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A Few Fundamental Aspects Related to the Modelling of an Accidental Massive Jet Release of Nanoparticles

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Nanotechnologies are increasingly used in various industries. The risks associated with nanoparticles are currently not well-known and then need to be further studied. Among the different possible hazardous scenarios with nanoparticles, the massive jet release seems to have received very little attention. Beside experimental approach, Computational Fluid Dynamics (CFD) tool constitutes an interesting approach to evaluate source term of a jet release. However, specific properties related to nanoparticles introduce new challenges in the modelling of such phenomenon compared to classical jet with particles. In that context, a new modelling framework has to be defined. In this paper, current qualitative and quantitative modelling available approaches are reviewed for jet release of nanoparticles and their relevance are discussed.

1. Introduction

Research in nanotechnology is growing rapidly and a lot of potential applications are identified in numerous fields over the whole industrial world, as well as colossal potential economic spin-offs (Kuhlbusch et al., 2011). Nanoparticles (NP) are nowadays used in variety of industrial processes including chemistry, aeronautics, biology and ecology process. Under this context, understanding and characterizing the potential damage that nanotechnology may cause to population and environment appears as a critical challenge. The risk study and management on NP process provide decision-making aid for public agency and a better understanding of population to this new technology. As an example of such accidental pipe leakage with NP, one can mention the one that occurred in Blanzy, France in 2012. The safety study of such accidental scenario should be able to provide information on variations of NP properties in the atmosphere, but there is, so far, no model that could predict the NP behaviour in such case. Literature studies concerning the modelling of release of powders are rather scarce and were devoted to the study of micropowders (Hadinoto et al., 2005). A few experimentations are available regarding the modelling of NP release: Ibaseta et al. (2006) experiment free falling of NP in a chamber test, Stahlmecke et al. (2009) investigates NP agglomerate stability flowing through an orifice under various differential pressure conditions. Although, experimental data in the literature about the NP release jet is insufficient to build a prediction model regarding the behavior of NP. Beside the experimental methods, the computational fluid dynamics (CFD) based methodology is developed recently thanks to computer power development. CFD is expected to give precise results of evolution of NP along time and space but is very time consuming. The aim of the present paper is to provide a better fundamental understanding of NP release jet phenomena and potential approaches of NP dispersion modelling. The modelling of NP behavior is expected to produce crucial information for better estimation of accidental scenarios including release of nanopowder in the environment and better estimate the toxic impact of NP on population or their capacity to form an explosive atmosphere.

2. Physical specificities regarding nanoparticles transport

The accidental scenario case considered is a massive release of NP in atmosphere in case of leakage or rupture of conveying pipe. For this configuration, the two main physical phenomena of NP considered are

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Brownian motion and agglomeration. Brownian motion is defined as the random motion of NP due to impact of NP with air molecule. The agglomeration is the process in which agglomerates are formed. Agglomerates are a cluster of loosely bound particles in which the resulting surface area is of similar magnitude to the sum of the surface areas of the individual particles. The NP in agglomerate, i.e. primary particles, are held together by weak forces. Agglomeration modifies the particle shape and size distribution in time and space and then influences the dynamics of NP flow. Agglomerates can have a non-spherical form and agglomerate size is often in microscale (Ibaseta et al., 2007). Therefore, the modelling of Brownian motion and agglomeration becomes a great challenge. Beside those two specific phenomena for NP, all physical phenomena that occur in particle laden jet should be accounted for. Those classical phenomena, presented in Figure 1, influence strongly the agglomeration and increase the complexity of modelling NP jets. Because of the complexity of the physical interaction in the NP jet, it is important to note that the other physical phenomena related to phase change as nucleation, condensation, vaporization, etc… and chemical reaction of the system are not commented in this study.

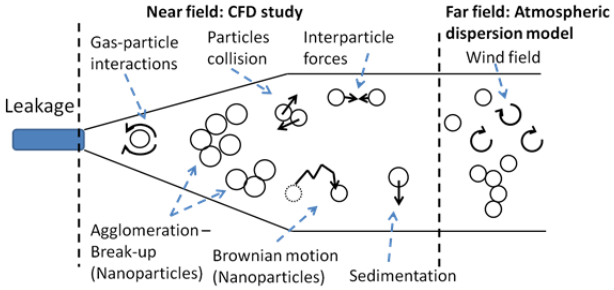


Figure 1: Schematic view of physical phenomena in case of massive release of nanoparticles.

