A MODEL FOR TRANSITIONAL BREAKAGE PROBABILITY OF DROPLETS IN AGITATED LEAN LIQUID-LIQUID DISPERSIONS

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Abstract—A model for transitional breakage probability of droplets in agitated lean liquid-liquid dispersions is proposed based on the mechanism of breakage of droplets due to their oscillations resulting from relative velocity fluctuations. A universal transitional breakage probability in terms of non-dimensionalized drop diameter is derived for all dispersed phases whose density and viscosity are almost the same as that of continuous phase. The maximum stable drop diameter $d_{\text{ms}}$, derived from the model, shows a dependence of $N_{\omega e}^{0.6}$. It is shown that a "power law" approximation $K d^m$ is valid for transitional breakage probability for $d/d_{\text{ms}}$ up to 2. The exponent $m = 0.67$, predicted by this model corresponds rather well with an estimate of 0.6 obtained from experimental observations. A functional relation for the rate constant $K$ in terms of the parameters and physical properties of the system is derived. A universal non-dimensionalized equilibrium drop-size distribution for agitated lean liquid-liquid dispersions is derived by analytical solution of a population balance equation simplified by order of magnitude estimates. Interestingly enough, this analytical solution is the same as the Gaussian distribution suggested empirically by Chen and Middleman.

INTRODUCTION

Drop size distributions in liquid-liquid dispersions evolve due to the dynamics of breakage and coalescence. Evolution of drop size distribution is important for prediction of, interfacial area, heat and/or mass transfer in liquid-liquid dispersions. Attempts have been made [1-3] to predict the drop size distribution in liquid-liquid dispersions using population balance equation. If considerations are restricted to lean dispersions (i.e. with low dispersed phase fractions), only breakage need be considered as coalescence is negligible due to very little interaction of droplets. Dynamics of breakage in agitated dispersions have been characterized by transitional probability of breakage [1-3] defined as,

$$\frac{d_2}{L} = c(N_{\omega e}^{-0.6}, c = \text{a constant})$$

Measurements of energy spectrum in the impeller stream of a baffled agitated vessel [12-14] have shown the existence of a "$-5/3$ slope" region, as predicted by Kolmogorov's theory of local isotropy. The applicability of the above theory in the case of agitated liquid-liquid dispersions was illustrated experimentally [7].

The purpose of this paper is to derive an expression for the transitional breakage probability for agitated lean dispersions on the basis of a model proposed for breakage of droplets in a turbulent field, using Kolmogorov's theory of local isotropy.

MODEL FOR TRANSITIONAL BREAKAGE PROBABILITY

A droplet exposed to a turbulent field will be subject to both inertial as well as viscous forces [8]. If the droplet is much larger than the macroscale of turbulence, the viscous forces can be neglected. In agitated vessels, the Reynolds numbers are so high that the macroscale of turbulence is found to be much smaller than the size range of the droplets encountered [7]. Such a case, the droplet will oscillate about its spherical equilibrium. The oscillations are brought about by the kinetic energy of the turbulent motion in the continuous phase [7, 8], or equivalently, by the relative velocity fluctuations between points near the vicinity of the droplet surface. In other words, the kinetic energy of the turbulent motion brings about the increase in the surface energy of the droplet through deformations. Fragmentation of the droplet occurs, if the turbulent motion provides the maximum increase in the surface energy for breakup.

In a turbulent field, velocity fluctuations at a point can
be thought of as due to arrival of eddies of different scales (frequencies). Similarly, the relative velocity fluctuations around the surface of a droplet exposed to a turbulent field can be viewed as due to arrival of either an eddy or eddies of different scale (frequency) on the surface of the droplet.

Indeed, oscillations of a droplet induced by a particular eddy may be interrupted by the arrival of subsequent eddies. Whether or not this occurs, is governed by the relative magnitudes of the time scales of, (i) the eddy arrival process and (ii) oscillations of the droplet. If the two time scales are comparable, the effects of successive eddies continually interfere with each other. Since oscillations of a droplet can be caused only by eddies of scale smaller than the droplet diameter, the smaller droplets require very small eddies to set them into oscillations. Furthermore, the time scale of oscillations should be inversely proportional to the eddy frequency. Thus the smaller eddies may be expected to create high frequency oscillations. In what follows, we assume that the time scale of oscillation is smaller than that associated with eddy arrival so that once an eddy of sufficiently high energy arrives the droplet would break certainly.

