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Historical Perspective

A critical review on turbulent collision frequency/efficiency models in flotation: Unravelling the path from general coagulation to flotation

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ABSTRACT

Flotation is a very important separation process in the mining industry. In addition, it finds important application as a water treatment process. The better design of flotation devices and operation strategies requires development of reliable and consistent mathematical models. Flotation is much more complex than typical unit processes, involving physicochemical interactions in small size scale and hydrodynamic interactions between bubbles, particles and liquid in a variety of size scales. The only feasible integrated approach to modeling the flotation process is by incorporating multiple scales. In the heart of such an approach there is a submodel for the frequency of collisions between bubbles and particles. Literature on this subject in the absence of intense turbulence is very extensive and there are many well-accepted models. Yet, the situation is quite different for the case of turbulence being an important collision mechanism, which is exactly what happens in industrial dispersed air flotation devices. The corresponding literature models are limited and focused on different aspects of the process. The present work is a review study attempting to unify these models in a general framework. The review is not restricted to presenting existing models but all relevant physical principles and fundamental theories are examined and assessed properly. In this respect, there are two levels of classification of literature material in this work. The first is a classification as general collision models and flotation models. It is important to critically examine the general collision models of engineering and physics literature since they constitute the basis on which flotation models rely. The second classification is with respect to the level of detail and sophistication of models (from distributed multibubble/multiparticle model to lumped models based on statistical theory of turbulence). The outcome of the work comes to the conclusion that existing models focus only to specific parts of the phenomena leading to bubble-particle collisions and for this, further improvement is needed to integrate them to obtain a better and more general picture. The material and comments presented in this work are meant as a decisive milestone towards this integration procedure.

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List of symbols

E_i	collision efficient with respect to mechanism i
f_{db}, f_{mb}, f_{Bb}	correction terms to account for deviation from linearity of the bubble motion equation
f_{dp}, f_{mp}, f_{Bp}	correction terms to account for deviation from linearity of the particle motion equation
g	gravitational acceleration
K	encounter frequency
k	turbulent kinetic energy
K_a	attachment frequency
K_c	collision frequency
m_{fp}, m_{fb}	mass of liquid having the volume of particle and mass respectively
m_p, m_b	particle and bubble mass respectively
P_a	attachment efficiency
P_c	collision efficiency
R_b	bubble radius
R_p	article radius
t	time
T_L	Lagrangian integral time scale
t_v	vorticity diffusion time
u	x-component of the relative entity-entity velocity
U_1, U_2	turbulent velocities of the two entities
U_b	bubble deterministic velocity
U_{bt}	combined turbulent-gravitational bubble velocity
u_p	particle deterministic velocity
$\mathbf{V}_p$, $\mathbf{V}_b$	turbulent particle and bubble velocity vectors
$\mathbf{W}$	liquid velocity vector
W_{g1}, W_{g2}	gravitational velocities of the two entities
w_r	radial relative velocity between two entities
ε	turbulent energy dissipation rate
ζ	coefficient in equation (18)
η_k	Kolmogorov size scale
θ	normalized relaxation time
μ	liquid viscosity
ν	kinematic viscosity of liquid
ρ	entity density
ρ_f	liquid density
τ_k	Kolmogorov time scale
τ_p	relaxation time

1. Introduction

Flotation is a very important separation process that has been recently characterized as the workhorse of the mining industry [1]. Flotation has been also used extensively as a water purification technique (dissolved air flotation, DAF [2]). The devices corresponding to the aforementioned main two industrial flotation applications are the mechanically agitated flow cells and the flotation tanks; in the latter the only hydrodynamic energy entering the system is through the inlet streams. In both cases, the devices and techniques employed in practice have been developed empirically. Therefore, for further optimization of existing techniques the so-called chemical engineering approach (this term has been extensively explained and introduced in [3] in the context of chemical reactor design) is needed. The application of such an approach gets more difficult and its outcome is vaguer as the complexity of the physicochemical process increases. Unfortunately, flotation is a very complicated process combining hydrodynamics and several modes of physicochemical interaction forces [4]. It has been stated that the flotation process is the encyclopedia of Colloid Science meaning that almost all subjects of Colloid Science are required to describe the flotation process. In fact, it is more than that since phenomena like bubbly flow and interplay between particle inertia and turbulent flow are barely part of Colloid Science. It is noted that in the following sections the term flotation in the modeling context refers always to flotation slurry and not to froth.

Further to the physical complexity of the flotation process (many theories must be simultaneously invoked), there is also an excessive computational complexity. Even if having set up a model, it is very difficult to solve it using reasonable computational resources. The disparate size scales involved in the process is the main reason for this difficulty. A multiscale approach is necessary to deal with the problem. Such an approach has been implicitly introduced in the theories of flotation for quiescent liquid developed very extensively in the past decades [5–7]. These theories are appropriate for flotation in bubble columns where small amounts of turbulence is found. However, in the main industrial flotation devices there is considerable amount of turbulence. A first attempt to formally exemplify the multiscale nature of the flotation process has been in the context of developing a generalized expression for turbulent flotation rate [8]. In that work the flotation process model is separated at three (size) scales. Scale I is the device scale which is to be treated by CFD (Computational Fluid Dynamics) codes. Scale II is a single point (or a finite dimension cell with uniform properties) in scale I. At this scale a mean field (i.e. statistical description) model for the occurring phenomena, is the appropriate tool (i.e. population balances). This scale model has no spatial dependence (zero dimensional model) and treats the bubbles and the particles as part of a homogeneous continuous phase. Scale III is the bubble/particle size scale which treats bubbles and particles as discrete entities. Regarding the flow of information, scale III supplies rate laws to the equations of

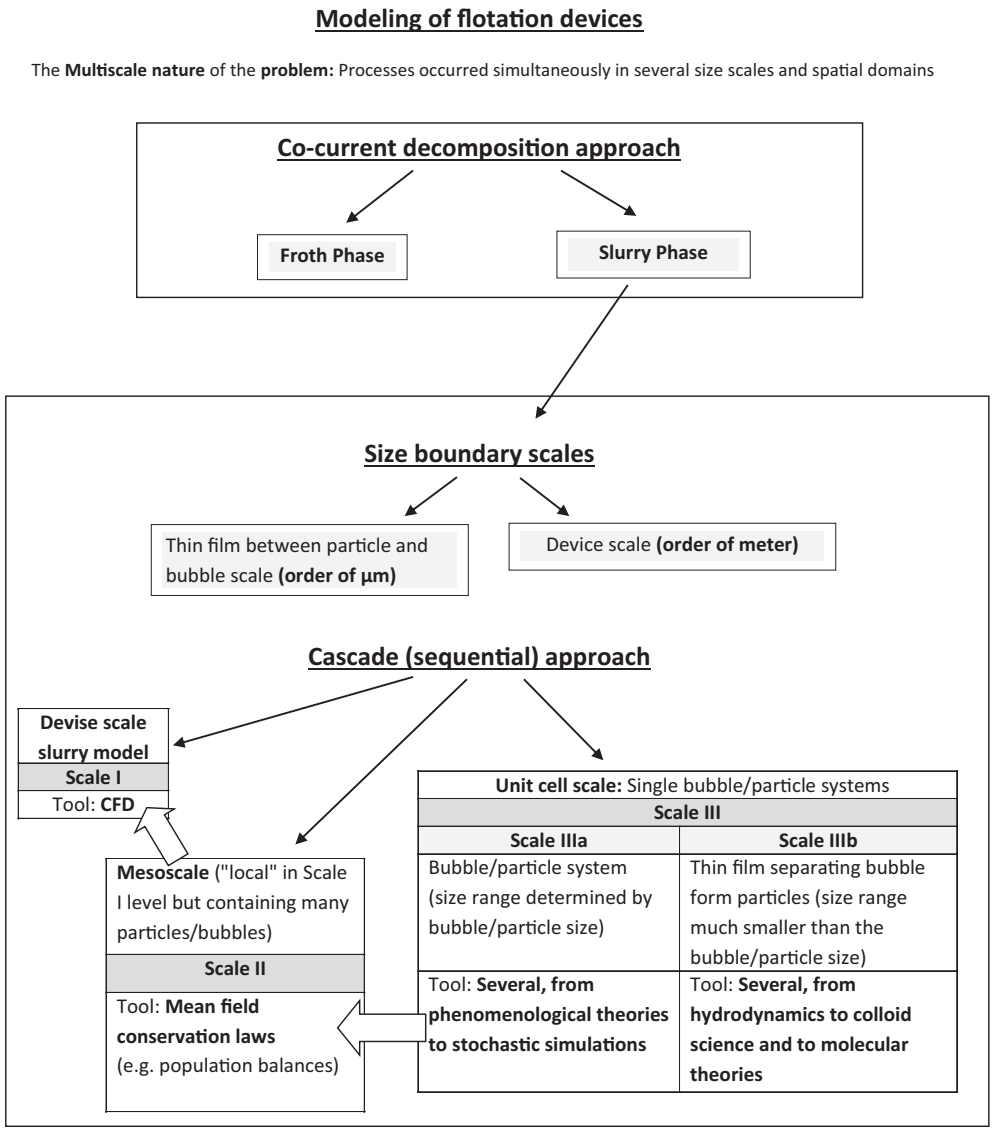

Fig. 1. A schematic of the multiscale structure considered for the modeling of flotation devices.

scale II and scale II provides the state equations appropriate for scale I CFD approach. The classical flotation models are based on decomposition of scale III to two subscales: The first is the size scale of the bubble/particle (Scale IIIa) and the second is the size scale of the thin film created between the bubble and the particle (Scale IIIb). A very recent review work on multiphase structures in particle/fluid systems [9] classifies in a strictly formal way the multiscale problems and their treatment methods. In general, there are two boundary scales (i.e. Scales I and IIIb in the flotation case). The larger the number of intermediate scales (i.e. mesoscales) the large the complexity in modeling and simulation. Direct handling of a multiscale problem is not possible since simultaneous solution of the governing equations in all scales is needed. There are two approaches for treating approximately a multiscale problem: the *cascading* and the *co-current* approach. In the first approach, the model is solved in different size scales and the communication between scales is made through constitutive laws or rate expressions or correlations or data sets everywhere in the physical domain. In the second approach, the physical domain is separated to subdomains to which different scale models are applied. The communication in this case is made through the spatial interfaces between the subdomains. In the context of flotation, the *cascading* approach has been proposed for the slurry modeling whereas the *co-current* approach has been used to separate the modeling of slurry from the modeling of froth. A detailed analysis of the multiscale approach (but using the equivalent term *sequential* instead of *cascading*) to the modeling of a flotation cell is given in [10] without referring to the previous suggestions in [8]. An overview of the above discussed methodology for the modeling of flotation process appears in Fig. 1.

Unlikely the extensive progress for the Scale III model in case of insignificant turbulence (this case is typically called “deterministic” flotation), the corresponding development in case of prevailing of turbulence is not adequate. Several reviews on the subject have appeared after the one of the present authors 15 years ago. They have been stand-alone reviews devoted to the subject [11], part of more general reviews on flotation rate [12] or part of the reviews on the multiscale modeling of the flotation cell [10]. These works suggest that there is no definite model for turbulent flotation and further research is needed.

Traditionally, detachment has been supposed to be part of the bubble-particle attachment process so the detachment rate is not an independent problem constitutive law but only a part of the collision

process [4]. An improved version considers that the detachment frequency is independent from the attachment but there is a detachment efficiency that affects both detachment and attachment process [13]. Kostoglou et al. [8] pointed out that detachment is a completely independent process that can occur at different locations and different moments from attachment. Such an approach is compatible to the development of detailed multiscale models considering spatial distribution of the detachment phenomenon [14]. Given the independency between collision (also attachment) and detachment it is possible to focus here only on the collision process in a turbulent flow field.

Although literature on turbulent collision rate for flotation is limited, literature for the more general case of two particles collision in a turbulent flow is vast. The origin of these studies ranges from the understanding of fundamentals of turbulent flow to more practical issues such as meteorology, dispersion flocculation, two phase flow etc. The basic characteristic that makes the flotation unique is the combination of bubbles and particles.

This work presents a detailed critical review of the existing approaches for the development of turbulent flotation rate models with a parallel assessment of all the background material on which they are based. The structure of the work is the following: At first some material relevant to turbulence is presented as background to the model development. Then, after an introduction to the deterministic flotation rate formulation, a review of the models on the collision rate between particles is presented. This review divides the models in levels regarding their sophistication. Moreover, compared to the previous review on the subject [15], it is expanded to include additional work, focusing on landmark and more critical contributions. This material is a necessary background for the development of the flotation models discussed next in detail. Finally, a summary and discussion of the present situation for flotation modeling closes the work. The general flowchart of the work is displayed schematically in Fig. 2. The present work is not a simple neutral numeration of relevant works on the subject but mainly reflects the personal opinion, point of view and thoughts of the authors. In addition, it is not a stand-alone material to provide directly correlations to the reader. Instead it guides the reader to the appropriate literature and indicates all the complex interrelation between the existing computational/theoretical approaches.

