics of Liquid–Liquid Dispersions

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A dispersion of a liquid in another liquid is produced by stirring a mixture of the two components in a vessel with, say, rotating impellers. Because of the importance of such systems in a number of industrial applications, there is an extensive literature on various aspects of their dynamics, from both the experimental and the mathematical point of view, beginning with the celebrated papers of M. von Smoluchowski [20], S. Chandrasekhar [5], and Z.A. Melzak [17]. Our research group in Florence became interested in this subject a few years ago, when Snamprogetti, a large Italian firm, involved us in the study of dispersions of mineral oils in water.

An understanding of the dynamics of systems of evolving droplets has a fundamental role in a variety of settings, such as the food, cosmetic, and drug industries, meteorology, and the study of photographic emulsions [4]. There are also more exotic applications: For instance, emulsification is a basic step in the preparation of catalysts for the Ziegler–Natta polymerization process (see [16]). The dynamics of polymer chains are strikingly similar to those of droplets in dispersions; indeed, the coagulation and fragmentation of molecule segments are close analogues of the coalescence and breakage of drops. A number of recent studies of coagulation and fragmentation processes have emphasized such interesting properties as sol–gel transitions (see, for example, [8], [11]). The dynamics of particle clusters in a suspension is also driven by a coagulation–fragmentation mechanism (see the recent paper [2]).

Traditional Models Reconsidered

The state of a spatially homogeneous liquid–liquid dispersion is described by a distribution function $f\,(v,t)$, such that $f\,dv$ represents the number of droplets whose volume is in the interval $(v,\ v\ +\ dv)$. The main processes influencing the evolution of f are coalescence and breakage. The physics of the coalescence and breakage of droplets in dispersions has been examined in a large number of papers. Both processes can result from different kinds of interactions of pairs of droplets, or of a droplet with the continuum phase (see [6] for some references).

The first significant mathematical paper [17], which appeared in 1957, was followed by many others. A remarkable overview can be found in the recent paper of H. Amann [1], which deals with the particularly difficult aspects of spatially nonhomogeneous dispersions. All mathematical models proposed prior to the one developed by our group in Florence [6] are of the type

$$\frac{\partial f}{\partial t} = L_c f + L_b f, \tag{1}$$

where L_c and L_b are the coalescence and breakage operators, to be described later.

In the construction of L_c and L_b, v is usually allowed to take any positive value. Although it is clearly meaningless to consider drops of arbitrarily large volume, writing an evolution model is much simpler if v varies in $(0, \infty)$. Indeed, coalescence does tend to produce “large” drops, and the step from the vague concept of “large” to infinity has always been considered physically irrelevant. Of course, $f(v,t)$ has to tend to 0 sufficiently fast when v tends to ∞.

This article reconsiders the question of consistently including an upper limit on droplet volume in the model, for the following reasons:

(1) experimental evidence indicates that for a given agitation speed of the mixture, there is indeed a maximum observable volume of the dispersed droplets (see, for example, [19]);

(2) eliminating the unphysical range of droplet volume is not just an aesthetic operation; on the contrary, it emphasizes the presence of a different physical mechanism in the evolution of the system, as discussed in this article;

(3) as is quite often the case, when the physics is respected, the mathematics becomes simpler.

Our recently developed model [6] introduces a maximum admissible volume: When a droplet produced by coalescence has a volume that exceeds the imposed threshold, it must immediately decay into two (or more) droplets that are within the admissible volume range. This mechanism is called *volume scattering,* being nothing but the scattering of a scalar quantity. The corresponding term in the evolution equation for the distribution function $f(v,\ t)$ looks very much like the collisional operator in Boltzmann’s equation.

In this article, we analyze the implications of the new approach, referring to the simple case of a spatially homogeneous system with one dispersed phase, sufficiently diluted that only binary collisions among droplets can be considered.

Coalescence and Breakage

These processes are far more complicated than simple intuition might suggest. Because space constraints do not permit a detailed analysis of the literature, we cite [9], [14], [21], [22] and confine the discussion here to a sketch of some general ideas.

In the turbulent motion generated by impellers, droplets can be brought to collision by various mechanisms. In the simplest, two droplets approach each other in a relatively slow motion, in which we can define an incidence angle. Roughly speaking, we can say that (in the unit volume) *coalescence frequency* = *collision frequency* × *coalescence efficiency*, with the latter quantity measuring the fraction of collision events that lead to coalescence.

Considering the ideal case of two spherical (nonspinning) droplets of equal size, once we have fixed the physical properties of the system (density and viscosity of each phase, interfacial surface tension, shape and speed of the impellers), the two drops may or may not coalesce, depending on the incidence angle [9]. It is intuitively understood that grazing droplets will not coalesce; even head-on collisions may not lead to coalescence, however, if the drops are too small or too large. Indeed, during collision the two droplets are separated by a film of the continuum phase, which has to be drained and eventually broken to produce coalescence. However, the situation can change radically for droplets of different sizes (see [9]), for which the coalescence efficiency can be close to one; in principle, then, we can say that the formation of large droplets by coalescence is possible.