At sufficiently high Reynolds numbers, the flow field in an agitated lean liquid—liquid dispersion is locally isotropic[7, 12–14]. Hence we need to consider only the relative velocity fluctuations between any two diametrically opposite points on the surface of the droplet[I], i.e. the oscillating droplet can be considered as a one-dimensional simple harmonic oscillator, in which the restoring action of the drop is due to surface tension. Neglecting viscosity effects the simple harmonic oscillator can be considered undamped. For an undamped oscillator, the sum of potential and kinetic energy is constant; the potential energy signifying the surface energy of the droplet. Taking the datum of surface energy to be that at the spherical equilibrium position, we have

\[
\text{Maximum specific surface energy} = \text{Energy of the arriving eddy}
\]

\[
\text{Maximum increase in the specific surface energy above the equilibrium value} = \text{Energy of the arriving eddy}
\]

Here we make a postulate that the number of eddies arriving on the surface of a droplet is a Poisson process, i.e.,

(i) The numbers of eddies arriving on the surface of a droplet in disjoint time intervals are independent,

(ii) \( \Pr \) [one eddy arrives on the surface in time interval \( t, t + dt \)] = \( \lambda dt + 0(dt^2) \),

(iii) \( \Pr \) [more than one eddy arrives on the surface in time interval \( t, t + dt \)] = \( 0(dt^2) \),

where \( \lambda = \text{average number of eddies arriving on the surface of a droplet/unit time} \)

We expect \( \lambda \), the parameter of the Poisson process, to depend both on the diameter of the droplet and energy input per unit mass \( \varepsilon \). In the absence of a priori information about the dependence of \( \lambda \) on the diameter, we assume it to be independent of the diameter of the droplet. Since we need to consider only the inertial subrange of Kolmogorov’s universal spectrum and the effect of eddies of scale less than or of the order of microscale of turbulence is negligible, we can neglect the effect of \( \varepsilon \) on \( \lambda \), i.e., \( \lambda \) can be regarded as a constant.

We consider a small time interval \( \tau \), and define two events \( A \) and \( B \) as

\[
\begin{align*}
A & \text{ An eddy arrives on the surface of a droplet in the time interval } \tau \\
B & \text{ The arriving eddy has energy greater than or equal to the minimum increase in the surface energy, } E_{\text{min}}(v) \text{ required to break a droplet of volume } v
\end{align*}
\]

Clearly we have \( P(A) = \lambda \tau \)

\[
\Pr[\text{Droplet of volume } v \text{ breaks in time interval } \tau] = P(A)P(B|A)
\]

\[
= \tau P(B|A) \lambda
\]

Therefore,

\[
\lim_{\tau \to 0} \frac{\Pr[\text{Droplet of volume } v \text{ breaks in time interval } \tau]}{\tau} = \Gamma(v) = P(B|A) \lambda
\]

The surface energy of a droplet of volume \( v \) equals

\[
\sigma \pi^{1/3} \sigma^{2/3} v^{2/3}
\]

It can easily be shown that the increase in the surface energy required for fragmentation is minimum if binary equal breakage occurs. Therefore, the minimum increase in the surface energy for fragmentation equals

\[
(2^{1/3} - 1) \sigma \pi^{1/3} \sigma^{2/3} v^{2/3}
\]

This energy is provided by the kinetic energy of oscillation of the droplet.

Therefore, the minimum relative velocity of oscillation required for fragmentation is given by

\[
\frac{1}{2} \left( \rho \nu \right) u_{\text{min}}^2 = (2^{1/3} - 1) \sigma \pi^{1/3} \sigma^{2/3} v^{2/3}
\]

\[
\frac{1}{2} u_{\text{min}}^2 = (2^{1/3} - 1) \sigma \pi^{1/3} \sigma^{2/3} v^{2/3}
\]

If the characteristic velocity of an eddy of scale \( \alpha \) is \( u_{\alpha} \), then its kinetic energy is \( \frac{1}{2} u_{\alpha}^2 \), and for the breakage to occur, we must have \( \frac{4}{3} u_{\alpha}^2 \geq 2 u_{\text{min}}^2 \).

In order to evaluate \( \Gamma(v) \), we need to know the probability distribution of the relative velocity between two points separated by a distance \( r \). Experimental measurements of probability distribution of velocity at a point in the impeller stream in an agitated vessel[14] at an impeller speed of 300 rpm have shown that this probability distribution may not be far from Gaussian. The Gaussian approximation may be better at higher impeller speed (or higher Reynolds number) as intermittent flow conditions and non-isotropic conditions tend to become less pronounced. Given that the probability distribution of the velocity at a point in an agitated vessel is normal, the most natural assumption about the joint probability distribution of velocities at two points is that it is normal...
This, according to Batchelor[15], follows from the central limit theorem, since the turbulent velocities are subject to the influence of a large number of random eddies or local flow. On the other hand, such an assumption cannot be exactly true especially for very small values of \( r \), because it amounts to neglecting non-linear terms in the dynamical equations, or, equivalently, the non-linear modulations of the energy spectrum[15]. Due to lack of adequate information regarding the joint probability distribution of 2-point velocities in agitated vessels, we make the assumption that the joint probability distribution is normal. From this assumption, it follows that the probability distribution of relative velocity between two points is also normal.

If \( u \) is the relative velocity between two points separated by a distance \( d \) at any time \( t \), from Kolmogorov's theory of local isotropy

\[
\overline{u^2(d)} = 2(\overline{e_d})^{2/3} \tag{4}
\]

Equation (4) was obtained by integrating the energy spectrum in the inertial subrange over all wave numbers greater than that which corresponds to \( 1/d \).