The approach proposed in the present paper for modelling NP release jets considers that there are two fields within the jet. In the first field, the so-called near field, the concentration of NP is high and all the physical phenomena presented in Figure 1 have to be modeled. In the second field, called the far field, the NP jet becomes diluted in the atmosphere and the NP dispersion will be driven by the gas velocity. The limits between near field and far field are not well known and may depend on space and temporal scale considered. In the near field, the space and temporal scale are in the order of meters and seconds respectively. Meanwhile in the far field, the space and temporal scale are in the order of kilometers and hours respectively. Therefore, the model chosen for the near field is based on CFD and the model chosen for the far field is based on atmospheric dispersion models. The argument about the use of those models will be detailed latter in the present paper.

2.1 Brownian motion

In continuum and free molecular approach, the criteria to account Brownian motion is the dimensionless Knudsen number as Eq(1):

$$K_n = \frac{2\lambda}{d_p} \tag{1}$$

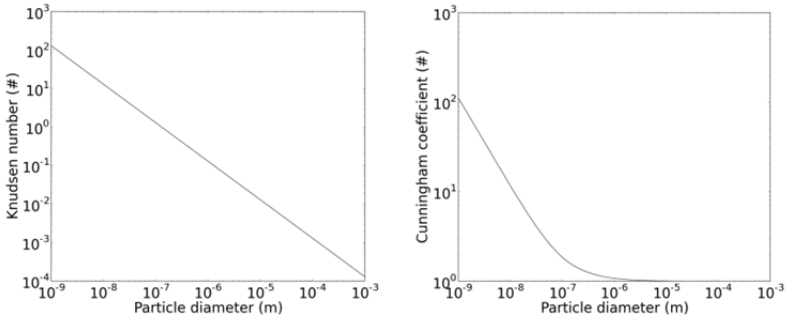
In this expression, d_p is particle diameter and λ is mean free path length of the fluid. In the atmosphere condition, Friedlander (2000) estimates $\lambda \approx 60\,nm$ for the air. For $K_n \gg 10$, the "free molecular regime" is considered and the Brownian motion strongly influence particle displacement. If $K_n \ll 1$, the particle is in "continuum regime" and the Brownian motion can be neglected. $1 < K_n < 10$ corresponds to the transition regime. Figure 2a represents the Knudsen number as a function of particle diameter in atmosphere. The figure shows that the NPs in atmosphere are generally in free molecular regime. The simplest approach to consider the Brownian motion is to extrapolate the particle movement in a continuum regime by a parameter called Cunningham coefficient, C_c. For example, the particle diffusion coefficient estimated by Stokes – Einstein can be modified as Eq(2):

$$D_{br} = C_c \frac{k_B T}{3\pi\mu_g d_p} \tag{2}$$

In this expression, $k_B = 1.381 \times 10^{-23} J/K$ is the Boltzmann's constant, μ_g is gas viscosity, T is the gas temperature. The Cunningham coefficient C_c is evaluated as Eq(3).

$$C_c = 1 + \frac{\lambda}{d_p}\left(A_1 + A_2 \exp\left(\frac{-A_3 d_p}{\lambda}\right)\right) \quad (3)$$

Where A_1, A_2, A_3 are model constants. By experimentation with modulated dynamic light scattering method, Hutchins et al. (1995) proposed that $A_1 \approx 1.23$, $A_2 \approx 0.469, A_3 \approx 1.178$. The Cunningham coefficient as a function of particle diameter is plotted on Figure 2b.



(a) (b)

Figure 2: Knudsen number (a) and Cunningham coefficient (b) in function of particle diameter.

For NP of 10nm diameter, $C_c \approx 11.5$ which means that the NP diffusion can be 11.5 stronger than Stokes – Einstein diffusion. As the particle size increases, C_c tends to 1, the particle diffusion coefficient is equal to Stokes – Einstein diffusion coefficient.

