Evolution of the Cluster-size Distribution in Stirred Suspensions

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Based on combinatorics, a simple model for predicting the steady-state cluster or drop-size distribution in suspensions undergoing simultaneous coagulation and break-up due to rapid stirring was recently proposed (R. D. Cohen, *J. Chem. Soc. Faraday Trans.*, 1990, **86**, 2433). This work extends that model to account for the evolution of the size distribution in stirred systems. The method utilizes the concept of the distribution entropy, and suggests a means for predicting the characteristics of the size distribution as the system approaches steady state. Among the important results is that the distribution functions (size, volume *etc.*) are path dependent. Furthermore, along the 'most probable entropy path', the cluster-size distribution remains closely related to the Poisson distribution up to and including steady state. Another interesting finding is that, along the mentioned path, the distribution functions are concentration specific (intensive property) as long as they are in their transient state. These ultimately become number specific (extensive property) once they reach steady state.

Owing to its important implications in the chemical industry, the behaviour of liquid droplet and colloidal dispersions in stirred vessels arouses great interest within the chemical engineering field. As noted from the amount of relevant papers in the literature, this subject has been studied extensively.

It is well known that the mixing of two immiscible liquids forms a dispersion in which coalescence and break-up of the liquid droplets occur simultaneously. Likewise, the same applies when the dispersion comprises colloidal particulates, in which case the end result is the coagulation and break-up of the aggregates. Also known is that if mixing persists over a sufficiently long period of time, a dynamical equilibrium or steady state is established where, beyond this point, the drop- or cluster-size distribution attains a form which remains practically unchanged with time.

Numerous investigations related to this topic have produced measurements of drop-size distributions in stirred vessels. Some of these have concluded that this dynamical equilibrium is accomplished when the rate of break-up equals exactly the rate of coalescence.[1] Many others, on the other hand, have conclusively demonstrated that equilibrium can be achieved even when there is no further coalescence.[2] This was shown to occur when the turbulence microstructure acts together with the particle–fluid and particle–particle interactions in such a manner that, beyond a certain limit, any further break-up of the droplets is completely prevented.

This paper is concerned primarily with the case where both coagulation and break-up occur simultaneously within the agitated system. This, of course, is in contrast to the situation mentioned above which involves only the fragmentation of larger clusters or drops into smaller ones.[2,3] The main objective of this work is to extend a recently proposed steady-state model[4] to account for the evolution of the cluster-size distribution during rapid mixing. A brief discussion of the steady-state model and the derivation for the present case follow in the next sections.

Problem Formulation

Consider a suspension that initially contains a large number of clusters, each composed of a certain number of primary particles or units. Depending on the nature of the primary units, the clusters may be agglomerates of solid colloidal particulates or drops of liquid formed by, respectively, aggregation or coalescence.

Related studies have consistently shown that vigorous stirring carries the cluster-size distribution through a transient or temporal stage until ultimately steady state is achieved.[2,5] Furthermore, if both coagulation and break-up were to occur at random due to stirring, then the steady-state size distribution becomes independent of the input cluster sizes.[1]

As mentioned above, the clusters in the system may be either aggregates or drops. The primary units forming these clusters will be assumed to be monodisperse, each with diameter d_{min}.

Consider now an experiment in which a suspension is being stirred so rapidly that all effects due to Brownian motion and surfaces interactions (such as DLVO) are overwhelmed by the shearing forces and pressure fluctuations of the mixing which cause coagulation and break-up to occur. At some point in time during mixing, there will be a given number of clusters in the suspension. This number shall be denoted by N. We should realize that while N changes with time, the total number of the primary particles in the system remains a constant, equal to N_0. Consequently,

$$N = \sum_{i=1}^{N_0} N_i \tag{1}$$

and

$$N_0 = \sum_{i=1}^{N_0} iN_i \tag{2}$$

where i is the cluster size or the number of primary units in a cluster and N_i is the instantaneous number of clusters with size equal to i.

Following the scheme proposed by Cohen,[4] we assume that the coagulation and break-up processes occur completely at random so that at any stage, the size distribution is determinable by combinatorics. This is a result of the vigorous and homogeneous stirring overcoming all effects due to surface interactions. Avoiding the details, we make use of the expression

$$\Omega(N_1, N_2, N_3, \ldots) = \frac{N_0!}{\prod_{i=1}^{N_0} N_i! [i!]^{N_i}} \tag{3}$$

where $\Omega(N_1, N_2, N_3, \ldots)$ is the degeneracy or the total number of ways in which the particles in the dispersion can be distributed into N_1 clusters of size $i = 1$, N_2 clusters of size $i = 2$, N_3 clusters of size $i = 3$ and so on. Upon combining eqn. (3) with the conservation constraint of eqn. (2), we obtain