Hence the probability density of the relative velocity \( u \) between two points separated by distance \( d \) is given by

\[
P(u) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[ \frac{u^2}{2\sigma^2} \right] \tag{5}
\]

where \( \sigma^2 = \overline{u^2(d)} \) Thus the transition probability \( \Gamma(u) \) is obtained as

\[
\Gamma(u) = \Pr[u^2 \geq \overline{u^2}] = \lambda \text{erfc} \left( \frac{u_{mm}}{\sqrt{2\pi}\sigma} \right)
\]

\[
\approx \lambda \text{erfc} \left( \frac{\sqrt{a(\pi/6)^{1/3}u^{-5/6}}}{2\varepsilon^{1/3}} \right) \tag{6}
\]

where

\[
a = 2(2^{1/3} - 1)\pi^{1/3}6^{2/3}\sigma^2 \rho
\]

Similarly

\[
\Gamma(d) = \lambda \text{erfc} \left( \frac{\sqrt{a(\pi/6)^{-1/6}d^{-1/6}}}{2\varepsilon^{-1/3}} \right) \tag{7}
\]

We define a maximum stable drop diameter \( d_s \), such that

\[
\frac{\sqrt{a(\pi/6)^{-1/6}}}{2\varepsilon^{1/3}} d_s^{-1/6} = 3.5 \tag{8}
\]

as \( \text{erfc}(\beta) = 0 \), if \( \beta \geq 3.5 \) From squaring eqn (8) we have

\[
2(2^{1/3} - 1)\pi^{1/3}6^{2/3}\sigma(\pi/6)^{-1/3}d_s^{-5/3} = 12.2
\]

Thus,

\[
d_s^{-5/3} = C_1 \frac{\varepsilon^{2/3}\rho}{\sigma}
\]

where

\[
C_1 = \frac{12.2}{(2^{1/3} - 1)6}
\]

For a baffled agitated vessel[16],

\[
\varepsilon = C_2 N^3 L^2, \quad \varepsilon^{2/3} = C_3 N^2 L^{4/3} \tag{9}
\]

Substituting,

\[
d_s^{-5/3} = C_1 C_3 N^2 L^{4/3} \rho
\]

\[
\left( \frac{d_s^2}{L} \right) = C_4 \left( \frac{N^2 L^3 \rho}{\sigma} \right)^{-0.6} = C_4 N^2 \sigma^{-0.6} \tag{10}
\]

where

\[
C_4 = (11/3)^{-0.6}
\]

The functional form of this expression is identical to the empirical relations obtained for average drop diameter of equilibrium distribution in well baffled agitated batch vessels[9–11].

Redefining the transition probability in terms of the dimensionless drop diameter we get

\[
\gamma \left( \frac{d}{d_s} \right) = \lambda \text{erfc} \left( 3.5 \left( \frac{d}{d_s} \right)^{-5/6} \right) \tag{11}
\]

We recognize that this is a universal relation for all liquid dispersions whose viscosity and density are not very different from those of the continuous phase. The behaviour of \( \gamma \) with \( d/d_s \) is shown in Fig 1.

From Fig 2, we see that a power law expression for \( \gamma \) is a good approximation for \( d/d_s \), up to 2. An evaluation of the slope yields a value of about 8 for the exponent, i.e.

\[
\gamma \left( \frac{d}{d_s} \right) \approx \left( \frac{d}{d_s} \right)^n \approx \left( \frac{1}{u_t} \right)^{2.67} \tag{12}
\]

Fig 1. Transitional breakage probability \( \gamma \) as a function of \( d/d_s \),
From the experimental data of Madden and McCoy [5] on cumulative volume distribution of dispersed phase in a batch agitated vessel, Ramkrishna [4] has found that a power law expression for the transitional breakage probability holds well. The exponent obtained with respect to volume v, by a preliminary analysis, was 2. This value agrees fairly well with the exponent of 2.67 obtained from this model. The higher value for the exponent predicted by this model indicates an even stronger dependence of the transitional breakage probability γ on the dropsize than what has been observed.

Now,

$$\gamma\left(\frac{v}{v_*}\right) = b\left(\frac{v}{v_*}\right)^{8/3}$$

where b is a universal constant obtained by taking the intercept of the straight line at $d/d_* = 1$.