2.2 Agglomeration

The agglomerate is formed by interactions between primary particles as weak force. The principal weak force considered is van der Waals force. In the atmosphere, Friedlander, (2000) has shown that NP are affected also by the electric force. In wet atmosphere, the capillary force should be considered and modeled as proposed by Butt et al., (2009). In pneumatic conveying system, the particle charging by interaction with wall and between particles is modeled by Bunchatheeravate et al. (2013). Those weak forces can be accounted for depending on different configurations. For simplification in the accidental release of NP case, the van der Waals force can be considered as the only weak force between primary particles in agglomerates.
The number of primary particle N_{pp} in agglomerates is found related with their radius of gyration R_g by a power law such as Eq(4) (Friedlander, 2000).

$$N_{pp} = k_f \left(\frac{R_g}{a}\right)^{D_f} \quad (4)$$

In this relation, a is the radius of primary particle. $1 \leq D_f \leq 3$ is the fractal dimension which represents the agglomerates morphology. k_f is a fractal prefactor. In diffusion – limited agglomeration that corresponds to agglomeration in free molecular regime, $k_f = 1.3$ and $D_f = 1.78 \pm 0.05$. (Goudeli et al., 2015). This relation is obtained by averaging over many aggregates and it requires self – similarity of primary particle. The fractal model is useful to describe the agglomerate morphology but cannot predict the evolution of agglomerate in time and space. This model could be coupled with CFD model.
The population balance method consists in describing agglomeration process by using Smoluchovski type equation on the number particle density c_k as Eq(5) (Friedlander, 2000).

$$\frac{dc_k}{dt} = \frac{1}{2}\sum_{i+j=k} \beta(v_i, v_j) c_i c_j - c_k \sum_{i=1}^{\infty} \beta(v_i, v_k) c_i \quad (5)$$

In this expression, v_i and v_j are respectively the volume of particulate class *i* and *j*, c_i and c_j are the number particle density of class *i* and *j*, $\beta(v_i, v_j)$ is the agglomeration rate which has unity of m^3/s. $\beta(v_i, v_j)$ represents the number of agglomeration per time within a volume considered of two particulate class *i* and *j*. The estimation of agglomeration rate $\beta(v)$ is complex and depends on various parameters such as particle diameter, flow regime, turbulence, etc... Friedlander (2000) has reviewed different models of $\beta(v_i, v_j)$ but its formulation remains uncertain. Kiparissides (2006) provided a review of numerical schemes to solve Eq(5) but those numerical schemes are highly complex and time consuming. Because of those limitations, population balance method still needs more research and cannot be currently used in industrial applications. Although, a

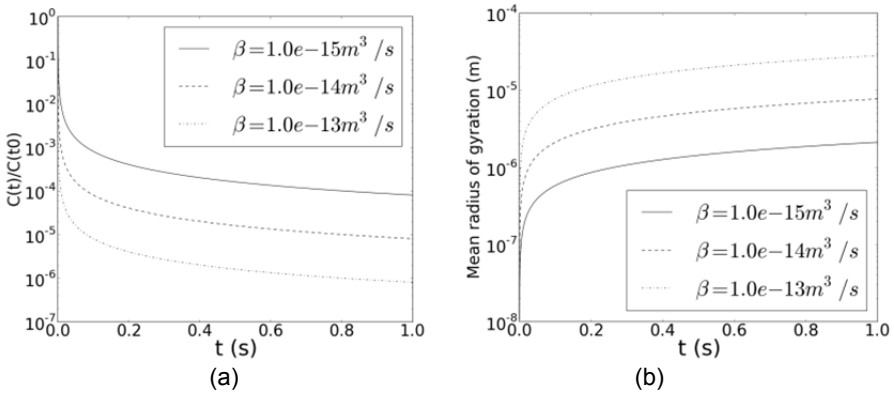
simple agglomeration configuration of NP monodisperse can be considered. In this case, the Smoluchovski equation becomes Eq(6).

$$\frac{dc(t)}{dt} = -\frac{1}{2}\beta(v)\, c^2(t) \tag{6}$$

The solution of this equation can be obtained analytically as Eq(7).

