



Understanding nano-impacts: Reversible agglomeration and near-wall hindered diffusion



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ABSTRACT



The effects of reversible agglomeration and near-wall hindered diffusion are investigated in the context of nano-impact experiments. A significant reduction in the mass transport to the electrode is observed due to the formation of slow-moving agglomerates. It is further demonstrated that in the presence of a rapid agglomeration process, larger agglomerated species are virtually unobservable, since the monomer is the dominant flux carrier. This observation is consistent with previously reported experimental data.

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1. Introduction

Nanoparticles have gained a significant importance in the past 20 years and found a wide range of applications in medical [1–3] and industrial spheres [4]. In addition nanoparticles can offer improved catalytic activity and are also trialled in the next generation of batteries [5]. As the production and usage of nanoparticles increase there is a distinct need for better understanding of the behaviour of nanoparticles in electrolytic environments. In such environments, nanoparticles are known to aggregate or agglomerate resulting in a change of their stability and properties, which have an impact on the potential applications. Agglomeration is inherently and by definition [6] a reversible process and allows the conversion between different agglomeration states, while aggregation is an irreversible clustering of particles. Hence understanding such agglomeration or aggregation processes is crucial for the efficient development of novel materials and applications.

A wide range of surface-detection based techniques has been developed in the search for an inexpensive and robust method of sizing and investigating the properties of numerous nanoparticle systems. In order to provide an accurate characterization of nanoparticles in colloidal suspensions through such surface-based methods, the effect of near-wall hindered diffusion often has to be taken into account as it is universally present at liquid–solid boundaries and may have a significant impact on the results. The nano-impact technique is an example of such surface-based in-situ characterization methods and has been shown to provide accurate size distributions of a range of nanoparticle systems [7–18] and also to yield information regarding the particles' agglomeration state [19]. This in-situ solution phase technique involves a micro-electrode, typically a carbon fibre, held at a suitable over-potential to enable the full oxidation or reduction of an impacting nanoparticle, while the experiment is shielded by a Faraday cage. Upon a collision due to Brownian motion with an electrode, charge transfer takes place and a spike is recorded in the chronoamperogram. From such a spike, the transferred charge can be calculated and the number of atoms in the colliding particle can be deduced in accordance with Eq. (1).

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$$N_{\text{atoms}} = \frac{Q}{ez} \quad (1)$$

where N_{atoms} is the number of atoms in a particle, Q is the charge transferred, z is the number of electrons transferred, and e is the electron charge.

If the particles form clusters, the resultant charge per spike will be larger and the frequency of the impacts per scan is expected to be lower. It has been demonstrated previously that nano-impact technique is capable of detecting large clusters of nanoparticles and the overall observed frequency of the impacts was lower [20,21]. Recent reports [19] showed that for a system of large ($r = 50$ nm) citrate-capped nanoparticles no such clusters were observed even at high ionic strength, but the frequency of spikes was lowered, suggesting that the concentration of the monomeric species was reduced. Since the particles are stable in the chosen electrolyte (KCl) a potential explanation is the reversibility of the clustering process i.e. agglomeration. Particle agglomeration is a complex process and the rates of agglomeration/de-agglomeration are very system-dependent and in most cases are unknown due to difficulty of accurate measurements.

In the following work we investigate the effect of the rate of reversible agglomeration on the flux of nanoparticles to the electrode and explain the non-observation of large agglomerates in some nano-impact experiments when a fast reversible agglomeration/de-agglomeration process takes place. In addition we contrast this observation with slow agglomeration or aggregation processes where large aggregates are detectable as reported in literature [20,22].

2. Theory

2.1. One dimensional diffusion

The diffusion of particles to an electrode in one dimension can be calculated via Fick's second law:

$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial r} \left(D \frac{\partial c}{\partial r} \right) \quad (2)$$

where c is the concentration, t is the time, r is the distance from the boundary, and D is the diffusion coefficient, which may be a function of r . The knowledge of the concentration gradient at the boundary allows the calculation of the time-dependent flux as is discussed below.