If

$$\Gamma(v) = K v^r,$$

then

$$\Gamma(v) = b v_*^{-8/3} v^{8/3},$$

i.e. the rate constant

$$K = b v_*^{-8/3},$$

$$K \propto v_*^{-8/3}.$$  \hspace{1cm} (13)

From the expression for maximum stable drop diameter $d_s$, we see that

$$K \propto d_s^{-8} \propto \frac{24^{4/3} \varepsilon^{16/5}}{\sigma^{24/5}}.$$  \hspace{1cm} (14)

EQUILIBRIUM DISTRIBUTION

In an agitated batch liquid-liquid dispersion, continuous break up and coalescence of drops occur. Eventually, a dynamic equilibrium between break up and coalescence is established and a spectrum of drop sizes results. For a lean liquid-liquid dispersion, the rate of coalescence, though small, becomes important near the equilibrium as the equilibrium is dynamic. Hence, at equilibrium the rate of breakage, in order to compensate for the rate of coalescence, has to be small. So, we can

\[\gamma\left(\frac{d}{d_*}\right) = \frac{\lambda}{\sqrt{\pi}} 3.5 \left(\frac{d}{d_*}\right)^{5/2} \exp \left[-12.2\left(\frac{d}{d_*}\right)^{-5/3}\right]\]

For $d/d_* = 1$

\[\gamma\left(\frac{d}{d_*}\right) = \frac{\lambda}{\sqrt{\pi}} 3.5 \left(\frac{d}{d_*}\right)^{5/2} \exp \left[-12.2\left(\frac{d}{d_*}\right)^{-5/3}\right] \]  \hspace{1cm} (14)

$d$ denoting an average diameter.

From Fig 3, it can be seen that this approximation is quite good up to $d/d_* = 1.5$.

We shall later use this expression of $\gamma$ in the derivation of an equilibrium drop size distribution in a batch vessel.

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**Fig 2** "Power law" approximation for transitional breakage probability $\gamma$

**Fig 3** Approximation for transitional breakage probability $\gamma$ near $d_*$. 

From the above expression for functional dependence of the rate constant $K$ on $\rho$, $\varepsilon$ and $\sigma$, we see that $K$ increases as $\varepsilon$ increases, and decreases as $\sigma$ increases. This behavior is of course as it should be.
expect the equilibrium distribution to be narrow around the maximum stable drop diameter $d$. Experimental observations of equilibrium distribution do show that they are narrow [16].

A population balance equation for a batch liquid-liquid dispersion is given by,

$$\frac{\partial \phi}{\partial t} = \int_{v}^{x} p(v')\Gamma(v')\phi(v', t) dv' - \Gamma(v)\phi(v, t)$$

$$+ \frac{1}{2} \int_{0}^{x} \mu\phi(v', t)\phi(v - v', t) dv'$$

$$- \int_{0}^{\infty} \mu\phi(v, t)\phi(v', t) dv'$$

(15)

At equilibrium

$$0 = \int_{0}^{x} \nu(v')\Gamma(v')p(v, v')\phi(v') dv' - \Gamma(v)\phi(v)$$

$$+ \frac{1}{2} \int_{0}^{x} \mu\phi(v')\phi(v - v') - \int_{0}^{\infty} \mu\phi(v)\phi(v') dv'$$

(16)

We assume that the coalescence frequency $\mu$ is a constant as the equilibrium distribution is narrow. Moreover, at equilibrium, the rate of breakage is small, i.e., the energy of oscillation available from the turbulence of the continuous phase is only slightly higher than the minimum increase in the surface energy for breakage. Hence we can expect the breakage to be mostly binary. We also assume that the daughter droplet size distribution is uniform (perfectly random), that is

$$\nu(v) = 2, \quad p(v, v') = \frac{1}{v'}$$

Hence the population balance equation is

$$0 = 2 \int_{0}^{x} \Gamma(v')\phi(v') dv' - \Gamma(v)\phi(v)$$

$$+ \frac{\mu}{2} \int_{0}^{x} \phi(v')\phi(v - v') - \int_{0}^{\infty} \phi(v)\phi(v') dv'$$

(17)

Recently, Bajpai et al. [19] have proposed an equilibrium dropsize model with viewing the coalescence-redispersal process as a single step process based on a constant coalescence frequency and a perfectly random redispersal. This model, which showed good agreement with experimental dropsize distributions, is not applicable for very low dispersed phase fractions in which both breakage and coalescence rates are very small. This is the situation, which the present model is aimed at.

As $\phi(v) = f_v(v)/v$, the population balance equation can be written in terms of volume density $f_v(v)$, as

$$0 = 2 \int_{0}^{x} \Gamma(v')\frac{f_v(v')}{v'^2} dv' - \Gamma(v)\frac{f_v(v)}{v}$$

$$+ \frac{\mu}{2} \int_{0}^{x} \frac{f_v(v')}{v'} \frac{f_v(v - v')}{v - v'} dv' - \int_{0}^{\infty} \frac{f_v(v')}{v'} \frac{f_v(v)}{v} dv'$$

Let $v^*$ be the volume at which the equilibrium density $f_v(v)$ exhibits a maximum. We define a non-dimensional

volume $x = v/v^*$. In terms of non-dimensional volume $x$ eqn (18) becomes

$$0 = 2 \int_{0}^{x} \gamma(x')\frac{F'(x')}{x'^2} dx' - \gamma(x)\frac{F(x)}{x}$$

$$+ \frac{\mu}{2} \int_{0}^{x} F(x') \frac{F(x - x')}{x'^2} dx' - \mu\frac{F(x)}{x} \int_{0}^{x} F(x') dx'$$