High-energy collisions may instead produce breakage—a possibility contemplated in a very recent paper [26], refining the model of [6]. Besides such shattering events, there are other, more usual mechanisms by which breakage occurs. The best known is breakage by elongation in a shear rate field, but in turbulent regimes there are also ruptures due to local pressure fluctuations, drop-eddy collisions, and even erosive breakage (stripping by turbulence), which generates a large number of tiny drops. Therefore, the rate of breakage must be understood as an average to which various mechanisms may contribute. Interesting simulations of breakage events can be seen at *http://www.math.vt.edu/people/renardyy/movies.html*. The underlying model is described in [12].

An effective way to describe the breakage rate is to introduce a breakage frequency (depending on the parent volume w) and a probability density for the production of daughter droplets of volume $v < w$. A very important quantity is the maximum size v_b of stable droplets, which will basically determine how fine the dispersion will be. For $v < v_b$, the breakage frequency is zero. It is generally agreed that the diameter d_{max} of unbreakable droplets is

$$d_{max} = cWe^{0,6}D, \tag{2}$$

where c is constant, D is the impeller diameter, and

$$We = N^2\rho D^3\sigma^{-1}. \tag{3}$$

We is the Weber number; N denotes the angular speed of the impeller, ρ the density of the dispersed phase, and σ the interfacial surface tension.

Volume Scattering

As mentioned earlier, for a given geometry and speed of the stirrer, we can observe not only the existence of unbreakable droplets, but also evidence that droplets beyond some volume v_0 cannot persist for any time. Of course, the former is much more important in the design of a dispersion-producing device, which probably explains why very little attention has been devoted to v_0. Some authors [23], [24] have included it in the evolution model for f, but only as an artificial cutoff. The question for our group was, How could we consistently describe the evolution of f, keeping an upper bound for droplet volume?

It would not make much sense to impose a cutoff on coalescence efficiency, because drops are not smart enough to guess the result of their coalescence. We could force breakage by letting the breakage frequency go to infinity as the volume approaches v_0. However, we would still have to deal with the question of excessively large droplets produced by coalescence.

The natural answer to this question is to say that on the coalescence of two droplets of volume v and w, with $v < v_0$, $w < w_0$, and $v + w > v_0$, the resulting droplet is just virtual and immediately decays into two or more droplets in the admissible range. If we confine ourselves to binary breakage, this process is simply the scattering of a scalar quantity (volume), which explains the name *volume scattering*. The main point is that volume scattering, coalescence, and breakage need to be considered as equally important mechanisms for the evolution of the system.

The Evolution Model

Having established the necessity of modeling volume scattering, we return to the evolution equation (1), replacing it with

$$\phi^{-1}\frac{\partial f}{\partial t} = L_c f + L_b f + L_s f, \tag{4}$$

where we have introduced not only the scattering operator L_s, still to be defined, but also an efficiency factor ϕ, which can be taken as

$$\phi(t) = \Phi(N(t),\sigma(t)), \tag{5}$$

with

$$N(t) = \int_0^{v_0} f(v,t)\,dt,$$

$$\sigma(t) = \int_0^{v_0} (4\pi)^{\frac{1}{3}} (3v)^{\frac{2}{3}} f(v)\,dv \tag{6}$$

representing the total number of droplets and their total surface area, respectively. The presence of ϕ is justified by the fact that the efficiency of the various processes depends on the power dissipated and, ultimately, on the structure of the system.

Referring, for simplicity, to the specific case of binary breakage, we write and briefly discuss the three operators in (5):

$$\begin{aligned} L_c f(v,t) = \int_0^{\frac{v}{2}} & \tau_c(w, v-w) \\ & f(w,t)\, f(v-w,t)\,dw, \\ & - f(v,t) \int_0^{v_0 - v} \tau_c(v,w) f(w,t)\,dw. \end{aligned} \tag{7}$$

Here, $\tau_c(v,w)$ is the coalescence kernel, a symmetric function of its arguments. The two integrals represent the gain and loss rates, respectively, of droplets of volume v due to coalescence,

$$\begin{aligned} & L_b f(v,t) = \\ & \int_v^{v_0} \alpha(w) \beta(w,v) f(w,t)\,dw - \alpha(v) f(v). \end{aligned} \tag{8}$$

The gain rate integral counts the droplets of volume v generated in one second in the unit volume by breakage of larger droplets: $\alpha(w)$ is the frequency; $\beta(w,v)$, the probability density for the fraction of breakage events leading from w to the pair $(v, w - v)$, is normalized as follows:

$$\int_0^{\frac{w}{2}} \beta(w,v)\,dv = 1, \quad \beta(w,v) = \beta(w, w-v). \tag{9}$$