2. Background material

2.1. Some key remarks regarding turbulence

Apparently, there is a huge literature on turbulence. Among these studies, one can find short essays on turbulent flow characteristics in the context of flotation studies [1,4]. The scope here is not to give formal reference to turbulence literature and not to repeat the very useful previous essays on the subject. Instead, the focus is to give a personal view on what we consider necessary knowledge in order to qualitatively understand the basic ideas of the models presented in the following sections. The fluid flow is well organized and steady in time for relatively small Reynolds number (laminar flow), but for large Reynolds number it becomes chaotic, three dimensional and transient. This transition is not evident from the solution of governing momentum transfer equations since a steady state solution always exists regardless the value of Reynolds number (*Re*). For many years the origin of turbulence has been one of the major mysteries in science [16]. The increasing power of computers and the theory of chaos brought up a quite trivial explanation of the appearance of turbulence. The momentum equations lose their stability as *Re* number (which is a measure of the degree of non-

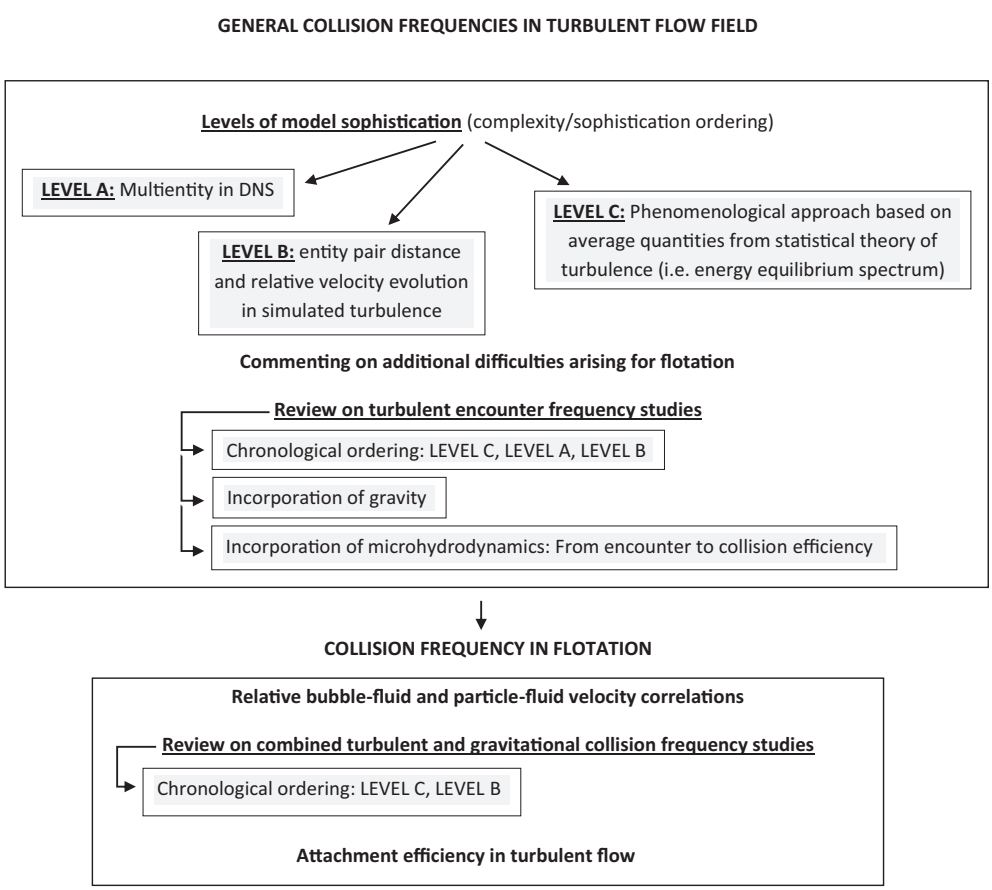

Fig. 2. A schematic of the structure of the present work.

linearity) increases. This means that the complete transient equations must be solved instead of seeking a steady state solution. The solution of these transient equations reproduces turbulence.

The transition from laminar to turbulent flow is an important issue. It depends on geometry and on Reynolds number. For a specific geometry there is a critical Reynolds number Re_c. For $Re < Re_c$ the flow is always laminar. For $Re > Re_c$ the flow may be laminar or turbulent (or transitional wherever there are coexisting spatial/temporal regions with laminar and turbulent features). The possibility of having laminar flow decreases as the difference Re-Re_c increases and depends on the magnitude of external disturbances applied to the flow. The main feature of turbulence is the existence of highly dissimilar size scales. This is important for the distinction between intrinsic turbulent flow and inherently transient laminar flow (e.g. vortex shedding behind a sphere [17], flow in membrane with spacers [18] etc.) where the size scales are imposed by geometry.

The next issue to discuss is how to model turbulent flow field. The obvious way, given the previous discussion, is to solve the transient form of the momentum transfer and continuity equations (Direct Numerical Simulation, DNS). The problem here is that turbulent flow exhibits features in such widespread size and time scales that the amount of information needed for their description is enormous. Unlike in the usual case of solving engineering models, the complexity here is not in the problem formulation or in the required mathematical solution techniques but in the solution itself. So, no practical problems can be modeled in this way. Only very simple geometries or idealized conditions, such as the isotropic and homogeneous turbulence (a situation in which only velocity fluctuations are present with no dominant motion and spatial variation of average flow properties), can be treated and this only by using large computational power.

The way of modeling turbulence many years before the understanding of its origin and in the absence of computer power was through a statistical approach. According to this, the flow is assumed to contain a superposition of eddies with sizes between a largest one, imposed by flow geometry, and a smallest one (Kolmogorov size scale) η_k. The flow is characterized by two variables: the one is the kinetic energy of the velocity fluctuations k and the other is the rate by which this energy is dissipated $\varepsilon = -dk/dt$. There is a distribution of these quantities among the size scales (eddy sizes) in the flow. The greatest part of k is concentrated in large size scales, affected by the geometry of the flow (integral size scales). On the other hand, the dissipation rate is concentrated in small size scales up to a few times the Kolmogorov one (dissipative subrange of turbulence spectrum). The size scales between the dissipative subrange and the integral scales is called the inertia subrange of turbulence spectrum. The dissipative and the inertia subranges constitute the equilibrium subrange which is "universal", i.e., it does not depend on the way of turbulence generation (geometry details). The kinetic energy is transferred from the integral scales to the inertial subrange without losses and then to the viscous subrange where it is dissipated through viscosity. This makes clear that k refers to velocities whereas ε refers to velocity gradients. The statistical description provides several flow features of the universal equilibrium range (i.e. velocity gradients, accelerations etc.) in the form of relations between their root of mean square and ε. A reasonable assumption for engineering purpose is that the corresponding probability density function is always a Gaussian one. This is not exactly true, as it has been shown by DNS [19], but it is a quite acceptable approximation. In the same manner it is assumed that the velocity fluctuation in the integral scales follows a Gaussian probability density function, too.

The statistical approach is sufficient to handle the isotropic homogeneous turbulence, but it is not effective in a real geometry. The appropriate approach in a real geometry is the so called Reynolds Averaged Navier Stokes equations (RANS). The momentum balances are averaged in time and equations for the time averaged quantities (velocities, pressure) are derived. Some rather weak (and questionable) approximations are introduced to achieve closure. The kinetic energy and turbulent dissipation rate appear as additional state variables of the flow. The implicit assumption in using RANS to simulate physicochemical processes through a scale decomposition is that the flow in a particular location can be described by the superposition of the time averaged variables and isotropic turbulence having as turbulent dissipation rate the value computed by RANS for the specific location. Finally, a compromise between RANS and DNS is the so called Large Eddy Simulation (LES) method where the time averaging refers only to small size scales (which are "filtered") and the complete transient equations are solved for the large scales. The LES method is much more accurate than RANS and computational affordable (in comparison to full DNS) for realistic geometries.

Further to the above general account of turbulence there are many technical details connected with the model derivation (e.g. a list of definitions of time, size and velocity scales in a turbulent flow field). Apart from the specific references in the present work, our suggestions for acquainting familiarity with the required turbulence details are the historical work of Batchelor for the statistical approach [20] and the book of Baldyga and Bourne [21] for modern developments.

2.2. An introduction to deterministic flotation rate formulation

At first a short discussion on the non-turbulent mechanism of flotation follows. Any relative velocity between a particle and a bubble leads to their collision. In case of non-Brownian particles (i.e. diameter larger than 1 μm) the only reason for this relative motion is gravity. Because of density difference with water, particles move downwards (sedimentation) and bubbles move upwards. The general treatment of the scale III process in the flotation literature is based on a flow field decomposition suggested by the fact that a particle is much smaller than a bubble. So, the particle is assumed to move in the flow field created by the bubble motion. The disturbance flow field created by the particle motion is typically not considered. At this point let us introduce a terminology about the several sub-processes. The encounter frequency is a nominal (artificial) quantity denoting the collision frequency resulting by ignoring the flow field created by the bubble. It is noted that the frequency can be transformed to rate by multiplying with the bubbles and particles concentration. The encounter frequency K can be simply found using a cylindrical formulation based on the unidirectional relative velocity between a bubble and a particle:

$$K = \pi\left(R_b + R_p\right)^2\left(U_b + u_p\right) \tag{1}$$

where R_b, R_p are the bubble and particle radius and U_b and u_p are the bubble and particle deterministic velocities (i.e. induced by gravity) respectively.

The collision frequency K_c is a "real" quantity and refers to the frequency at which the particle "touches" the bubble (there still could be a thin film between them being a part of the scale IIIb problem). The quotation marks in "real" means that it is much more realistic than the encounter frequency, but it is still somewhat imperfect regarding the definition of the thin film appearance (which is result of the scale decomposition procedure). The encounter and collision frequencies are related through the collision efficiency $P_c = K_c/K$. From the modeling point of view, the difference between collision and encounter frequencies is the consideration of the disturbance flow field created from the motion of the bubble. The particles in general do not follow the fluid streamlines due to gravity and inertia. The term interception refers just to the consideration of a finite particle size. So, gravity, inertia and interception determines collision efficiency. In addition, the attachment frequency K_a is a real quantity denoting the frequency of attachment of particles to the bubbles. The attachment efficiency is $P_a = K_a/K_c$ and refers to the fraction of the collisions that leads to permanent attachment. The model for P_a requires computations from both scales IIIa and IIIb. The literature on theories/correlations and computations for

the quantities P_a, P_c is very extensive and have been reviewed many times in the past [22–24].

Although in traditional studies on flotation modeling the particle disturbance flow field has not been considered in the computation of P_c, this issue came recently into play under the name "microhydrodynamics". In the case of particle disturbance flow field in the Stokes regime the inclusion of microhydrodynamics degenerates to appropriate corrections to the Stokes drag law. The coefficients for these corrections result from the solution of individual fluid mechanics problems being the subject of fluid mechanics literature [25]. A complete set of these coefficients (in the form of functions of the particle-bubble separation) has been developed and gathered in [26,27] and [28] for the case $R_p/R_b << 1$. The inclusion of "microhydrodynamics" in flotation collision efficiency computations was made for the first time for Brownian particles in [29]. Before that, it had been used for attachment efficiency computation [30]. However, the first detailed computations for non-Brownian particles being of interest here appeared in [31] for quiescent fluid/bubble and in [32] for moving fluid/bubble. The correction functions is a combination of analytical solutions and fittings of numerical data. A different form of the correction functions for stationary bubble (combinations of high degree polynomials-up to 10-th order with a blending function accounting for fast convergence to the far-field limit) has been used more recently in [33]. It must be noted that the microhydrodynamics functions have been of interest in many other engineering disciplines before flotation. As an example, a complete list of fitted functions for a pair of solid particles with very different sizes can be found in [34] in the context of modeling deep bed filtration (functional forms different than those used in flotation).

3. Modeling of collision frequency between entities in turbulent flow field

3.1. Description of levels of modeling of encounter/collision frequency in isotropic turbulence

The following sections present the levels of detail at which the encounter or collision frequency between entities (particles/droplets/bubbles) in an isotropic turbulent flow field is computed.

3.1.1. Level A

In principle, a three dimensional unit cell (scale II) must be considered, large enough to contain enough particles/bubbles for statistically significant results and small enough to be able to assume isotropic turbulence in it. The fluid flow equations (transient Navier-Stokes) must be solved simultaneously with the entity motion and rotation equations after applying a force to the fluid flow to initiate the turbulent motion. The fluid and entity motions are fully coupled since the boundary condition for the fluid can be set at each entity surface and forces/torques apply from the fluid to the entities. Then the particles/bubbles trajectories can be recorded and upon detection of collision the collision frequency can be derived. Such an approach is extremely demanding from the computational point of view, so a series of simplifications is applied hierarchically.