(19)

Differentiating with respect to $x$,

$$0 = -2\gamma(x)\frac{F(x)}{x^2} - \frac{d}{dx} \left[ \gamma(x)\frac{F(x)}{x} \right]$$

$$+ \frac{\mu}{2} \int_{0}^{x} \frac{F(x')}{x'^2} \frac{d}{dx} \left[ \frac{F(x - x')}{x'^2} \right] dx'$$

$$- \mu \left[ \int_{0}^{x} \frac{F(x')}{x'^2} dx' \right] \frac{d}{dx} \left[ \frac{F(x)}{x} \right]$$

(20)

Now $\lim F(x)/x = 0$ as the distribution tends much more rapidly to zero than $x$ as $x$ tends to zero.

Expressing the volume density $F(x)$ in terms of non-dimensionalized drop diameter $\xi = (d/d^*) = x^{1/3}$, and denoting it by $f(\xi)$, we have

$$0 = 2\gamma(\xi)f(\xi) - \frac{d}{d\xi} \left[ \frac{\gamma(\xi)f(\xi)}{3\xi^2} \right]$$

$$+ \frac{\mu}{2} \int_{0}^{\xi} f(\xi') \frac{d}{d\xi} \left[ \frac{f(\xi - \xi')}{3(\xi - \xi'^2)} \right] d\xi'$$

$$- \mu f(\xi) \left[ \int_{0}^{\xi} f(\xi') \frac{d}{d\xi} \left[ \frac{f(\xi - \xi')}{3(\xi - \xi'^2)} \right] d\xi' \right]$$

(21)

For a narrow equilibrium distribution, it can be shown that (see Appendix) the coalescence term is of a much smaller order of magnitude than the other terms in the above equation. Hence eqn (21) becomes

$$0 = -\frac{\gamma(\xi)f(\xi)}{\xi} - \frac{\gamma'(\xi)f(\xi) - \gamma(\xi)f'(\xi)}{\xi}$$

$$- \mu f'(\xi) + \frac{5f(\xi)}{\xi} \int_{0}^{\xi} f(\xi') d\xi'$$

(22)

where

$$\kappa = \int_{0}^{\xi} f(\xi') d\xi'$$

is a constant.
Thus

\[
\frac{f'(\xi)}{f(\xi)} = \frac{5\mu_k - \gamma(\xi) - \xi \gamma'(\xi)}{\xi[\mu_k + \gamma(\xi)]}
\]  
(23)

In the Appendix, we have shown that \( \mu_k \gg \gamma(\xi) \) so that (23) becomes

\[
\frac{f'(\xi)}{f(\xi)} = \frac{5\mu_k - \gamma(\xi) - \xi \gamma'(\xi)}{\xi \mu_k}
\]  
(24)

Since we expect the distribution to be narrow around \( d_\ast \), we use the approximate expression for \( \gamma \) near \( d_\ast \), given by eqn (14)

\[
\gamma(\xi) = A \exp[-\alpha B \xi^{-5/3}]
\]  
(25)

where

\[
A = \frac{\lambda}{3 \sqrt[4]{\pi}} \left( \frac{d}{d_\ast} \right)^{5/6}, \quad B = 3 S^2, \quad \alpha = \left( \frac{d_\ast}{d_\ast} \right)^{-5/3}
\]  
(26)

Substituting for \( \gamma \) in eqn (25) we get

\[
\frac{f'(\xi)}{f(\xi)} = \frac{5\mu_k - \frac{\lambda}{3 \sqrt[4]{\pi}} \left( \frac{d}{d_\ast} \right)^{5/6} \exp[-\alpha B \xi^{-5/3}] - A \alpha B \frac{5}{3} \xi^{-8/3} \exp[-\alpha B \xi^{-5/3}]}{\mu_k}
\]  
(27)

Since \( f'(1) = 0 \)

\[
5\mu_k - A \exp[-\alpha B] - A \alpha B \frac{5}{3} \exp[-\alpha B] = 0
\]  
(28)

Elimination of \( A \) from eqn (27) using (28) yields

\[
\frac{f'(\xi)}{f(\xi)} = 5 \left[ \xi^{-1} - \exp\{-\alpha B(\xi^{-5/3} - 1)\} \right]
\]  
(29)

Now \( 5\alpha B/3 \approx 18 \) and for \( \xi = 1 \) we have

\[
\frac{5}{3} \alpha B \xi^{-8/3} + \frac{\xi^{-1}}{3} = \xi^{-8/3}
\]

Hence

\[
\frac{f'(\xi)}{f(\xi)} = 5[\xi^{-1} - \xi^{-8/3} \exp\{-\alpha B(\xi^{-5/3} - 1)\}]
\]  
(30)