2.2. Near-wall hindered diffusion

Any freely-diffusing particle in a solution slows down its movement as it approaches a wall due to the existence of hydrodynamic forces [23], which is known as near-wall hindered diffusion. A particle in solution has an associated diffusion coefficient which is a proportionality constant between the gradient of the concentration of the respective species and its molar flux. For a spherical particle the diffusion coefficient can be approximated via Stokes–Einstein–Sutherland¹ [24,25] equation:

$$D_b = \frac{k_b T}{6\pi\eta a} \quad (3)$$

where D_b is the bulk diffusion coefficient, k_b is the Boltzmann constant, T is the temperature, η is the viscosity, and a is the radius of a nanoparticle,

This approximation is valid for spherical particles in an infinite uniform bulk solution; however it is inaccurate in the vicinity of a solid boundary as shown by the work of H. Brenner [26]. The effect of the

boundary can be taken into account by introducing a correction factor λ [23], which is dependent on the distance of the particle from the wall and the particle size as shown in Eq. (3):

$$\lambda = \frac{6h^2 + 2ah}{6h^2 + 9ah + 2a^2} \quad (4)$$

where h is the perpendicular distance from the electrode.

As a result it is possible to formulate the corrected spatially-dependent diffusion coefficient as shown in Eq. (5):

$$D_h = \lambda D_b \quad (5)$$

D_h is the position-dependent diffusion coefficient. Any experiment which involves freely-diffusing nanoparticles and solid walls will be influenced by near-wall hindered diffusion. It has been demonstrated that hindered diffusion has a significant influence on the flux of nanoparticles and becomes increasingly important as the size of a particle increases. It is therefore likely to be even more important for nanoparticle agglomerates which feature even larger sizes [27,28].

The variation of the diffusion coefficient with the distance from the electrode is shown in Fig. 1. As the particle size increases, a decrease in the diffusion coefficient is observed and as a particle gets closer to the electrode the diffusion coefficient tends to zero. In addition for larger particles near-wall hindrance is observed further from the boundary compared with smaller particles.

2.3. Diffusion coefficient of the agglomerates

The simulation requires the knowledge of the diffusion coefficients of the agglomerates, which will be dependent on their geometrical structure. For the purpose of our simulation we assume the structures shown in Fig. 2. The corresponding diffusion coefficients for such structures according to literature [20,29] are summarized in Table 1, where the relative diffusion coefficient is the ratio between the diffusion coefficients of agglomerate to the diffusion coefficient of the monomer. Aggregates and agglomerates are larger in size compared with monomeric species, have lower diffusion coefficients in accordance with Stokes–Einstein–Sutherland equation, and as a result move more slowly to the electrode.

2.4. Modelling agglomeration

The flux of nanoparticles towards an electrode will depend on the electrode geometry, the concentration and the diffusion coefficients of

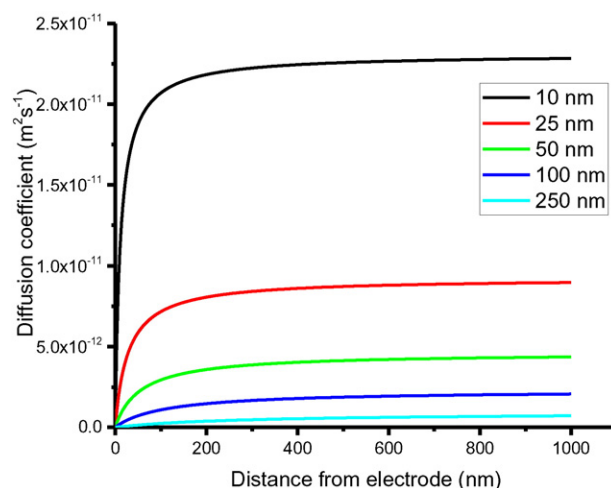


Fig. 1. Effect of the distance from the electrode on the diffusion coefficient of a nanoparticle shown for particles radii from 10 to 250 nm.

¹ W. Sutherland holds precedence in publication of the equation over A. Einstein but is rarely acknowledged.

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