The first step is to decompose the turbulent fluid motion from the entity motion. This allows the solution of transient Navier-Stokes equation via DNS for the fluid alone. The influence of particles/bubbles to the macroscopic fluid motion is ignored (but it may be considered in scale I by computing the effect of gas/solid phase on turbulence levels). When a "frozen" (i.e. statistically constant in time) liquid flow field is established a number of particles/bubbles is thrown in the unit cell. In that case the fluid flow around each entity has not to be resolved. Instead, the motion of each entity can be directly described by an integrodifferential equation with respect to time t. Since the interest here is primarily in flotation, separate equations for particles and bubbles are written. The governing particle equation is:

$$m_p\frac{d\mathbf{V}_p}{dt} = m_{fp}\frac{D\mathbf{W}}{Dt} - 6\pi\mu R_p f_{dp}(\mathbf{V}_p - \mathbf{W}) - f_{mp}\frac{m_{fp}}{2}\frac{d(\mathbf{V}_p - \mathbf{W})}{dt} - f_{Bp}6R_p\left(\pi\rho_f\mu\right)^{1/2}\int_{-\infty}^{t}\frac{1}{(t-\xi)^{1/2}}\left[\frac{d(\mathbf{V}-\mathbf{W})}{d\xi}\right]d\xi \tag{2}$$

where $\mathbf{V}_p$ is the particle velocity and $\mathbf{W}$ is the liquid velocity at the position of entity (in the absence of entity). Using this formalism entities can be assumed as material points so the position coordinates and fluid velocity can be assumed to refer to the entity center. The bold symbols stand for vectors. The mass of the particle is denoted as m_p, the mass of the fluid having the volume of the particle is denoted as m_{fp}, and the fluid viscosity, density are denoted as μ, ρ_f, respectively. The relation of the derivatives appearing in Eq. (2) to the partial spatial and temporal derivatives is:

$$\frac{D\mathbf{A}}{Dt} = \frac{\partial\mathbf{A}}{\partial t} + \mathbf{W}\cdot\nabla\mathbf{A} \tag{3}$$

$$\frac{d\mathbf{A}}{dt} = \frac{\partial\mathbf{A}}{\partial t} + \mathbf{V}\cdot\nabla\mathbf{A} \tag{4}$$

where $\mathbf{A}$ is an arbitrary vector field.

The initial form of the above equation was derived for rectilinear motion of Stokesian particles in a quiescent liquid and it has been known as Basset-Boussinesq-Oseen (BBO) equation [35]. The extension of the equation for moving liquid was made by Tchen [36] and the corresponding equation is called extended BBO. The above presented form includes some corrections made by Maxey and Riley [37]. The extension of the equation to non-Stokesian entities is a semiempirical one and it is a large issue of discussion in literature [38]. However, this approach is the only one that admits trajectory calculations for large number of entities.

Let us examine the terms in Eq. (2) one by one. The left hand term is the entity acceleration. The first right hand term is the pressure force arising from pressure gradient in the liquid. The second right hand term is the drag term in which the coefficient f_{dp} appears as a correction to the Stokes law. In general, f_{dp} is a function of a Reynolds number which incorporates the magnitude of the slip velocity between entity and liquid. The third right hand side term is the so-called added mass force and it is the force needed to move the liquid around the entity. Finally, the last integral term is the so called Basset or history term and has to do with the acceleration of the liquid around the entity. The f_{mp}, f_{bp} coefficients are corrections to account for the non-rectilinear, non-Stokesian character of the problem and they are described by empirical correlations in [39].

A quite similar equation can be written for bubble velocity $\mathbf{V}_b$:

$$m_b\frac{d\mathbf{V}_b}{dt} = m_{fb}\frac{D\mathbf{W}}{Dt} - 6\pi\mu R_b f_{db}(\mathbf{V}_b - \mathbf{W}) - f_{mb}\frac{m_{fb}}{2}\frac{d(\mathbf{V}_b - \mathbf{W})}{dt} - f_{Bb}6R_b\left(\pi\rho_f\mu\right)^{1/2}\int_{-\infty}^{t}\frac{1}{(t-\xi)^{1/2}}\left[\frac{d(\mathbf{V}_b-\mathbf{W})}{d\xi}\right]d\xi \tag{5}$$

where the subscript "b" denotes the bubble.

The entity properties (mass, size, density) are used only as parameters in Eqs. (4), (5). In addition, the entity size is used for the collision detection. Otherwise the particles are sizeless points with position to be found from the numerical integration of the system of Eqs. (4), (5). It is clear that the simplification over the original model of fully coupled fluid flow is tremendous allowing computation of encounter frequency.

However, there are several issues that need be discussed regarding the above equations:

i. In the derivation of these equations there is the underlying assumption that the liquid velocity profile (in the absence of entities) is

linear in the size scale of the entity. This assumption is quite valid for particles (due to their small size) but is questionable for bubbles in a turbulent flow field. There are scales of motion that cannot be linearized in the bubble size scale. The subject is complex since turbulent size scales much smaller than the bubble may be excluded from this discussion. The corrections for non-linear flow fields in the bubble scale are called "Faxen" terms [40] and their form brings up the addition of the term $-cR^2\nabla^2\mathbf{W}$ to the difference between entity and fluid velocity in Eq. (5). The coefficient c takes the value 1/10 for the added mass term and 1/6 for the drag force and history terms [41].

ii. The significance of the added mass term must be stressed because its negligence is a source of errors and misconceptions as will be shown latter. This term is insignificant for particles/droplets in gases, very important for particles in liquids and quite dominant for bubbles in liquids. The usual mistake is the consideration that a bubble in liquid has no inertia since its mass is insignificant. However, the motion of a bubble is associated with the motion of a considerable amount of liquid and this is the reason of appearance of bubble inertia. Quantitatively, this inertia is expressed through the added mass force.

iii. The Basset (history) force term is the one that creates the most computational problems in the solution of Eqs. (4), (5). This is why it is typically ignored (sometimes with no sound justification or scientific reasoning). Extensive analysis on the contribution of this term can be found in [42]. A time scale associated with this term is the vorticity diffusion time $t_v = R^2/\nu$ (where ν is the kinematic viscosity of the liquid). This has to be compared with the turbulence time scale to assess the influence of the Basset term. For fine particles t_v is of the order of 0.1 ms so it is reasonable to ignore this term. On the other hand, for bubbles t_v is of the order of 1 s and the omission of this term is questionable.

iv. The addition of a lift force that depends on the fluid flow field vorticity has been proposed to be added to Eq. (5) for bubbles [38]. This force makes bubbles (high Reynolds number) to behave very different than the small (low Reynolds number) particles in the turbulent flow field [43]. Another issue that must be considered is the (moderate) increase of the drag force on solid particles induced by turbulence [44].

v. The above system of equations ignores microhydrodynamics (i.e. hydrodynamic interaction between entities). Its inclusion to the above description is through the modification of the corresponding drag expressions in Eqs. (4), (5). The coefficients f_{dp},f_{db} are now a function of the position and velocity of all the entities in a cell. Their computation requires the solution of the fluid momentum equation for the disturbance flow field produced by the entities for each time step. In case that the disturbance flow field is not in the Stokes regime, there is no computationally acceptable way to proceed. However, in the Stokes regime the linearity of governing equations for the disturbance flow field allows several simplifications/approximations.

3.1.2. Level B

A second approximation step is to forget the three dimensional domain with the directly simulated turbulence and to create a single differential equation for the relative velocity and position of a pair of entities. The flow field in this case is represented by a linear flow field with a velocity gradient tensor that fluctuates stochastically in time in such a way that reproduces the statistical features of the homogeneous isotropic turbulence. There is no reason for solving Navier-Stokes equations and sampling in the Scale II in this case. The representative domain is a spherical one with a radius being few times the particle radius (i.e. 5 times). The particle pair distance evolution is followed up to the occurrence of an encounter event. The number of encounters determines the encounter frequency.

3.1.3. Level C

The final approximation is to handle turbulence in a statistical manner using mainly features of the equilibrium turbulence spectrum. This handling refers spatially to a unit cell having radius equal to the sum of the radius of the particles. An expansion of the unit cell (to some particle diameters) is made in some theoretical approaches (i.e. turbulent diffusion) or if an additional mechanism (e.g. Brownian motion in [45]) is to be considered.

3.1.4. Additional difficulties associated to flotation

Some additional complications to the above ideal picture are discussed next: Bubbles, in general, are not spherical but it has been shown that for bubble size (up to 1 mm radius) and bubble velocities met in flotation the spherical shape is a very reasonable approximation [4]. The motion of a bubble and the flow field around, depend largely on the amount and distribution of surfactant on the bubble surface. This distribution is determined by a very complex conservation equation which considers surfactant adsorption-desorption between the bulk and the air-liquid interface, surface convection and surface diffusion on the interface. The surfactant modifies the interface and the flow field by creating a layer on the surface but mainly by inducing Marangoni flow. The typical asymptotic cases considered in literature regarding the amount of surfactant on bubbles surface are i) no surfactant at all (i.e. fully mobile bubble surface). ii) surfactant existence over the whole surface (fully immobile bubble surface) iii) bubble is covered by surfactant up to a point and is free from surfactant in the rest of the surface (stagnant cup formation). The last situation arises when the surface convection dominates the other surfactant transfer mechanisms. It is probably the case in flotation, given that the adsorption-desorption process is dominated by diffusion of surfactants from the bulk which is typically slow compared to the residence time of bubbles in the flotation device. In addition, surface diffusion can spread the surfactant along the bubble surface for small bubbles but not for the bubble sizes found in dispersed air flotation.

In the stagnant cup case, the interface is assumed to be immobile for a part of the bubble and mobile for the rest [46]. Unlike what is showed pictorially in literature [32], the stagnant cup is not a compact region of accumulated surfactant that acts as barrier to the fluid motion. The stagnant cup contains a concentration profile from a maximum (at the rear of the bubble) to a zero concentration at the front edge of the cup. It is not the surfactant packing density but its surface concentration gradient which immobilize the interface (through Marangoni phenomenon). In the more general case the interface is neither mobile or immobile but there is a continuous profile of a slip velocity along the interface. It is noted that the local slip velocity depends not only on local surfactant surface concentration but mainly on the local surface gradient of this concentration. Most of the literature work for deterministic collision frequency in flotation refers to the extreme case of fully mobile/immobile surface and only a few works to the stagnant cup case (e.g [47]). It must be mentioned that even in the presence of a stagnant cup covering less than half of the bubble surface the front part of the bubble (where collisions occur) is mobile so a mobile interface may be a good approximation.

The above picture holds for deterministic bubble motion. The situation is by far more complex for a stochastic one. The highly transient character of the flow and the shear stress on the bubble surface lead to localized surfactant non-uniformities and possibly interfacial waves. These waves may be too small to alter the spherical shape of the bubble, but they could be comparable to the particle size leading to an immense alteration of the flow field in the vicinity of the particle, thus having a significant effect on collision efficiency.

Another complexity arises from the shape of particles. The so far discussion refers to spherical particles. However, particles can have a variety of shapes [33,48,49]. The collision efficiency can be very sensitive to the exact particle shape. Elongated particles are subjected to rotation as they move in the flow field around the bubble. This results to a collision

radius equal to the larger dimension of the particle. Even a spheroidal particle with a small aspect ratio (seemingly very close to sphere) could have a collision efficiency increased by 10% compared to the equivalent spherical shape. Furthermore, small protrusion on otherwise spherical particles are capable to affect collision efficiency [31].

The scope of mentioning the above difficulties and complexities arising in realistic flotation systems is to point out that predictive modeling of flotation process is rather a wishful thinking. Even if a huge effort is spent to resolve every detail of the flow field and collision process issues like slight oscillations of bubble shape and deviations of particles from sphericity can affect the model validity. This aspect should be taken into account during the model development procedure.

3.2. Review on turbulent encounter frequency studies

The fact that the majority of existing theories has been developed for the case of two entities of the same material and comparable size leads us start the presentation with this case. The modifications needed in the theories for a bubble-particle pair of flotation are discussed separately in another section. The analysis of the basic entity encounter theories is necessary because the corresponding flotation theories are based on them. The discussion here begins with the level C studies since historically they were the first that have been extensively developed. In the present section the terms particles and entities are used interchangeably.

3.2.1. Level C studies

A very important entity quantity is the so called relaxation time (or inertia response time) defined as

$$\tau_p = \frac{\left(2\rho_p + \rho_f\right)R^2}{9\mu} \tag{6}$$

where ρ_p, ρ_f are the particle and fluid densities, R is the particle radius and μ is the fluid viscosity.

The Cunningham coefficient typically appears to the definition of τ_p in literature. However, it can be ignored here since it is relevant only to aerosol particles (accounting for deviations from continuum regime) [50].

This is the characteristic time needed by the entity to adjust its velocity to external disturbances. It can be derived by the entity motion Eqs. (4), (5) and it refers to Stokesian entities (corresponding entity Reynolds number based on relative entity-fluid velocity, much less than 1). The relative value of τ_p and turbulence time scales determine the mechanism of turbulent collision. In general, turbulent encounters occur due to the motion of entities with the fluid and due to deviation of the motion of entities from the motion of the fluid. These correspond to mechanisms I and II, respectively, in the terminology of [8] which is adopted here. There are several other names for these mechanisms in literature. Mechanism I can be found as turbulent shear, turbulent orthokinetic or gradient collision mechanism. Mechanism II can be found as turbulent inertia or accelerative collision mechanism [15].