Integrating

\[
\ln f(\xi) = 5\left[ \ln \xi - \frac{3}{5\alpha B} \exp\{-\alpha B(\xi^{-5/3} - 1)\}\right] + C
\]  
(31)

where \( C \) is the constant of integration. Expanding \( \ln f(\xi) \) and \( \exp\{-\alpha B(\xi^{-5/3} - 1)\} \) in Taylor series around \( \xi = 1 \) and retaining terms up to second order, we obtain

\[
\ln f(\xi) = 5\left[ \frac{3}{5\alpha B} - \frac{5}{6}(\alpha B - 1)(\xi - 1)^2 \right] + C
\]  
(32)

Normalizing the non-dimensionalized volume density and denoting it by \( f_n(\xi) \), we have

\[
f_n(\xi) = \frac{1}{\sqrt{\pi \sigma}} \exp\left[-\frac{\xi - 1)^2}{2\sigma^2}\right]
\]  
(33)

where

\[
\sigma^2 = \frac{3}{25(\alpha B - 1)}
\]

From (33), we find that the non-dimensionalized equilibrium volume distribution is normal. Interestingly enough, this is the distribution obtained by Chen and Middleman[16]. Quantitative comparison of the derived distribution with the experimental data is possible only if the value of \( \alpha \) is known.

From (9),

\[
\frac{d_\ast}{L} = C_4 N^{-\alpha/6}
\]

From the correlations[9] for average drop diameter \( \bar{d}_{32} \) in batch agitated dispersions,

\[
\frac{\bar{d}_{32}}{L} = 0.053 N^{-\alpha/6},
\]  
(34)

It was observed that[16] the equilibrium distribution exhibits a maximum at \( \bar{d}/\bar{d}_{32} = 1.06, \) i.e.

\[
d_\ast = 1.06 \bar{d}_{32}
\]  
(36)

Therefore,

\[
\frac{d_\ast}{d_\ast} = 1.06 C_5
\]  
(37)

For a well-baffled stirred vessel[17],

\[
Pr_c = 6 N^3 L^5
\]

\[
\bar{\varepsilon} = \frac{Pr_c}{(\pi/4) T H} = 1.27 N^3 L^2
\]

for \( T - H \) and \( L/T = 0.54 \) the dimensional ratios being the same as those used by Chen and Middleman[16].

Using this empirical correlation for \( \bar{\varepsilon} \) for the evaluation of \( d_\ast/L \) we find that \( d_\ast/L \) turns out to be much greater than \( d_{32}/L \). This cannot be physically accounted for as this implies that breakage is absent at equilibrium.

From the observations of Cutter[18], we find that about 20% of the energy is dissipated in the impeller itself about 50% in the impeller stream, and about 30%
in the other parts of the tank. Measurements of $e/\bar{e}$ in the impeller stream showed an almost exponential variation from 70 near the impeller tip to about 3.5 near the wall. Outside the impeller stream $e/\bar{e}$ was found to be roughly 0.26. In view of such important inhomogeneities existing in a stirred vessel, it is felt that some statistical mean $\bar{e}$ should be used instead of $e$ in the probability distribution of relative velocity. It may be reasonable to use $e$ averaged over the residence time of the drops in different regions of the stirred vessel; i.e., in effect, $e$ may be the average rate of energy dissipation per unit mass a drop "experiences" in the stirred vessel. This will depend on the flow pattern in the agitated vessel. If we assume that most of the breakage takes place in the impeller stream, we can, in order to evaluate the order of magnitude of $\alpha$, take a geometric mean of $e$ at the impeller tip and wall (as $e$ varies almost exponentially).

$$(e)_{av} \approx 30\bar{e}$$

Using this $(e)_{av}$ in the evaluation of $d_s$, we find that,

$$\frac{d_s}{L} = 0.015 \frac{N}{\text{We}}^{0.6}$$

$$\left(\frac{d_{32}}{d_s}\right) = 1.03, \quad \left(\frac{d_{42}^*}{d_s}\right) = 1.092, \quad \alpha = 0.86$$

For this value of $\alpha$, eqn (33) and a numerical solution of eqn (29) are plotted in Fig 4. For comparison, the experimental data points as well as the empirical equilibrium density of Chen and Middleman[16] are plotted on the same figure.

It can be seen that the approximate Gaussian density as well as the numerical solution of eqn (33), both predicted by this model, are steep. This is consistent with the assumption made in the derivation of the equilibrium distribution. The equilibrium density obtained from (29) is skewed. This is understandable as only a very narrow cut of drops greater than $d_s$ can exist at equilibrium for the rate of breakage to be small, whereas, due to uniform breakage, one can expect a broad spectrum of drops less than $d_s$. The equilibrium density, predicted by the model, drops faster for drop diameters greater than $d_s$ and is broader for diameters less than $d_s$. This indicates that the rate of breakage near $d_s$, predicted by this model, increases faster with diameter than the estimates from the experiments of Madden and McCoy[4]. In fact, this is corroborated by the observation that the exponent of 2.67 for the power law approximation of transitional breakage probability, as predicted by this model, is greater than the exponent 2 obtained by Ramkrishna[4].