$$c(t) = \frac{c(t_0)}{1 + \frac{1}{2}c(t_0)\beta(v)\, t} \tag{7}$$

For a diameter range of primary particle from 1 nm to 1000 nm, $\beta(v)$ is computed from different formula in free molecular regime, transition regime and continuum regime (Friedlander, 2000) and takes values in range between $10^{-15}\ m^3/s$ and $10^{-13}\ m^3/s$. A simple computation can be made for a case of same size NP release in atmosphere. For example, a mass of 0.5 kg of NP is considered with 25 nm diameter and a density of 2500 $kg/\ m^3$. The number concentration and agglomerate diameter can be estimated by Eq(7) and the mean radius of gyration is obtained by Eq(4) for 1 s. The results are showed in Figure 3.



(a) (b)

Figure 3: Number concentration of agglomerates (a) and mean radius of gyration (b) in function of time.

The results show that the agglomeration rate $\beta(v)$ modifies significantly the agglomerate number concentration and the mean radius of gyration. Figure 3b shows that the agglomerate size tends quickly to microscale. This simple computation cannot give a precise result or morphology of agglomerate but it can be used to obtain a quick result and an idea about agglomerate number concentration and size in time.

3. Capabilities and limits of existing models for particles transport

In near field, the volume fraction or number concentration of NP is important. All the physical phenomena presented in Figure 1 strongly influence the NP behavior. On top of that, the information of the distribution of size, velocity and position of particulate phase at the end in the near field is crucial in order to model the behavior of NP in far field. Therefore, a CFD study has to be performed in this region and numerical results should be used as an input for atmospheric dispersion models which are used in far field.

3.1 Atmospheric dispersion models

Holmes et al. (2006) have reviewed different atmospheric dispersion models available which are Box models, Gaussian models and Integral models. Theirs common advantages are simple, quick computation while taking into account some other aspects as chemical reaction, wind field in terms of velocity and turbulence. However, those models cannot provide detail information about particles dynamics within the fluid and are not suitable in case of obstacles. The further limitation in simple models is that they are based on hypothesis of spherical particles while agglomerates of NP have often complex morphology as discussed above. In the far field, the dispersion of NP is studied for long temporal scale and in a large space scale. An approximation about information of NP is quite satisfying enough. Therefore, the simple modelling method is used to model the NP behaviour in the far field.

3.2 Computational fluid dynamics methods

The CFD methods based on numerical resolution of physical equation system can provide information about the evolution of particle dispersion in time and space. Two main approaches can be used for solving fluid

flows: the Euler approach which studies a quantity of a flow through a volume considered and the Lagrange approach which follows the trajectory of discrete phases and calculates their exchange quantity in the flow. In order to model multifluid system, the gas phase is modelled by Euler approach and the particulate phase can be modelled by Euler or Lagrange approach. The details of those models are presented in this paper.
In Euler multifluid approach, the gas phase and the particulate phase is modelled by Euler approach which means that the particulate phase is considered as a second continuum fluid. The fluid equations such as mass conservation equation Eq(8) and momentum conservation equation Eq(9) are solved for each phase.

$$\frac{\partial}{\partial t}\alpha_k\rho_k + \frac{\partial}{\partial x_j}\alpha_k\rho_k U_{k,j} = 0 \tag{8}$$

$$\frac{\partial}{\partial t}\alpha_k\rho_k U_{k,i} + \frac{\partial}{\partial x_j}\alpha_k\rho_k U_{k,j}U_{k,i} = \frac{\partial}{\partial x_j}\left[-\alpha_k\rho_k\langle u'_{k,j}u'_{k,i}\rangle_k\right] + \alpha_k\rho_k g_i + \alpha_k\frac{\partial P}{\partial x_i} + \sum_{k'=g,p} I_{k'\to k,i} \tag{9}$$