The pioneering work of flow induced encounters of entities is the one of Smoluchowski [51] for simple shear flow (unidirectional motion, uniform velocity gradient). An extensive literature work followed, starting from Camp and Stein [52], with a lot of discussion on how to extend the collision frequency expression of [51] to agitated tanks in turbulent regime. The outcome of the discussion [53] was that the expression of [51] holds under turbulent flow conditions for particles smaller than the Kolmogorov microscale η_k and with the shear rate replaced by the quantity $(\varepsilon/\nu)^{1/2}$. This correlation is used even today for modeling in the environmental technology domain [54]. It is noted that $\eta_k = \nu^{3/4}\varepsilon^{1/4}$.

The definite landmark work on the subject appeared in 1956 by Saffman and Turner [55] (referred henceforth as ST for brevity) based on the statistical approach to the isotropic turbulence. This is the most cited and the most tested work in the history of the subject. On the other hand, some aspects of this work have been extensively criticized by subsequent literature studies (from simple typos to major inconsistencies). There are two different approaches in this work: The first is for entities with $2R < \eta_k$ and $\tau_p << \tau_k$ where τ_k is the Kolmogorov time scale $(\nu/\varepsilon)^{1/2}$. A uniform strain relative motion field is assumed. The so called spherical formulation leads to the simple result for the encounter frequency

$$K = \frac{1}{2}\int_S |w_r|_{av} dS \tag{7}$$

where S is the spherical surface of radius $R_1 + R_2$, w_r is the radial relative velocity between the two entities and the subscript "av" denotes average with respect to orientation, space and time. The subscripts "1" and "2" refer to the two entities. For entities much smaller than the Kolmogorov eddies, the linear expansion of the velocity profiles and the isotropic character of the flow leads to:

$$|w_r|_{av} = (R_1 + R_2)\left|\frac{\partial u}{\partial x}\right|_{av} \tag{8}$$

where u is the x-component of the relative particle-particle velocity assumed to coincide with the corresponding fluid velocity. Considering the mean square of the velocity gradient from $\left(\left(\frac{\partial u}{\partial x}\right)^2\right)_{av} = \frac{\varepsilon}{15\nu}$ [56] and assuming a normal (Gaussian) probability density function for the velocity gradient leads to the classical relation for turbulent coagulation:

$$K = 1.3(R_1 + R_2)^3\left(\frac{\varepsilon}{\nu}\right)^{1/2} \tag{9}$$

Very surprisingly, the expression is quite similar (the coefficient 1.3 replace 4/3) to the one derived previously by extending the Smoluchowski work. The coefficient 1.3 can be found also as 1.29 in the literature. Its actual value is 1.2944. The above formula is the major contribution of ST. It has been proven over the years to be essentially valid even by comparison to detailed simulations of entity encounters in realistic (i.e. DNS) turbulent flow fields. Apparently, this is true also for the similar older approximate expression. However, Eq. (9) was derived in a more rigorous way admitting further analysis of the problem based on the statistical theory of turbulence. It is noted that many authors derived equations similar to the above with different coefficients in place of 1.3 that range from 0.365 to 5.65. (even in the ST work there is an alternative derivation). An even more rigorous approach to derive the encounter frequency using the detailed flow extensional axisymmetric flow field and the statistical theory of turbulence led to the Eq. (9) but with the coefficient 0.365 instead of 1.3 [57].

In ST there is also a different approach to find the encounter frequency. The so called cylindrical formulation. In this case the integration is performed over the projection area of the sphere with surface S and using the magnitude of the relative velocity $|\mathbf{w}|$ instead of the radial component w_r. ST assumed an approximate probability density function (PDF) for $\mathbf{w}$ (which does not obey isotropic behavior). The cylindrical formulation led to a result in the limit of small particles similar to Eq. (9) but with coefficient 1.67 instead of 1.3. The discrepancy was attributed to the approximate PDF of $\mathbf{w}$. Both formulations have been used by several authors but in [58] it was definitely proved that the reason for the discrepancy between the two methods was not the approximate PDF used by ST but the fact that the cylindrical approach is inherently wrong (at least for the case of turbulence in which the relative velocities depends on their orientation over the collision surface S).

ST used the cylindrical formulation in the case where particle relaxation time is not so small. This quantitatively means a ratio τ_p/τ_k being small but finite. In that case the relative velocity **w** is no more the fluid velocity since the particles deviate from it. In order to find **w,** ST used Eq. (4) retaining only the pressure force and the drag force terms. Then they performed direct evaluation of the variance of **w** through the particle motion Eq. (4) leading eventually to its relationship with the variance of the turbulent Lagrangian acceleration which can be found in Batchelor [59]. This is the part of the ST work that has been extensively criticized in literature.

A further important development has been made by Yuu [60]. According to him, the relative velocity of particles is expressed with respect to independent large scale particle turbulent velocities and correlated gradients of small scale particle turbulent velocities. The equation of motion (4) is considered separately for each particle ignoring history and pressure force terms and assuming Stokesian particles. The computation of the required quantities was based on the work of Hinze [61] who solved the equation of motion assuming a generalized flow field expressed through Fourier integrals. This allows analytical solution of the motion equations and derivation of algebraic relations between particle velocity and fluid velocity integral parameters. Unfortunately, the cylindrical formulation and the approximate probability density function of ST have been used in this work. However, the result is of interest since there is a term for the "particle motion imparted by the fluid" which degenerates to the corresponding term of ST (apart from the wrong coefficient 1.67 due to cylindrical formulation) and a term for "particle motion relative to the fluid" which depends not only on energy dissipation rate but also on fluid velocity variance (i.e. turbulent kinetic energy). In addition, the turbulent integral time scale appears in the equations. This parametric dependence appears more physically sound than the one of ST theory where ε is the only turbulence parameter.

The next landmark work on the subject is the one of Abrahamson [62]. He considered the limit of particles having a large inertia and moving through eddies. This is the opposite limit than the one considered by ST. The particle velocity variance is related to fluid velocity variance according to the equation found in [63]. It was derived by solving the particle motion equation for Stokesian particles, ignoring the history term, and assuming the fluid and particle motion as superpositions of sinusoidal motions. The encounter frequency resulted by applying the cylindrical formulation to the relative velocities. In the present case the relative velocity does not have spatial correlation, so the cylindrical approximation is correct and equivalent to the spherical one. The final result is

$$K = 5(R_1 + R_2)^2\left(\left(U_1^2\right)_{av} + \left(U_2^2\right)_{av}\right)^{1/2} \tag{10}$$

where

$$A_i = \frac{a_i T_L + b_i^2}{a_i T_L + 1} \tag{10a}$$

$$\left(U_i^2\right)_{av} = A_i\left(W^2\right)_{av} \tag{10b}$$

$$a_i = \frac{36\mu}{\left(2\rho_i + \rho_f\right)4R_i^2} \quad b_i = \frac{3\rho_f}{2\rho_i + \rho_f} \tag{10c}$$

where the index $i = 1,2$ refers to the two entities, W is the fluid turbulent velocity, T_L is the Lagrangian integral time scale of the flow (the relation $T_L = 1.4\ k/(3\varepsilon)$ can be derived based on the discussion in Abrahamson [62]). The somewhat different coefficient 0.53 instead of 1.4/3 was proposed by Yuu [60].

Further to the above general result, most of the analysis in Abrahamson [62] is restricted to gas as continuous phase. A detailed derivation led to the criterion that in order the theory to hold, the entity diameter d must obey the expression

$$d > \frac{15\mu\left(W^2\right)_{av}}{\rho_i \varepsilon} \tag{11}$$

In case of bubbles, the above relation should be corrected for the added mass effect (included in Eq. (10)) and for deviations from Stokes law (not included in Eq. (10)). Detailed multiparticle simulations [64] of Level A showed that the Abrahamson theory is approached (with slow algebraic convergence) in the limit τ_k/τ_p goes to zero.

Whereas Yuu was unaware of Abrahamson's work and tried just to correct ST, similar techniques to the one of Yuu have been used in [65] in order to find encounter frequency for the whole particle inertia range bridging the small inertia limit of ST to the high inertia limit of Abrahamson. This work ignored the added mass force and it is restricted to the accelerative (mechanism II) contribution to the collision rate. The models of [60,65] were improved in [66] by employing a more detailed time correlation function, including the added mass force term and incorporating turbulent shear (mechanism I) regime encounters. Their results are universal regarding the accelerative mechanism regime. However, the influence of the particle inertia on the shear regime (due to correlation of particle velocities) is accounted only through asymptotic relations for small and large relaxation times. The accelerative mechanism encounter frequency is given as

$$K = \left(\frac{8\pi}{3}\right)^{1/2}(R_1 + R_2)^2\left(U^2\right)_{av}^{1/2} \tag{12}$$

where

$$\frac{U^2{}_{av}}{W^2{}_{av}} = 31 - b^2 \times$$

$$\frac{\gamma}{\gamma - 1}\left[\frac{\theta_1 + \theta_2{}^2 - 4\theta_1\theta_2 1 + \theta_1 + \theta_2{}^{1/2} 1 + \theta_1{}^{-1/2} 1 + \theta_2{}^{-1/2}}{\theta_1 + \theta_2}\right] \tag{12a}$$

$$\times\left[\frac{1}{1 + \theta_1 1 + \theta_2} - \frac{1}{1 + \gamma\theta_1 1 + \gamma\theta_2}\right]$$

$$\theta_i = \frac{\tau_{pi}}{T_L}, \quad \gamma = \left(\frac{T_L}{\tau_L}\right)^2 \tag{12b}$$

where τ_L is the Lagrangian time scale [15] and $i = 1,2$.

The major feature of this relation is that it can reproduce the results of ST and Abrahamson in the limits of small and large inertia, respectively. However the cylindrical approximation leads to a wrong coefficient in case of small inertia. As the inertia of the particles increases the correlation between their velocities decreases leading to the correct result in the limit of high inertia.

The above constitute the first group of works on the subject. It is now time to stress that all the above works ignore any flow disturbance induced by particles and refer to particles smaller than the Kolmogorov microscale. Another interesting result refers to particles with sizes in the inertia subrange ($R_1 + R_2 >> \eta_k$) but with zero relaxation time (i.e. no inertia). In this case, a procedure similar to the one of ST can be used employing features in different scale of the turbulent flow field. A result for this case is given in [67]:

$$K = \left(\frac{8\pi}{3}\right)^{1/2}(R_1 + R_2)^{7/3}\varepsilon^{1/3} \tag{13}$$

The same result appears with a coefficient 1.37 in [66] and 1.37π/2 in [68]. An attempt to account for deviations from the quasi-steady nature of turbulence accounting for intermitency effects through a multifractal

formalism was made in [69]. The resulting correction term is quite insignificant for the level of accuracy needed here so it can be safely ignored.

It is straightforward to generalize the spherical approximation of ST for arbitrary particle sizes as far the particle inertia is not considered. Following the approach of ST but using the general interpolated function for the relative fluid velocity (based on the velocity gradient statistics through the whole equilibrium subrange) leads to the final relation [4]:

$$K = (8\pi)^{1/2}(R_1 + R_2)^2(\nu\varepsilon)^{1/4} f\left(\frac{(R_1 + R_2)\varepsilon^{1/4}}{\nu^{3/4}}\right) \tag{14}$$

where

$$f(x) = 0.26x\left(1 + 0.006x^2\right)^{-1/3} \tag{14a}$$

The above equation tends to the ST formula for particles in the viscous dissipation regime and to the formula (13) for particles in the inertia subrange. In this second limit, the coefficient is different from those discussed above probably due to incorrect derivation (not detailed description is given in the corresponding works). A possible suggestion is to assume this coefficient as an experimentally determined parameter. An approximating form of the above frequency has been used in [8] assuming $f(x) = 0.26\times$ for $x < 1$ and $f(x) = 1.41 \times^{2/3}$ for $x > 1$ (leading to discontinuous collision frequency). A remedy to overcome discontinuity has been proposed in [70] in the context of flocculation. The corresponding function is modular consisting from three spline functions with internal boundaries at $\eta_k/2$ and $2\eta_k$. However, the single smooth function in Eq. (14a) is much better for this purpose.

Hu and Mei [71] corrected the relation of ST for inertial particles by using the spherical formulation and including a term to account for the combined effect of spatial variation of fluid acceleration and particle inertia. Their result was further refined in [58] to include pressure force and the use of proper relaxation times to account for the added mass effect. The latter yields:

$$K = (8\pi)^{1/2}(R_1 + R_2)^2[(R_1 + R_2)^2\frac{\varepsilon}{15\nu} + \left(1-\rho_f/\rho_p\right)^2 D((\theta_1-\theta_2)^2 + 2\theta_1\theta_2\left(R_1^2 + R_2^2\right)\lambda_D^{-2}]^{1/2} \tag{15}$$

where D is the mean square Lagrangian fluid acceleration $D = \left(\left(\frac{Du}{Dt}\right)^2\right)_{av}$ (also known as "machine acceleration" in some studies [4]) and λ_D is the longitudal Taylor-type microscale of fluid acceleration. The problem in this equation (as in the one derived by ST) is that the inertial contribution to collision frequency appears to depend only on turbulent dissipation rate and not on turbulent kinetic energy. In literature, the terms "correlated" and "independent" [15] (referring to entity velocities) have been used to further characterize the mechanism II collision models. From the above review it follows that only the limiting model of Abrahamson is in the "independent" category. Evidently, the particular characterization of the models is useless since there is always a degree of correlation between entity velocities.