The last term in (8) is the cumulative rate of loss by breakage in the droplet class labelled v:

$$\begin{aligned} L_s f(v,t) = \int_{v_0 - v}^{v_0} dw & \int_{v+w-v_0}^{\frac{v+w}{2}} \\ & \tau_s(u, v+w-u; v, w) \\ & f(u,t)\, f(v+w-u,t)\,du \\ & - f(v,t) \int_{v_0 - v}^{v_0} f(w,t)\,dw \\ & \int_{v+w-v_0}^{\frac{v+w}{2}} \tau_s(v, w; u, v+w-u)\,du. \end{aligned} \tag{10}$$

The scattering kernel

$$\tau_s(a, b; c, a + \mathrm{b} - c) = \tau_c(a, b)\, \beta(a + b, c) \tag{11}$$

combines coalescence and breakage. The rate of gain by scattering is obtained by summing the events that lead from pairs of cumulative volume larger than v_0 to a drop of volume v. The loss rate counts all scattering events involving drops of volume v. Of course, we must again normalize β,

$$\int_{v_0}^{\frac{s}{2}} \beta(s,u)\,du = 1, \tag{12}$$

thus reducing the loss rate term in (10) to

$$-f(v,t)\int_{v_0-v}^{v_0} \tau_c(v,w)\,f(w,t)\,dw, \tag{13}$$

which is the natural continuation of the analogous term in (8). Equation (4) must be complemented with the initial condition

$$f(v,0) = f_0(v). \tag{14}$$

Assuming f_0 to be non-negative and Lipschitz continuous, and with some regularity properties on the kernels (in particular the boundedness of $\alpha(w)$), an existence and uniqueness theorem is proved in [6], showing that the solution f is non-negative, Lipschitz continuous in v, and continuously differentiable in t. In [3] the same results have been extended to cover the case $\lim_{w\to v_0}\alpha(w) = +\infty$, implying in particular $f(v_0) = 0$. Considerable simplification can be obtained by working in a space of summable functions. As pointed out in [26], the existence proof then becomes straightforward and requires fewer assumptions on the kernels.

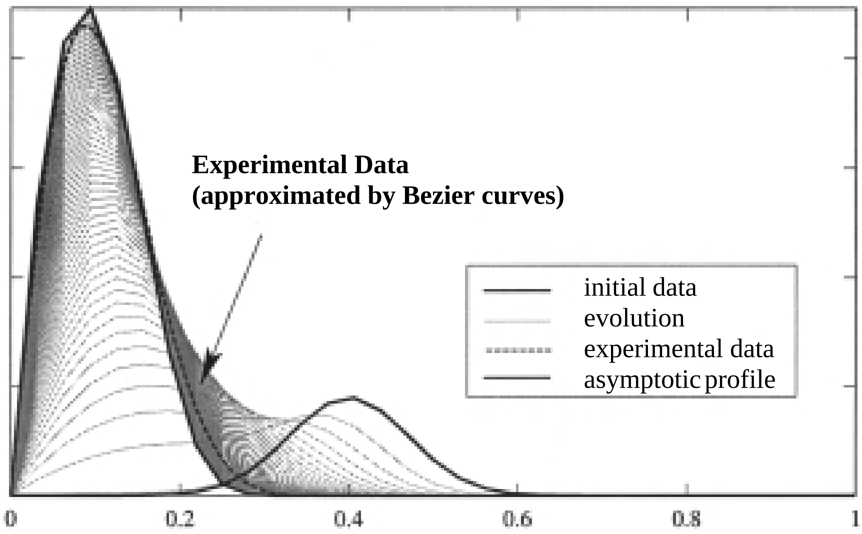

Figure 1. *Evolution from bell-shaped initial data toward a final distribution. The asymptotic shape fits one of the experimental curves in [18], obtained with a high-speed rotational impeller (ultra-Turrax).*

Passing from binary to multiple breakage is not difficult. It is of course necessary to remove the specific symmetry requirement on β (see(9)). A quite recent study analyzed the contributions of each breakage mode, assuming that the corresponding frequencies and probability distributions of products can be prescribed [7]. Numerical simulations can be found in [14], where the model is shown to fit the experimental data of [19] (see Figure 1).

An important open question is the study of the stationary solution of (4). Some results on long-time behaviour have been obtained [25].

Modeling the dynamics of the size distribution of evolving particles, with physical bounds imposed on their volume, seems even more important in other situations. This is certainly the case for systems of crystals growing in supersaturated solutions, governed by the so-called Lifshitz–Slyozov–Wagner equation [13],[25] (see in particular [10], [18]). It has been proved that when the crystal volume is allowed to take any positive value, the asymptotic behaviour of the system is essentially dominated by the tail of the distribution function as it extends to infinity, i.e., into the nonphysical range. How the model can be modified so to eliminate the leading role of the distribution tail is also a very interesting open problem.

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