**CONCLUSIONS**

A model for transitional breakage probability of droplets in agitated lean liquid-liquid dispersions is proposed based on the mechanism of breakage of droplets due to their oscillations resulting from the relative velocity fluctuations. The joint probability distribution of two point velocities in an agitated vessel is assumed to be normal Kolomogorov's theory of local isotropy is used in estimating the probability distribution of the relative velocity between two points in an agitated vessel. A universal transitional breakage probability, applicable for all dispersed phases whose density and viscosity are almost the same as that of the continuous phase, is derived in terms of non-dimensionalized drop diameter. The expression for $d_s$, derived from the model, shows a dependence of $N_{\text{We}}^{0.6}$. It is shown that a "power law" approximation $K^\alpha$ for the transitional breakage probability is valid for $d/d_s$ up to 2. The value of the exponent $\alpha$, predicted by this model, is 2.67 which compares reasonably well with the value 2.0 obtained from experimental observations[4]. A functional relation for the rate constant $K$ in terms of the parameters and physical properties of the system is derived.

A universal non-dimensionalized equilibrium drop size distribution for agitated lean liquid-liquid dispersions is derived using a population balance equation. In its derivation, it is assumed that (i) breakage near equilibrium is binary uniform breakage and (ii) the equilibrium volume density is steep. Only a qualitative comparison of the derived equilibrium distribution with the experimental observations[16] was possible as the parameter $\alpha$ could not be evaluated accurately due to lack of information. The predicted equilibrium volume density was found to be steep, consistent with the assumptions. It is inferred that the rate of breakage near $d_s$ as predicted by the model, increases faster than available estimates.

**NOTATION**

- $d$: drop diameter
- $d_{32}$: Sauter mean drop diameter
- $d_s$: maximum stable drop diameter
- $d^*$: drop diameter at which the equilibrium volume density exhibits a maximum
- $E_{\text{min}}$: minimum increase in specific surface energy of a drop for fragmentation
\[ f_v \] density function of droplet volume in terms of volume
\[ f \] density function of non-dimensionalized droplet volume in terms of volume
\[ f_n \] normalized \( f \)
\( H \) tank height
\( K \) rate constant in power law expression for transitional breakage probability
\( L \) impeller diameter
\( N \) impeller speed, rotations/unit time
\( N_w e \) \( L^3 N^2 \rho / \sigma = \text{Weber number} \)
\( n \) exponent in power law expression for transitional breakage probability
\( p \) density function of daughter droplet volume arising from breakage of a parent droplet in terms of number
\( p \) power input
\( T \) tank diameter
\( u \) relative velocity between two points
\( u_c \) characteristic velocity of an eddy of scale \( \alpha \)
\( v \) drop volume
\( v_* \) drop volume at which the equilibrium volume density exhibits a maximum
\( V \) dispersed phase volume fraction
\( x \) non-dimensionalized droplet volume

**Greek symbols**

\( \alpha \) parameter defined in eqn (26)
\( \gamma \) universal transitional breakage probability in terms of non-dimensionalized droplet volume or diameter
\( \Gamma \) transitional breakage probability
\( \lambda \) average number of eddies arriving on the surface of a droplet/unit time
\( \sigma \) interfacial tension, also used as variance of equilibrium volume density
\( \rho \) density of continuous phase
\( \bar{\rho} \) average power input/unit mass
\( (\bar{e})_{av} \) average power input/unit mass a droplet experiences
\( \mu \) coalescence frequency
\( \nu \) mean number of droplets from breakage of a parent droplet
\( \phi \) density function of droplet volume in terms of number
\( \xi \) non-dimensionalized droplet diameter

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**APPENDIX**

For an equilibrium distribution narrow around the maximum stable drop diameter \( d_\alpha \), we can divide the distribution into three zones as shown in Fig 5:

Z1 Zone of droplets of small volume, \( \xi \ll 1 \)
Z2 Zone where most of the distribution is concentrated, \( \xi \gg 1 \)
Z3 Zone of droplets of large volume \( \xi \ll 1 \)

For Zone 1 the population balance equation at equilibrium in non-dimensionalized volume is

\[ 0 = \frac{2}{\xi} \int_{\xi}^{\infty} y(x) F(x) \frac{1}{x^2} \, dx - \frac{\mu}{3} \int_{0}^{\xi} F(x) \frac{1}{x} \, dx \quad (A1) \]

As (i) droplets do not break in Zone 1, (ii) production of droplets in Zone 1 due to coalescence of smaller drops is negligible

Differentiating (A1) with respect to \( x \)

\[ 0 = -2 \gamma(x) F(x) \frac{1}{x^3} - \frac{\mu}{3} \frac{d}{dx} \left[ \frac{F(x)}{x} \right] \]