A very sophisticated and elaborate approach to computation of collision frequency for particles of the same or different size has been developed in [72,73]. Actually, two different models have been presented. The first one is based on the assumption that the joint probability density function of particle and fluid velocities has a correlated Gaussian form. This model allows an analytical manipulation but cannot include the preferential concentration effect (this effect is explained later in the context of detailed simulations since it was discovered that way). The second model is based on the derivation of a kinetic equation for the probability density function for the relative velocity of two particles. The central assumption is that the probability distribution of the fluid velocity difference between two points is Gaussian. The mathematical treatment is cumbersome and ends to a system of three ordinary differential equations for the radial distribution, second order transverse structural and second order longitudal structural functions, respectively. The collision frequency is derived from these functions (including the effect of preferential concentration). Extensive comparison with the results from multiparticle studies of Level A confirmed the validity of the model. The above models are for particles smaller than the Kolmogorov scale. Extension for entities of larger size can be found in [74]. In summary, the mechanisms of turbulent encounters between entities are shown schematically in Fig. 3.

As it has been discussed above, the entity inertia magnitude is determined by the relaxation time τ_p. However, the effect of the entity inertia on the encounter frequency is determined by the ratio τ_p/T where T is a characteristic time of motion. This characteristic time is $T = \tau_k$ for the turbulent encounters and $T = R/U_d$ (U_d is the deterministic-gravitational entity velocity) for the deterministic encounters. Therefore, it becomes evident that for a given entity inertia may be important for turbulent encounters and unimportant for deterministic ones or vice versa depending on other conditions. In this context, particle turbulent inertia and particle deterministic inertia effect can be considered as different quantities although the particle inertia is a single parameter.

Turbulent diffusion approach

A rather different approach to turbulent coagulation for entities with size much smaller than η_k was introduced by Levich [75]. It is assumed that these particles are transported from place to place in isotropic turbulence in a manner similar to Brownian motion. The corresponding diffusion coefficient is assumed to depend on the distance between particle centers. Levich assumed the diffusivity to be the product of the root mean square of the relative velocity between particles with the distance between their centers and a constant. The solution of the resulting diffusion equation leads to an expression for the coagulation frequency equal to the one of ST but with a much larger coefficient (5.65 instead of 1.3). However, this coefficient was based on the value of the empirical constant of diffusivity-velocity root mean square relation. A different choice of this constant can lead to coincidence between diffusion approach and validated ST approach. Latter, Pismen and Nir [76] generalized the approach to include particle inertia but their result that the diffusivity increases with particle inertia is physically unreasonable. A more rational extension of the theory to include inertia was proposed in [77,78]. The final expression derived leads to the Levich non-inertial and to the ST

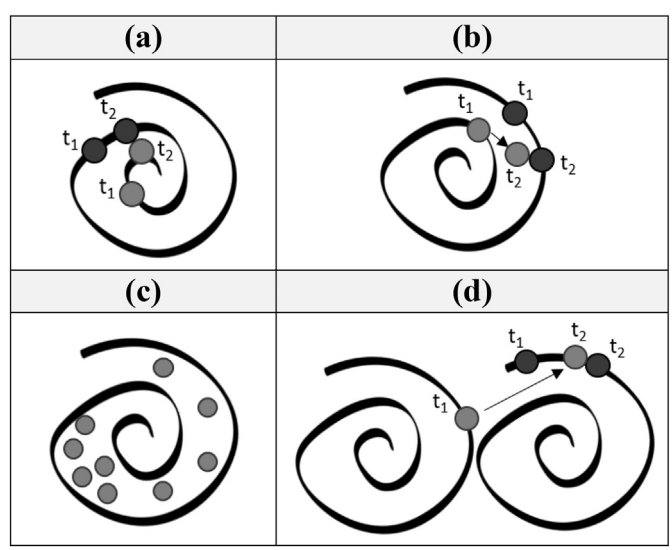

Fig. 3. A schematic of the encounter mechanisms in turbulent flow. In order of increasing ratio (τ_p/τ_k) of entity relaxation to Kolmogorov time scales: (a) mechanism I, (b) mechanism II correlated, (c) preferential concentration, (d) mechanism II uncorrelated.

inertial terms of the coagulation frequency as limiting cases. Lundgren [79] showed that turbulent diffusivity has not only radial but angular component also. A very sophisticated formulation of the diffusion approximation for the case of non-inertial particles is presented in [80]. In this work it was stated that the turbulent diffusion and the ST approximations refers to two different limits of the flow structure. In case of flows with small total strain, each particle interacts with many eddies during the characteristic time of encounter so its motion can be assumed to be stochastic (diffusive). In the other limit of large total strain, the flow field can be assumed to be constant in the time scale of encounter. In this case, the ST picture of the physics is valid and the averaging can be made over the possible flow fields. The resulting relationship differs from all previous ones in that the encounter frequency has an additional proportionality dependence on total strain of the flow field as far as it is smaller than unity.

3.2.2. Level A studies

Some important results from multientity numerical simulations are presented here. In Wang et al. [81] the turbulent flow field is produced through DNS. A total of 1000 to 10,000 particles that completely follow the fluid motion are introduced into the computational cell. The entity size is considered to be of the order of η_k. The essential finding of this work is that apart of technical, statistical, finite domain issues of the techniques used, the ST theory (for mechanism I) holds for practical purposes [81].

Almost in parallel to each other, in [64,82] multiparticle simulations similar to the above but for inertial particles were performed. Only acceleration and drag forces (Stokesian particles) considered in the equation of particle motion. The results are quite interesting showing that an order of magnitude increase of the encounter frequency occurs with respect to the ratio $\alpha = \tau_p/\tau_k$ with a maximum around to $\alpha = 0.5$. This behavior is not predicted by anyone of the stochastic approaches described above. Only the independent velocity approach [62] can be considered as the limit of computations since α goes to infinity. The failure of the stochastic approaches is due to the fact that they consider a spatialy uniform entity concentration. A simple analysis of the equation of particle motion in the presence of inertia [83] reveals that the particle velocity field (unlike the fluid flow field) is not incompressible. In particular, particles are concentrated in regions of the flow field having low vorticity and high rate of strain. The encounter rate is a second order process with respect to particle concentration and this is why any spatial non-uniformity of concentration increases encounter frequency. The phenomenon is termed as preferential concentration can be studied only through multientity simulations. In [64], an improved encounter frequency relation with respect to the one of [66] has been proposed based on a stochastic eddy-particle interaction model. The result is for monodisperse entities, considering only Stokes drag and acceleration terms for entity motion and ignoring preferential concentration.

Additional simulation work, with similar to the above features regarding the flow field generation and the particle motion equations, was made in [84]. Here the focus was the development of relations (by fitting simulation data) for the encounter frequency incorporating the preferential concentration effect. The final result refers to monodisperse particles. More general simulations for particles of different size were performed in [85]. The size ratio in these simulations does not appear to exceed 5. This work has suggested the most general encounter frequency relation. The preferential concentration effect is multiplier of the encounter frequency and it is a complicated piecewise function of relaxation and turbulent times resulted by fitting the simulation data. The final relationship is proposed as the most general candidate to be used by mean field approaches of coagulation (i.e. population balances). However, there is the restriction that the model refers to particle with density much larger than the density of the fluid (i.e. particles in gases).

A very interesting level A simulation work based on DNS appears in [86]. It is the first occasion in literature where entities not only of different size but also of different properties (i.e. bubbles vs particles) are dealt with. Results are provided for four combinations of bubble and particle parameters and three combinations of flow field parameters. The examined particle diameters are smaller than the Kolmogorov microscale whereas the bubble sizes are one to three times the Kolmogorov microscale. Both particles and bubbles are considered to be Stokesian and they are treated as point particles. The equation of motion is used ignoring the Basset and lift forces although it is recognized that the Basset force may be important for bubbles. The results section of [86] contains extensive comparison of the DNS data with the level C model of [73,74] discussed before with particular focus on the preferential concentration effect. A very important outcome of this study is that whereas preferential concentration appears to increase the collision frequency between similar type entities (particle or bubbles) this is not the case for collisions between particles and bubbles. This is because particles and bubbles accumulate in different regions of the flow (due to different responses to the flow field) leading to lower collision frequencies. This effect is not captured by the model of [73] which works well only for entities of the same type.

3.2.3. Level B studies

The approach based on the numerical solution of the evolution of the relative position between two particles are developed and tested extensively in a series of papers by Koch and coworkers (e.g [87,88]). Such a technique refers to particles much smaller than the Kolmogorov microscale since the flow field is locally linearized. Only the acceleration and drag forces are considered to affect particle motion. The technique is not able to predict the preferential concentration effect so a correction using an empirical radial distribution function has been proposed in [87] as post processing of the simulation results for small particle inertia. The approach is restricted to similar size particles. The results of the diffusion approach were compared to the results of multiparticle Level B simulation for non inertial particles in [88]. The dependence of encounter frequency on the total strain was confirmed and the transition between the two limits is found to occur in a smoother manner than what it had been considered previously in [80]. Finally, it is suggested that the ST theory overpredicts slightly (e.g 5%) the collision frequency because it ignores the flow field rotation adverse effect.

3.3. Incorporation of gravity effect in turbulent encounter frequency

The gravitational field creates relative velocities and encounters only between dissimilar particles. The combined effect of turbulence and gravity has been considered in literature as follows: Regarding level A and B models, none of the above referenced works included gravity in their computations. The inclusion of gravity is straightforward; only the addition of the gravitational acceleration to the right hand side of the particle trajectory equation is needed. A few works of Level A can be found in literature for droplet encounters (from the discipline of cloud microphysics) [89]. For example in [90] the flow field is produced by DNS and the trajectory equations for Stokesian particles with inertia and gravity (no microhydrodynamics) is considered. The important outcome here is that gravity influences the turbulent encounter frequency even for particles of the same size (for which there are no gravitational encounters). This is called gravitational aerodynamic effect and leads to a slight reduction of the encounter frequency of monodisperse particles in turbulent flow. On the other hand, it is found that gravity does not affect the radial distribution of particles (i.e. preferential concentration phenomenon). Based on this, a model to modify the turbulent encounter frequency of monodisperse particles has been proposed in [90]. The modification is made only to the terms expressing the relative velocity of particles to the fluid.

The next step is to examine Level C derivations of expressions for the encounter frequency. The most straightforward approach is just to add

the encounter frequencies due to turbulent and due to gravity. In the limit of small inertia particles ST handled g as an effective acceleration in the liquid. Their final result after being corrected latter in [58] corresponds to addition to the right hand side of Eq. (15) (under the square root) of the term

$$+\frac{\pi}{8}(\theta_1-\theta_2)^2\left(1-\frac{\rho_f}{\rho_p}\right)^2 g^2 \tag{16}$$

where g is the gravitational acceleration.

The original derivation in ST had the coefficient 1/3 instead of π/8. A few years after the heuristic modification of the ST formula in [58], a more rigorous approach has been followed in [91]. The final formula for encounter frequency is somewhat more complex than Eqs. (15) and (16) but numerically it is very close to those.

Abrahamson [62] used a completely different approach which is valid at the limit of large inertia particles. He modified the probability density functions of the particle velocity components to have their average at the gravitational velocities W_{g1} and W_{g2} (sedimentation or buoyancy). The resulting encounter frequency is

$$K = 5(R_1+R_2)^2\left(\left(U_1^2\right)_{av}+\left(U_2^2\right)_{av}\right)^{1/2}\exp\left(-\frac{1}{2}\frac{(W_{g2}-W_{g1})^2}{\left(U_1^2\right)_{av}+\left(U_2^2\right)_{av}}\right) + \pi\frac{(W_{g2}-W_{g1})^2+\left(U_1^2\right)_{av}+\left(U_2^2\right)_{av}}{W_{g2}-W_{g1}}\times erf\left(\frac{1}{2^{1/2}}\frac{W_{g2}-W_{g1}}{\left(\left(U_1^2\right)_{av}+\left(U_2^2\right)_{av}\right)^{1/2}}\right) \tag{17}$$

where erf(x) is the well-known error function.

It must be stressed that there is no general relationship for turbulent-gravitational coagulation for the whole range of particle inertia.

3.4. Incorporation of microhydrodynamics- collision efficiency

Let us discuss now the inclusion of microhydrodynamics in the above approaches for the computation of the entity collisions (the inclusion of microhydrodynamics renders "encounters" to "collisions").

LEVEL A. Starting from the Level A models, a procedure to include microhydrodynamics in the simulation of collisions in turbulent flow has been developed in [92]. Only the acceleration and Stokes drag force terms are considered in the equation of motion. The flow field is assumed to be the sum of the turbulent flow field and of the disturbance flow field produced by the entities. The disturbance flow field is assumed to be the superposition of the Stokes flow fields produced by all entities. A consistency requirement for the particle velocities leads to a linear system of 3 N equations where N is the number of entities. Typical simulations were made for $N = 100{,}000$ particles. The disturbance flow field must be solved at each time step of the basic turbulent flow field evolution. It is evident that the computational effort for this approach is enormous. Suggestions have been made to truncate the disturbance field equations to a sphere with radius of 30 entity radii. The method can be trivially extended to handle particles with non-uniform sizes. In any case, the approach is extremely computationally demanding whereas it handles only approximately the hydrodynamic interaction at very close distances between particles. However, this interaction mainly determines the collision efficiency.