In those equations, the subscript k can be written as subscript g for the gas phase and as subscript p for the particulate phase. α_k represents volume fraction of phase k, ρ_k is the density, U_k is the phase velocity, u'_k is the velocity fluctuation, g_i is the gravity, P is the pressure, I represent the momentum exchange between phase (drift, collision, etc..), subscript *i* and *j* are dimensions in space, $\langle . \rangle_k$ is an average operator on phase k.
To model the Brownian motion, Drossinos et al. (2005) proposed to introduce a dedicated term in equation of momentum conservation derived from Fokker-Planck relation. To model agglomeration, the population balance method presented in chap 2.2 can be used. The main limitation of using Euler multifluid approach to model Brownian motion and agglomeration is the complexity of numerical resolution and an approximation of information of particulate phase. However, the Euler multifluid approach can give satisfying results with short computation time.
In Euler Lagrange approach, the gas phase is modelled by Euler approach and the balance equations as Eq(8) and Eq(9) are only solved for the gas phase. For the particulate phase, the fundamental equations that govern particle displacement are solved for each particle in the flow as Eq(10) and Eq(11).

$$\frac{dx_p}{dt} = u_p \tag{10}$$

$$m_p\frac{du_p}{dt} = F_d + F_c + F_{pp} + F_g + F_{Br} \tag{11}$$

In this expression, m_p is the particle mass considered as constant in our study, F_d is the drag force, F_c is the force caused by collision between particles, F_{pp} represents the forces created by interaction between particles, F_g is gravity force and F_{Br} is the force created by Brownian motion.Therefore, the detailed properties on particle can be obtained. Although, this approach requires tracking a very large number of particle trajectories to achieve a satisfying solution. Therefore, this method can be very expensive for engineering calculations but very useful for research purposes. To model Brownian motion, Ibaseta et al. (2007) added a random displacement for each particle after each time step as Eq(12).

$$\Delta x_{Br} = \zeta\sqrt{2D_{SE}\Delta t} \tag{12}$$

In this expression, ζ is a random variable taking into account random properties of Brownian motion. D_{SE} is the Stocks-Einstein diffusion coefficient and Δt is the time step. The theoretical demonstration of this method is detailed by Mädler et al. (2007). This model is easier to solve numerically than Drossino et al. (2005) model with Euler multifluid approach. To model agglomeration of NP, Sommerfeld (2010) has simulated the agglomeration of primary particle by considering only the van der Waals force. Two models are proposed. The first is a simple agglomeration model that allows to compute, by using a spherical hypothesis for agglomeration process, the properties of the new agglomerates as the mean of the properties of primary particles. The second is structured agglomerates model that creates different agglomerate morphologies but the fluid effect on agglomerate becomes very complex to be taken into account.
The turbulence of the fluid strongly affects the particle displacement, therefore Brownian motion and agglomeration. By numerical methods, there are three levels to model the turbulence depending on numerical resources. The first is DNS (Direct Numerical Simulation) which solves all the turbulence scales of the fluid. The second is LES (Large Eddy Simulation) which solves the turbulence big scales and models the smaller scales. The third method is RANS (Reynolds Average Navier-Stokes) which models all the turbulence scales. The LES and RANS demand less numerical resources than DNS and are feasible for industrial applications. Due to computer limitations, Elghobashi (1993) classified the influence between particles phase and fluid turbulence depending on the volume fraction of particulate phase. For the massive NP release case, influence of the presence of particles in fluid turbulence needs to be considered.

In order to model the Brownian motion and agglomeration of NP by CFD, a numerical simulation was achieved for a microparticle dispersion case using Neptune_CFDv3.0 with Euler multifluid approach and Code_Saturnev4.0 with Euler – Lagrange approach. A good agreement between numerical simulation results (Le et al., 2015) and experimental data (Hadinoto et al., 2005) was obtained for the two CFD tools. Therefore, the two CFD tools using different approaches are both well evaluated for a microparticle dispersion case. The next step consists in implementing the Brownian motion and agglomeration models as discussed above into CFD tools in order to be able to address NP specificity.

4. Conclusions

The present paper reviews the main physical phenomena to be taken into account for an atmospheric release of NP: Brownian motion and agglomeration. The current qualitative and quantitative approaches to model those phenomena with their current advantages and drawbacks are detailed. To model NP jet from the release source, CFD simulation should be performed in the near field and, atmospheric dispersion model can be used in the far field. CFD simulation for microparticles dispersion case was achieved by the authors before implementation of Brownian motion and agglomeration models into CFD tools.

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