For \( x \in I \), \( \gamma(x) = 0 \) so that \( (d/dx)[F(x)/x] = 0 \) and we write

\[ F(x) = n^{-1} x \]

where \( n \) = number of droplets in Zone 1 per unit interval of non-dimensionalized drop volume \( x \)

Thus

\[ f(\xi) = 3n^{-1} \xi^3 \quad (A2) \]

From (A1) we have

\[ 0 = \frac{2}{\xi} \int_{\xi}^{\infty} y(x) f(x) \frac{1}{x^2} \, dx - \frac{\mu}{3} \xi \int_{0}^{\xi} f(x) \frac{1}{x} \, dx \]

so that dividing by dispersed phase fraction \( V \)

\[ \int_{\xi}^{\infty} \gamma(x) f_{av}(x) \frac{1}{x} \, dx \sim \frac{\mu}{3} \xi \int_{0}^{\xi} f(x) \frac{1}{x} \, dx \quad \xi \in I \quad (A3) \]
Since \( f_0(\xi) \) is concentrated around \( \xi = 1 \), taking the order of magnitude of terms in (A3)

\[
\gamma(\xi) \sim \frac{\xi}{2} n^* \quad \text{where } \xi \in I \text{ or II}
\]
or

\[
\mu - \frac{2\gamma(\xi)}{n^*} \approx \frac{2\gamma(\xi)x'}{n^*x'} \quad x' \in I
\]  \hspace{1cm} (A4)

Since \( n^*x' \) is the volume of drops in unit non-dimensionalized volume interval around \( x' = \xi^3 \) we may write from (A4)

\[
\mu \sim \frac{2\gamma(\xi)x'}{\Delta V} \quad x' < 1, \Delta \ll 1
\]
or equivalently \( \mu \gg \gamma(\xi) \)

Since \( \gamma(\xi) = A \exp \left[-B\xi^{-3}\right] \) it can easily be seen that for \( \xi \in II \)

\[
\gamma'(\xi) \sim \frac{5B}{3} \gamma(\xi) \sim 20y(\xi)
\]  \hspace{1cm} (A5)

Now

\[
f'(\xi) = \frac{1}{[\xi - 1]}
\]  \hspace{1cm} (A6)

and

\[
\int_0^\infty f(\xi) d\xi = \frac{\xi}{V} - 1
\]  \hspace{1cm} (A7)

For Zone II, the population balance equation is given by eqn (21), which on division by \( V^2 \) yields

\[
0 = -\frac{\gamma(\xi)f_0(\xi)}{V\xi} - \frac{1}{V} \gamma'f_0(\xi) - \frac{\gamma(\xi)f''(\xi)}{V}
\]

\[
I \quad II \quad III
\]

\[
+ \frac{\mu^2}{2} \int_0^\xi f(\xi) \frac{d}{d\xi} \left[ \frac{f(\xi)}{\xi^2} \right] d\xi - \frac{\mu \xi f_0(\xi)}{V}
\]

\[
IV \quad V
\]

We now consider the coalescence integral for \( \xi \in II \)

\[
f = \int_0^\xi f(\xi) \frac{d}{d\xi} \left[ \frac{f(\xi)}{\xi^2} \right] d\xi
\]

The contribution to this integral can come from any one of the following cases

(i) \( \xi' \in I, \xi \in II \), (ii) \( \xi' \in II, \xi \in I \), (iii) \( \xi' \in I, \xi \in I \)

If we denote the corresponding values of I by \( I_0, I_{00}, \) and \( I_{000} \), then from (A2) we have

\[
\frac{d}{d\xi} \left[ \frac{f_0(\xi)}{\xi^2} \right] = 0
\]

which implies that \( I_{00} = I_{000} = 0 \) so that \( I = I_0 \), or

\[
I = \int_0^\xi 3n^* \xi^2 \frac{d}{d\xi} \left[ \frac{f_0(\xi)}{\xi^2} \right] d\xi', \quad \xi' \in I, \xi \in II
\]

Considering the order of magnitude of different terms in (A8) it can be shown that

\[
I \sim \frac{\gamma(\xi)}{V}, \quad \text{II} \sim \frac{20\gamma(\xi)}{V}, \quad \text{III} \sim \frac{\gamma(\xi)}{V} \frac{1}{[\xi - 1]}
\]

\[
IV \sim \frac{3n^*}{\xi^2} \frac{d}{d\xi} \left[ \frac{f_0(\xi)}{\xi^2} \right] V, \quad \text{V} \sim \frac{2\gamma(\xi)n^*\xi^3}{\Delta V^2[\xi - 1]}, \quad \text{VI} \sim \frac{5\gamma(\xi)n^*\xi^3}{\Delta V^2}
\]

where \( \xi \gg 1, \xi' \ll 1, \Delta \ll 1, \) and \( \Delta \ll \xi^3 \). From these estimates it is clear that the coalescence integral IV is of a smaller order of magnitude than the other terms in (A8)