LEVEL B. The microhydrodynamics interaction has been treated in an exact way in the Level B simulations in [89,90]. The relative velocity between two solid spheres in a linear flow field (far from the spheres) has been derived in [93]. This velocity depends on four functions (two for hydrodynamic relative mobility and two for relative mobility) having as arguments the normalized distance between spheres and the ratio of the sphere sizes. This ratio is unity for the simulations in [89,90]. For the same ratio, tabulated results and asymptotic formulas of the required functions along with appropriate fittings can be found in [94]. In case of inertial particles the hydrodynamic interactions are more complex but still they can be expressed in terms of a small number of functions. The analysis and computational procedure can be found in [95] whereas several asymptotic formulas are presented in [94].

LEVEL C. There is a large amount of work on the computation of collision rate in laminar flow for non-inertial particles with an exact treatment of microhydrodynamics as it has been described above (e.g., [96–98]). A simple way to exploit this work for the case of turbulent collisions is to invoke the old approaches of considering the turbulent collisions frequency equal to the laminar simple shear one with the replacement of shear rate by $(\varepsilon/\nu)^{1/2}$. This type of calculations requires computation of trajectories of a pair of approaching particles. The basic assumption is that microhydrodynamics act on turbulent collisions in the same way as on laminar shear collisions which is not improbable [99,100]. It is noted that according to the exact treatment of microhydrodynamics the drag force to the particle goes to infinity as the gap between particles goes to zero. The result of this behavior is that turbulent collisions (as it is the case for Brownian collisions also) cannot occur. This is why microhydrodynamics for the above collision mechanisms must be combined with the presence of an attractive force (e.g. Van der Waals) to produce finite collision rate. None of the approaches considered in the Level C models, based on statistical approach of turbulence, takes into account microhydrodynamics. The only exception is when the model of ST is applied to the case of two particles with large size ratio. In the latter, the flow disturbance to the extensional flow field of ST created by the Stokesian large particles is considered and an expression for the collision efficiency due to interception is derived [45].

On the other hand, the inclusion of microhydrodynamics in the turbulent diffusion theory is quite straightforward. Microhydrodynamics can be treated in a strict manner by considering the corresponding functions described in the Level B simulations [80]. It is stated that the particle velocity field taking into account hydrodynamics is no more incompressible so a convective current must be added to the diffusive one to account for this incompressibility. Simpler approaches to handle hydrodynamics in the framework of turbulent diffusion approach can be found in [101,102]. The quiescent fluid microhydrodynamic functions have been used in [101] but in [102] the linear flow field functions are proposed in line with [80]. The major significance of the turbulent diffusion approach to computation of the collision frequency is that it can incorporate in a relatively straightforward fashion other mechanisms of collision, hydrodynamics and force fields.

3.5. What about non-homogeneous and isotropic turbulence?

An issue which arises from the decomposition of the velocity field to locally homogeneous turbulence and to mean flow is discussed here. Velocity gradients appears in the mean flow. The question is how these gradients affect collision rate. The simplest approach is to add the turbulent and mean shear encounter frequencies. This leads to a modified version of ST equation with new coefficient $(1.3(\varepsilon/\nu)^{1/2} + 1.33G)$ where G is the generalization of shear rate referring to mean velocities in a 3-dimensional flow field [52]. A modification to the definition of G has been latter proposed in [103]. A different coefficient in the modified ST has been proposed in [104]: $1.3(\varepsilon/\nu + G^2)^{1/2}$. A slight improvement of the previous relation has been suggested in [105] by using a generalized Churchill interpolation [106] to bridge the gap between small scale isotropic collisions and mean velocity gradient induced collision. Their suggestion for the coefficient of encounter frequency is $[1.3^{2.2} + (1.33G(\varepsilon/\nu)^{-1/2})^{2.2}]^{1/2.2}(\varepsilon/\nu)^{1/2}$. The question on which is the encounter frequency of entities in non-homogeneous turbulent flows remains open. There are no more rigorous derivations of frequencies and corresponding efficiencies than the above heuristic suggestions. Furthermore, no detailed simulations of level A and B

exists. The simulations for these levels of detail are extremely difficult since the mean flow variation imposes a break to the multiscale approach.

4. Review of turbulent flotation collision frequency studies

Having reviewed all the major developments regarding the collision of two entities in a turbulent flow field, the next step is to review their application to the flotation process. It is noted that there are no studies on bubble-particle collision in turbulent flow out of the flotation context (e.g. in physics literature) with only exception [86] discussed before.

4.1. On relative bubble fluid and particle fluid velocities in turbulent flow

A very important issue is the relative bubble-fluid and particle-fluid velocities. The relations derived and used in the above mentioned studies refer to Stokesian particles. However, in flotation, the bubbles are almost never Stokesian and the particles may or may not be Stokesian. This means that the complete equations of motion (4, 5) must be solved which is a formidable task. Some simplified expressions for the relative velocity root mean squares are extensively used for this purpose in flotation literature. The starting one is the correlation of Liepe and Moeckel [107] which is usually referred as "experimental" or "empirical":

$$\left(U_i^2\right)_{av}^{1/2} = \zeta \frac{\varepsilon^{4/9} R_i^{7/9}}{\nu^{1/3}} \left(\frac{\rho_i - \rho_f}{\rho_f}\right)^{2/3} \tag{18}$$

where i take the values "b" or "p" for particle and bubble, respectively. The coefficient ζ originally in [107] had the value 0.68 but the value 0.57 can be also found in literature [11]. Our opinion is that this is simply a result of confusion and there is no fundamental issue behind this discrepancy. Eq. (18) can be found with the different order of the variables in parentheses. It is suggested here to put the numerator of the parenthesis term in absolute value to avoid computational failure. In particular, in case of bubbles the whole parenthesis term approximates unity and can be omitted. Despite its characterization as experimental or empirical, Eq. (18) has a fundamental origin. It is the result of considering turbulent inertia subrange acceleration and Allen's drag law. The formula was later corrected in [4] and the value 0.83 was found for the coefficient ζ. This formula holds for bubbles/particles in the inertia subrange. For smaller particles, the balance between turbulent viscous subrange acceleration and Stokes drag leads to [4]:

$$\left(U_1^2\right)_{av}^{1/2} = \frac{2\varepsilon R_p^3}{135\nu^2} \frac{\rho_p - \rho_f}{\rho_f} \tag{19}$$

It is also suggested here to put in absolute values the density difference to ensure non-negativity of the results. Another less used approximate expression has been proposed in [108] as

$$\left(U_2^2\right)_{av} = (4\varepsilon R_b)^{2/3} \tag{19a}$$

The suggestion of taking the harmonic average of Eqs. (18) and (19) in order to derive an expression appropriate for all particle sizes is made in [8].

4.2. On combined turbulent and gravitational collision frequency

4.2.1. Level C studies

The structure of the presentation in this section is different than in the previous sections for general collisions. There are specific reasons for this choice: Most of the existing models are of Level C and only very few can be considered as Level B (i.e. multiparticles with a single bubble). No simulation of Level A (multibubble-multiparticle in DNS turbulence) exists. The more important problem is that there is no clear distinction between encounter frequency and collision efficiency (like the one defined in section 2.2) in flotation literature. In addition, the different mechanisms (deterministic and stochastic) are totally coupled to each other and to the efficiency so the only reasonable way is to examine the issue of collision frequency in a single step. In order to demonstrate the complexity of the situation it suffices to say that there are models in which the turbulent encounter rate is multiplied by an efficiency derived for deterministic collisions but, on the other hand, there are models that consider the stochastic collision mechanism just as a contribution to the efficiency of the deterministic mechanism (as will be analyzed below). The only process that is absolutely distinct in flotation literature is the attachment process so the few models for bubble-particle attachment in turbulent flow will be examined separately.

It is important to stress that literature on the subject of turbulent flotation functions development was rather non-existent (with the exception of Schubert's work [109,110]) before 2000, unlike the very rich literature for the case of deterministic collisions. There were general references to the subject but not specific models development. It is interesting the following comment in 2003 from a well-known group with long experience in flotation "As far as we are aware, the literature is silent both experimentally and theoretically on these issues at present, so there is a task defined for the future" [111]. The source reference for modeling of turbulent encounters in flotation literature has been the work of Abrahamson [62]. The contribution of the deterministic forces is totally ignored so the Eq. (10) is used for the calculation of encounter frequency. However, the collision efficiency used in [109] and in [111] is the one that corresponds to deterministic collision mechanism. It must be stressed that this is not simply a rough approximation but a purely misleading approach since it implies that the encounter frequency is independent from gravity and the collision efficiency is independent from turbulence levels.

The next step to the development of a turbulent flotation rate model was done in [112] as a sequel to a series of papers devoted to the modeling of deinking by flotation [113]. These authors rederived the Eq. (17) but they used the relative particle/bubble to fluid velocities of [107] instead those of [62].

However, there are several subtle points in their work. The derivation of Eq. (17) was made in a incorrect way. As showed later in [8], there are two ways to derive (17). The one (employed by Abrahamson) is to modify the probability density functions of the velocity components such as to have as mean values the deterministic velocity components. The other way (employed in [8]) is to modify the relative velocity magnitude accounting for deterministic velocity in addition to stochastic velocity. In the derivation of [112] both relative velocity magnitude and probability density functions were modified. Strangely enough (it is believed no real integration was performed), the final result of integration was the same with that of [62].

Although the problem of contribution of the gravitational motion on the collision frequency was dealt with in [112], there was no improvement regarding collision efficiency. The relation corresponding to deterministic collisions continued to be used [113]. The condition (11) for the validity of Abrahamson theory was analyzed in [112] and it was found that it marginally holds for bubbles. This outcome was adopted by following studies in flotation. Unfortunately, this outcome is deceptive because the relation (11) refers to particle-gas system and ignores the added mass effect. In addition, instead of fluid velocity, the total bubble velocity including the deterministic contribution is employed in Bloom [112] which is totally inappropriate. A proper derivation incorporating the added mass effect and the correct fluid velocity shows that the two corrections are counterbalanced and the relation holds for the size of bubbles employed in dispersed air flotation and for high turbulence levels. As the turbulent intensity decreases the error in

using Abrahamson's theory increases but, on the other hand, the turbulence contribution to the encounter frequency is reduced leading to overall acceptable results. Of course, at this stage this is just a crude estimation and detailed calculations are required.

The next attempt to present an integrated model for the collision rate between bubbles and particles in a turbulent flow field can be found in [4]. The basis is again the Abrahamson's model which is presented in the form:

$$K = \pi\left(R_p + R_b\right)^2\left(|U_b| + |u_p|\right) F\left(\frac{\left(\left(U_1^2\right)_{av} + \left(U_2^2\right)_{av}\right)^{1/2}}{|U_b| + |u_p|}\right) \tag{20}$$

where

$$F(x) = 2^{3/2}\pi^{-1/2}x\,\exp\left(-0.5x^{-2}\right) + \left(1 + x^2\right)\,erf\left(2^{-1/2}x^{-1}\right) \tag{21}$$

and U_b, u_p are the deterministic bubble and particle velocities and the U_1, U_2 the corresponding turbulent velocitites.

The turbulent relative mean square velocities are computed from the corrected Eq. (18) (i.e., $\zeta = 0.83$). The collision efficiency for the turbulent collisions is taken from the turbulent diffusion approach of [75] as

$$P_c = 8.05\frac{1}{\left(\rho_p/\rho_f - 1\right)}\left(\frac{\eta_k}{R_p + R_b}\right) \tag{22}$$

The total collision efficiency (in the absence of inertia relative to deterministic motion) is proposed to be the sum of the turbulent collision efficiency given above and of the deterministic collision efficiency for which several relations can be found in the literature. The proposed set of equations is indeed the first integrated approach to turbulent coagulation.

However, several issues still remain open. First, the collision efficiency relation holds only for particles much smaller than the turbulence microscale. It is consistent to the fact that it was derived for the turbulent diffusion regime. On the other hand, the Abrahamson relation for the encounter frequency, holds in the limit of high inertia (relative to turbulent motion) and certainly is not compatible to a turbulent diffusion approach.

The second issue is that the Eq. (22) appears to diverge as particle density approaches liquid density. It gives reasonable values only for particles much denser than the liquid.

The third issue has to do with the addition of the two efficiency functions to get the overall efficiency function. It is surely an improvement over previous approaches to use efficiency and frequency functions derived from combined collision mechanisms. However, the encounter frequency is derived for coupled mechanisms but the collision efficiency is just the sum of the efficiencies derived for the isolated mechanisms.

The fourth issue is not restricted to the particular model discussed but is of a more general interest. In [62,112] it is argued that their resulting relation (equivalent to Eq. (21)) approaches the limits of turbulent and deterministic encounter frequency as the non-relevant velocities go to zero. This is quite true for the limit of deterministic encounters but regarding the limit of turbulent encounters both of the works argue that it is also a good approximation because $\mathrm{erf}(x)/x \to 0$ as $x \to 0$. The exact words of Abrahamson are "$\mathrm{erf}(x) \to 0$ faster than x". However, this is not correct since the single term Taylor of expansion of $\mathrm{erf}(x)$ near zero is $2/\pi^{1/2}x$. The limit of relation (18) for purely turbulent conditions is Eq. (10), as it should be, but the coefficient is 7.5 instead of 5 (i.e. a 50% error). This suggests that Abrahamson's analytical integration leading to the Eq. (21) is incorrect. This is pointed out for the first time in [8]. Nevertheless, Eq. (21) is still extensively used in spite of the fact that it is incorrect. There is no notification of this even in the extensive review in [15]. It must be stressed that is not the approach of Abrahamson (that has been validated against DNS Level A simulations) but the analytical integration which is wrong. There are no comparisons in literature between detailed (Level A) simulations and Abrahamson equation in the presence of gravity that could have revealed the error in Eq. (21). The problem can be overcome with numerical integration of the model equation as in [8]. Sherrel [114] reviewed all available particle-bubble collision frequency models and concluded that there is no model to take into account all turbulent effect and conditions.

Kostoglou et al. [8] attempted to develop a unified approach that covers all the aspects of the problem discussed previously. In the spirit of Abrahamson [62], it was assumed that the relative to fluid velocities of particles and bubbles are random, uncorrelated and follow a Gaussian probability density function. In the spirit of ST, the approach was expanded to account for the relative velocity from the mechanism I collisions. The deterministic velocities were included in the computation of the total relative bubble to particle velocity magnitude. The stochastic nature of the model is considered through the use of probability density functions. In this way, a probability is assigned to each pair of relative particle-fluid and bubble fluid velocities. The computation of the collision efficiency (via deterministic theories) using the representative velocity pairs is a quite reasonable approximation in this case. An integration over all the relative velocity magnitudes and collision efficiencies is required to achieve a closure to the problem. Using generalized relations for the mechanism I collisions and for the inertia dominated particle and bubble velocities, the model can be applied to all possible conditions and this is its main distinction from the previous models for turbulent flotation rate. However the main problem is its complexity since it is expressed by a 9-fold integral. Using mathematical problem reduction techniques the model computationally complexity is significantly reduced to 4-fold integral without any sacrifice of its parametric dependence.

The model of [8] for the attachment rate has the form (the more accurate 6-fold integration version is presented instead of the approximate 4-fold integration version):

$$K = \frac{\pi\left(R_p + R_b\right)^2}{(2\pi)^3\left(U_{cb}u_{tp}\right)^3}\int\int\int\int_{-\infty}^{\infty}\int\int PC\,\exp\left(-\frac{U_x^2 + U_y^2 + U_z^2}{2U_{cb}^2} - \frac{u_x^2 + u_y^2 + u_z^2}{2u_{tp}^2}\right)dU_x dU_y dU_z du_x du_y du_z \tag{23}$$

$$P = P_c\left(\left[U_x^2 + U_y^2 + (U_z + U_b)^2\right]^{1/2}, \left[u_x^2 + u_y^2 + \left(u_z - u_p\right)^2)\right]^{1/2}\right) \times P_a\left(\left[U_x^2 + U_y^2 + (U_z + U_b)^2\right]^{1/2}, \left[u_x^2 + u_y^2 + \left(u_z - u_p\right)^2)\right]^{1/2}\right)$$

$$C = \left[(U_x - u_x)^2 + \left(U_y - u_y\right)^2 + \left(U_z + U_b - \left(u_z - u_p\right)\right)^2\right]^{1/2}$$

$$U_{cb} = \left(U_{tb}^2 + W_{tr}^2\right)^{1/2}$$

where P_c, P_a are the deterministic collision and attachment efficiencies as function of the bubbles and particles velocities, U_{tb} is the mechanism II bubble-fluid relative root mean square (rms) velocity, u_{tp} is the mechanism II particle-fluid relative velocity rms and W_{tr} the mechanism I relative bubble-particle velocity rms. The attachment probability is included in the model for latter reference. Putting $P_a = 1$ the model gives the collision frequency.

The main drawback of the model is that its derivation is based on the cylindrical approximation. According to the above discussions this means than in the limit of mechanism I collision, it leads to an overestimation of the collision rate (by 28%). This limit is actually quite improbable for the case of dispersed air flotation. On the other hand, in the case of dissolved air flotation the mechanism I is the dominant turbulent

collision mechanism. In this case, a simple addition of the ST model to the deterministic mechanisms has been proposed [115]. It is noted that the error in the analytical integration of Abrahamson [62], employed by most of the other models, is avoided in the model of [8] by performing the integration numerically. The problem of the numerical complexity of the final expression has been further reduced by the use of special designed integration techniques. However the computational effort is still much higher than the existing algebraic models.

Koh and Schwarz [116–118] proposed a combination of Abrahamson and ST expression for the turbulent collision frequency. The switch between the two models is proposed to be done using Eq. (11). The problem is that, as it has been already discussed above, this equation cannot be applied to bubbles.

About ten years after the work in [8], a review of stochastic description of the turbulence effect on bubble-particle interactions in flotation appeared in literature [11]. The key and interesting points of this review are the following: i) An integrated form of the particle and bubble motion equations is presented. This is actually the one developed in [60] but it did not appear in an explicit form there. ii) The spherical approximation is considered. iii) A linear addition of the deterministic and stochastic collision efficiencies is proposed formally by decomposing the bubble-particle relative motion to deterministic and fluctuating parts. But the most important feature in [11] is that the collision efficiency is defined with respect to the deterministic encounter frequency. This is a huge difference from the previous models and from the definitions given in the present work. In this new definition of collision efficiency, turbulence is not considered to affect the encounter frequency but is accounted only as a modifier to the efficiency that multiplies the deterministic encounter frequency. In the previous models [4,8], the encounter frequencies are functions of both turbulent and deterministic (gravitational) conditions. iv) In case of small particles the corrected in [58] equation of ST for inertial particles is suggested (Eq. (15) with the gravity term (16)). A further modification that is proposed for this flotation regime is the generalization of the mechanism I contribution to the collision frequency using Eq. (14). This is analogous to the modification previously proposed in [8]. In case of high inertia particles the model of [4] is presented. So there is no a really innovative general model for flotation arising from [11].

Some of the authors of the previous review published a novel integrated model for collision frequency in turbulent flow after two years [1]. Despite the reference they make to the importance of the spherical approximation in their previous work [11] the same authors used in [1] the (wrong) cylindrical approximation. The model development follows the approach of [60]. The relative particle/bubble velocity is expanded to a linearized form around the particle and bubble and the velocity at the contact point is computed. Then the mean square relative velocity is computed in terms of mean velocity and velocity gradient products. Finally, the particle velocities are related to fluid velocities through the (analytical, considering an exponential Langrangian structure function of the flow) solution of the corresponding motion equations. The main modification with respect to the model of [60] is that the particle and bubble velocities are computed directly from Eq. (18) (with $\zeta = 0.83$) and (19). However, their correlation term is computed from the solution of the equations of motion. The effect of deterministic velocities is added to the rate not as a simple addition (like in ST for example) but using the Abrahamson approach. The final result for the collision frequency is

$$K = \pi\left(R_p + R_b\right)^2 \left|U_b + u_p\right| F\left(\frac{(Z/3)^{0.5}}{U_b + u_p}\right) \tag{24}$$

$$Z = 2.0667\frac{\varepsilon^{8/9}R_b^{14/9}}{\nu^{2/3}}\left(1-\rho_b/\rho_f\right)^{4/3} + \frac{4R_p^6\varepsilon^2}{6075\nu^4}\left(\rho_p/\rho_f - 1\right)^2 - 2B\left(W^2\right)_{av} + \left(A_bR_b^2 + A_pR_p^2 + 2BR_bR_p\right)\frac{\varepsilon}{3\nu} \tag{24a}$$

$$B = 1 + \frac{1}{a_b + a_p}\left[\frac{(b_b-1)\left(a_p + a_b b_b\right)}{1 + a_b T_L} + \frac{(b_p-1)\left(a_b + a_p b_b\right)}{1 + a_p T_L}\right] \tag{24b}$$

where the coefficients a_i, b_i, A_i ($i = b,p$) and the time scale T_L have been already described in Eq. (10) and the function F(x) is given in Eq. (21). The significance of each term on the collision frequency is assessed in detail in [1] by omitting this term and computing the collision frequency using the remaining terms. A comparison of the modified to original frequency indicates the significance of the omitted term.

Apart from the obvious errors associated with the use of the cylindrical formulation to compute the collision frequency and the use of the incorrect form of the function F(x) there are a few other issues to be discussed on this model derivation. The first refers to the computation of the drag coefficients. The original model of [60] is exclusively for Stokesian entities since it is the only case that admits analytical solution of the governing motion equations. The problem is overcome partially in [1] by using the velocities of Eqs. (18), (19) instead of those resulting from the motion equation. However, the integration of motion equations cannot be avoided in the computation of the bubble-particle velocity correlation term. In order to proceed to analytical integration of the equation, it is apparent that the drag coefficient was assumed to be independent from the velocity (which of course is not true). So the constant drag coefficient appears in the final equations. It is not explained at which velocity this coefficient corresponds (if it is the turbulence root mean square relative to fluid velocity, it is implied that a trial and error computational procedure is needed). Another issue is that the particle/bubble velocities and their correlation were derived using different theories. This leads to the strange issue that the velocities depend on turbulent dissipation rate ε whereas their correlation depends on turbulent kinetic energy k. The inconsistency is clear here since k is uncorrelated to ε so it is not possible for the correlation of ε-dependent functions to depend on k.

The work has no discussion on the computation of the real collision efficiency (i.e accounting for the bubble flow field). However, several results of a collision efficiency defined as (combined deterministic and stochastic collision frequency)/(deterministic collision frequency) are presented. The inadequacy of this definition is evident because the presented efficiency takes values up to 250 whereas one should expect the efficiency not to exceed unity. Extensive comparisons of the collision frequencies resulting from the proposed model in [11], model of [60], model of ST (cylindrical formulation), model [112] and model of [4] are presented. The new model gives very similar results to the one of [60]. The deviation between the two models increase as the significance of gravity increases which is reasonable since Yuu's [60] model does not include gravity. The other three models give much smaller values (about half) of the new one implying that mechanism I and II contributions are comparable for the studied cases.

An integrated model of turbulent flotation has been proposed in [119]. The collision frequency is the one of Abrahamson accounting only for turbulent velocities computed by Eqs. (18) with $\zeta = 0.68$ for particles and (19a) for bubbles. The collision efficiency for deterministic collision is used. However, it is not stated at which velocities this efficiency is computed.

Recently, the turbulent energy dissipation rate distribution in a flotation cell is computed based on particle image velocimetry measurements [120]. Based on this distribution the corresponding distributions of particle-bubble encounter frequency and collision efficiency are computed and presented. The encounter frequency is computed employing only the turbulent mechanism II as expressed in the large inertia limit by Eq. (10). The particle/bubble velocities are computed by Eqs. (18), (19). The turbulent collision efficiency is computed using Eq. (22). The inconsistency of using the large inertia limit encounter frequency with the small inertia limit collision efficiency is obvious. In addition, a total collision efficiency is computed using the relation proposed in [4]:

$$1-P_c = \prod_j (1-E_j) \tag{25}$$

where the index j takes the values: turbulent, inertia, interception and gravitational and E_j refers to partial collision efficiencies. It is questionable how such a global efficiency, affected by all collision mechanisms, can be combined with the turbulent encounter frequency presented in [120] to give meaningful results for the collision rate, as no details are offered by the authors.

4.2.2. Level B studies

The only approach that can be considered as Level B for bubble particle turbulent collision is the one of Liu and Schwarz [121,122]. The basic difference between these two works is that in the first the methodology is applied to a bubble with an immobile surface and in the second is applied to a bubble with mobile surface. So, only the first of the two will be discussed in detail here. This particular work is made in the spirit of multiscale simulation of flotation process [117,118]. This multiscale formulation is furthermore refined in [121]. The main suggestion is the use of CFD approaches not only in Scale I simulations but also in Scale IIIa. In this respect, several model problems are proposed and solved using the CFX10 CFD code. The first is the computation of the drag force for the motion of the bubble in the Non-Newtonian slurry. The non-Newtonian character is due mainly to the effect of particles existence. The second model problem is the computation of the microhydrodynamics functions in non-Newtonian fluids using CFD. An objection here is that the fluid in the particle scale is Newtonian, unlike in the bubble scale. Another objection is that the superposition approach is considered leading to the use of microhydrodynamic functions. However this approach holds only for linear problems. The non-Newtonian fluid renders the problem non-linear which means that the computations must be done for every possible particle velocity and flow field around the bubble (in addition to the geometric variables: sizes and separation distances). The third model problem, which is of main interest here, is the turbulent collision frequency. The relative particle-bubble motion is decomposed as follows: The bubble has a velocity with respect to liquid. This velocity comes from the combination of the turbulent inertia motion of the bubble and of the buoyant motion. The velocity of bubble due to turbulence is computed from the relation (18) and the composite bubble-liquid relative velocity rms is computed using the Abrahamson approach as

$$\left(U_{bt}^2\right)_{av}^{1/2} = |U_b| F\left(\frac{\left(U_1^2\right)_{av}^{1/2}}{|U_b|}\right) \tag{26}$$

where the function F(x) is given in Eq. (21).

Then a parallepiped unit cell is assumed in which the bubble remains stagnant and the fluid with the particles enters having as velocity the previously computed relative bubble-liquid velocity. The flow field is computed using a RANS approach (time averaged quantities). Unlike in most cases in literature, turbulence is not produced in the computational cell (since the bubble Reynolds number is small) but it exists in the inlet stream and it is the one computed form the device scale CFD simulation (Scale I). The detailed trajectories of the particle entering the cell are predicted using the equation of motion (4) (excluding the history term) augmented by a term to account for turbulent dispersion of the particles (in this case the terms "dispersion" and "diffusion" are equivalent). This term is of stochastic nature and it is extensively used in CFD codes for Lagrangian simulation of particulate flows. The microhydrodynamics is also considered by employing the appropriate functions for drag corrections. This refers only to interactions between particles and bubble and not to the interactions between particles. No encounter frequency is presented in this work but the collision efficiency is computed directly in microscale as the fraction of particles reaching the surface of the bubble.

The model is absolutely consistent with the analysis presented in the previous sections. The bubble and the particle turbulent motions are treated separately using the Abrahamson approach for the high inertial bubble and the turbulent diffusion approach for the much smaller particle that meet many eddies before colliding to the bubble. All collision mechanisms are taken into account. Specifically, it is the only case in which microhydrodynamics is taken into account in modeling of turbulent flotation. The collision efficiency that corresponds to the above computation procedure is a novel one. The bubble turbulent inertia motion contributes to the encounter frequency whereas the particle turbulent motion contributes to the collision efficiency.

The main problem of this approach originates from the fact that the dispersion term in particle trajectories is a stochastic one. This means that a limiting trajectory procedure is not possible and several thousands of trajectories have to be tracked in order to get convergent results for the collision efficiency. Considering that the number of input parameters of the unit cell problem is large (sizes, velocities, turbulence features etc.), it is apparent that the method can be used only for indicative calculations and not to resolve the complete parameter space. Such indicative results are presented in [121] for cases in which it is clearly shown that microhydrodynamics has an adverse effect to the collision efficiency. It is suggested that the effect of microhydrodynamics decreases as particle size decreases so for fine particles can be ignored. A very elegant detail of the model is the notification that only eddies with size between the Kolmogorov scale and the bubble size contribute to particle dispersion so the relevant kinetic energy must be employed in the calculations. This energy is found by integrating the universal equilibrium spectra. The authors also discuss about the sampling of bubble to fluid relative velocity from a distribution instead of using a single value for the calculation of collision efficiency, an approach that has been previously followed in [8]. The approach of [121] is recently followed in [123] using the CFD code Fluent. The main improvement is that LES is used to resolve the flow field in the unit cell instead of RANS. In this case, the use of k and ε are not enough to define the inlet conditions and a realistic turbulent energy spectrum is employed to simulate the inlet flow. Additional differences from [121] is that the lift force is taken into account but microhydrodynamics is ignored. It is not clear if a particle dispersion term accounting for turbulence wavelengths filtrated by LES is taken into account. Some results for particles with density slightly larger than that of water are presented. The effect of particle inertia is examined. It is shown that turbulence increases collision efficiency. An interesting observation is that the existence of particles in the bubbles wake may modify considerably the local turbulent characterestics affecting significantly the detachment process.

Let us review the basic schemes of accounting for encounter frequency and collision efficiency mentioned above. The general coagulation Scheme is the one used for collision between general entities. The notation TI, TII refers to turbulent encounter mechanism I and II, respectively. The terminology GB, GP refers to gravitational motion of bubble and particle, respectively. In general, the letters "B" and "P" are used to denote the bubble and the particle motion. The term microhydrodynamic refers to bubble and particle only for the general coagulation scheme. In all flotation schemes it refers only to the particle disturbance flow field. The flotation Scheme I is what we propose here as the most physically sound. This scheme has been followed in [8] (ignoring microhydrodynamics and particle deterministic inertia). The flotation Scheme II is the one employed in [112]. The flotation Scheme III is the one proposed in [4]. The flotation Scheme IV is the one employed in [1]. Finally, the flotation Scheme V is the one employed in [121,122]. The same scheme ignoring microhydrodynamics is employed in [123]. The basic aspects of the Schemes discussed above are presented in Fig. 4. It is noted that the extension to include attachment efficiency is the same for all Schemes so it does not appear except in Scheme I for which the attachment efficiency has already been included in [8].

4.3. On attachment efficiency in turbulent flow field

The final issue remaining for discussion is the consideration of the attachment efficiency in turbulent flotation models. There are only two approaches to the subject based on the two different approaches to attachment efficiency for deterministic flotation models. According to the first approach, the two main variables for attachment is the contact time and the induction time [4]. The induction time depends only on physicochemical forces. The increase of relative bubble-particle velocity leads to decrease of contact time and decrease of attachment efficiency. The second approach has as key variables the relative velocity at contact (more specifically at the thin film distance) and the energy barrier (computed using DLVO theory) [124]. In this framework the relative velocity increases the attachment efficiency. The controversial nature of the two approaches is shown in more detail in [125]. A recent correlation of experimental data for attachment time

General coagulation Scheme

Encounter Frequency	Collision Efficiency
Turbulence (TI+TII)	Microhydrodynamics (disturbance flow field for both entities)
Gravity (both entities)	Interentity forces

Flotation Schemes

Scheme I [8]		
Encounter Frequency	Collision Efficiency	Attachment Efficiency
Turbulence (TI+TII)	Bubble disturbance flow field (TI +TII+GB)	Particle-bubble forces
Gravity (GB+GP)	Particle deterministic inertia	Microhydrodynamics
	Particle gravity	
	Interception	
	Microhydrodynamics	

Scheme II [112]	
Encounter Frequency	Collision Efficiency
Turbulence (TII)	Bubble disturbance flow (GB)
Gravity (GB+GP)	Interception
	Particle gravity (GP)

Scheme III [4]	
Encounter Frequency	Collision Efficiency
Turbulence (TII)	Bubble disturbance flow (GB)
Gravity (GB+GP)	Interception
	Particle gravity (GP)
	Turbulence (TI)
	Particle deterministic inertia

Scheme IV [1]	
Encounter Frequency	Collision Efficiency
Gravity (GB+GP)	Turbulence (TI+TII)
	Gravity (GB+GP)

Scheme V [121]	
Encounter Frequency	Collision Efficiency
Bubble turbulent inertia motion (BTII)	Bubble disturbance flow (BTII+GB)
Bubble gravitational motion (GB)	Interception
	Microhydrodynamics
	Particle turbulent motion (PTI+PTII)
	Particle gravity (GP)
	Particle deterministic inertia

Fig. 4. The several schemes for consideration of encounter frequency and collision efficiency employed in the literature.

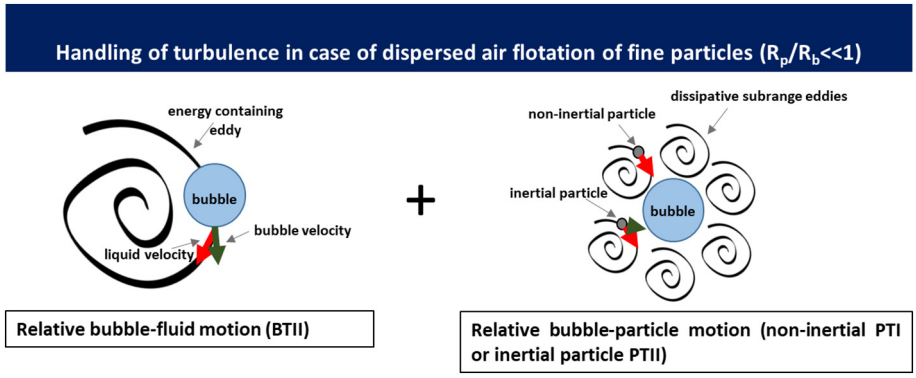

Fig. 5. Proposed treatment of turbulent encounter frequency between fine particle and bubble sizes representative of dispersed air flotation.

shows that it depends on approach velocity [10,49]. This may be the point that connects the two approaches to attachment efficiency. The contact/induction time attachment efficiency approach has been incorporated in turbulent flotation rate model of [8] where the kinetic energy/energy barrier approach has been incorporated in turbulent flotation rate of [119].

4.4. Additional discussion

The importance of including a gravity-induced contribution in a turbulent flotation rate model should not be overlooked. This contribution is insignificant for high levels of turbulence or in the more exotic case of microgravity (e.g. mining in space). The point is that there is always a distribution of turbulence intensity in a flotation device. Examining the bubble-fluid relative velocities and the cumulative distribution of ε in a small laboratory Denver cell presented in [121], it is concluded that the deterministic collisions prevail for up to 80% of the cell volume so the gravity effect must be always taken into account. An alternative approach is to divide the flotation device in high turbulence and low turbulence regions [126]. The turbulent and deterministic flotation mechanism can be considered to prevail in different regions. Another important issue is that the above mentioned models mainly refers to the case of small particles and large bubbles. There are applications in which the bubbles are smaller than the particles [127,128]. Turbulent flotation rate models for this case do not even exist and development from first principles is needed. This is clearly a subject of future research.

To this end, our personal opinion is that increasing the complexity of the models in all scales will not lead to real predictive modeling for flotation, because there are always additional phenomena and additional complications. The proper employment of detailed simulations (usually focusing on a subspace of the existing phenomena) is to use them for the design of phenomenological approaches in several scales (supported also by experimental data) which then can be integrated to large scale models appropriate for engineering design and optimization. At present, a prototype application of this procedure in computational fluid mechanics is the DNS (detailed model of excessive computational complexity that makes it useless for realistic problems) and RANS (phenomenological model of affordable computational complexity appropriate for design-not predictive-calculations).

At this moment, there are three available turbulent flotation rate expressions of the required type. All of them contain some inconsistencies with that in [8] appearing to have the least. However, its computational complexity is orders of magnitude higher than that of the others. Regarding the use of the particular rate expressions in scale I (device scale) models, the one of [4] has been used extensively in literature, the one of [1] has never been used and the one of [8] have been used by just one group [129]. Our suggestion for the future is the modification of the statistical model of [8] using the decomposition of turbulent encounter mechanisms as introduced in [121]. This decomposition for a particle much smaller than the bubble appears schematically in Fig. 5 and shows clearly the difference of the turbulent encounter mechanisms between general coagulation and flotation of fine particles.

The present manuscript up to this point describes the situation on the subject up to the end of 2019. However, after the completion of the present work and right before submission at January of 2020 an outstanding work that completely redefines the scientific subject appeared in literature [130]. It is the first Level A simulation study for flotation. Unlike the other Level A studies, this particular one does not focus only on fundamental issues but it extends the simulations accounting for parameter values relevant to actual flotation process. Several thousands of particles and bubbles are considered as point particles in the computational domain. In some cases the domain has size (side of 10 cm) of the order of macroscopic scale. The particles and bubbles have diameters of 57–60 and 190–300 μm, respectively, and they are treated as being smaller than the Kolmogorov microscale although it is not always the case. Both gravity and hydrodynamic interactions are taken into account using the approximate technique developed in [92]. The particle and bubble trajectory equations are solved (for general non-Stokesian entities) ignoring the Basset and lift forces. Several results for the probability density functions of bubble and particle velocity components and for collision frequencies are presented. The simulations show that the effect of the relative velocity on the collision frequency is much more important than the effect of preferential concentration as turbulent intensity increases. A very relevant discussion on the limitations and prospects of the particular approach closes the manuscript. To our opinion the work in [130] is very significant as it presents important results and ideas at several levels. It can be considered complementary to existing level B simulations for flotation since it accounts for bubble populations but it cannot resolve accurately (for computational economy reasons) the flow field around each bubble. The Level A and B simulations cannot be conclusive since they cannot include all the phenomena so they are focused to different aspects of the process. However they are invaluable to support the development of Level C models.

5. Conclusions

A quite exhaustive review of the possible approaches, of the background material and of the existing models of flotation rate (i.e. encounter and collision frequencies between bubbles and particles) is presented in this work. The collision frequency model is independent from detachment but the effect of gravity should always be taken into account. The turbulent collision frequency can be treated only in a multiscale framework. The complexity of the idealized process and the additional uncertainties arising in practice (e.g. particle shape) renders the predictive modeling rather out of question for the time being. So, the focus must be on models appropriate for sensitivity analysis and

process optimization. In that respect, a flotation rate model should exhibit consistency and appropriate parametric dependence and has to be of realistic algebraic complexity. Three models (i.e. [1,4,8]) that more or less (at least after some modifications) offer these features can be found in literature. All of them are based on three pioneering works on turbulent collision modeling (i.e. [55,60,62]). It appears that these models need further refinement (based also on more recent detailed simulations) in order to be able to be used in multiscale flotation process simulation tools.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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