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Short Communication

On the diffusion-controlled rate coefficient for chemical reactions and collisions of nano-particles

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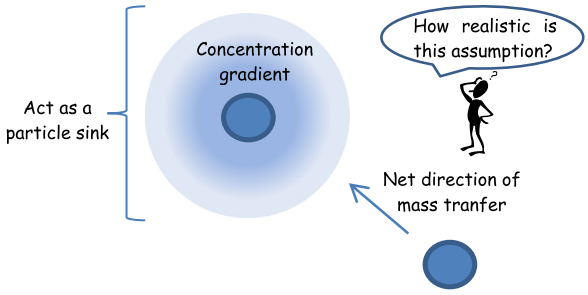
HIGHLIGHTS

- Collisions of chemical reactants and nanoparticles are very important.
- Smoluchowski's collision rate coefficient is questioned.
- An equation for estimating the collision rate coefficient k_c was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the validity of the Smoluchowski collision rate coefficient (SCRC) to describe random collisions of nano-particles and molecules is questioned and an alternative equation for this purpose is proposed. This latter is based on geometric considerations and basic concepts of diffusion. The proposed equation agrees, at least qualitatively, with experimental data of the coagulation rate coefficient reported in the literature for particle radii <50 where the SCRC equation deviates by up to three orders of magnitude. To quantitatively validate the proposed equation more experimental data is needed. Implications of these findings on chemical kinetics are briefly discussed.

1. Introduction

Random collision between molecules or colloidal particles is ubiquitous in many different fields of nature and engineering, including the estimation of the rate coefficient for diffusion-controlled chemical reactions (e.g. polymerization) and the growth of particulate matter like in combustion, in the early stage of formation of planets from interstellar dust, aggregation/coagulation of colloidal particles, etc. The particle aggregation/coagulation refers to two particles colliding and adhering together, leading to the increase of average particle size and the decrease of particle number concentration.

For the mathematical description of random collisions between particles or solute molecules in solution (from now on "entities") separated a distance much greater than their own size, the Smoluchowski's equation (1917) has been widely used. An analytical solution to this equation is only possible in the case of simple collision kernels $k_{i,j}$ between particles i and j (Kruis et al., 2000). For monodisperse particles its measurement is done at the early stages of coagulation experiments. In this case, the collision rate coefficient k_c for particles of the same size (i.e. $k_{1,1}$) in the length scale mentioned at the beginning of this paragraph, is given by

$$k_c = 8\pi r D \tag{1}$$

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where D is the diffusion coefficient of the particle which, for the case of spheres, can be calculated with the well-known Stokes-Einstein equation.

$$D = \frac{K_B T}{6\pi\eta r} \tag{2}$$

where K_B, T and η are the Boltzman constant, the absolute temperature and viscosity of the medium, respectively. Substitution of Eq. (2) in (1) yields

$$k_c = \frac{4K_B T}{3\eta} \tag{3}$$

Notice that according to Eq. (3), k_c is independent of particle size. Eq. (1) can be obtained by applying Fick's laws in steady-state and spherical coordinates, to the collision of a single moving particle with a target particle of the same radius (r) in a stagnant fluid (Hiemenz, 1986).

If the restriction is removed that the "target" particle is stationary, then the diffusion coefficient of the moving particle is replaced by relative diffusion coefficient of the two, which is simply $2D$ when the particles are the same size (Hiemenz, 1986). With this change and using the Stokes-Einstein equation for calculating D, Eq. (1) becomes

$$k_c = 16\pi r D = \frac{8K_B T}{3\eta} \tag{4}$$

Eq. (4) is referred as the Smoluchowski's collision rate coefficient (SCRT). Although the differences between theoretical and experimental values were rather high, the validity of SCRT equation was postulated (Gedan et al., 1984) so that it has been used for decades. Furthermore, given that Eq. (1) is derived from Fick's laws, it implies, obviously, that collision depends on the concentration gradient around the target entities, which should act as a sink. However, how can a single molecule or particle by itself give rise to a "sink" such that a concentration gradient around it can be formed? If there is not a concentration gradient then simply Fick's laws do not apply.

In this work, the Smoluchowski coefficient is questioned for entity radii <50 nm and an alternative equation that exhibit better agreement with experimental data (Higashitani et al., 1991) is proposed.

2. Development of the mathematical model

If $[N]$ represents the number of entities per volume unit, then its inverse represents the volume v' associated with one entity:

$$v' = \left(\frac{1}{[N]}\right) \tag{5}$$

Assuming cubic geometry and that the entities are located in the center of their corresponding cube (see Fig. 1a), then the length of one side of a cube is equal to the characteristic distance δ between entities. Accordingly, δ can be calculated by

$$\delta = \left(\frac{1}{[N]}\right)^{1/3} \tag{6}$$

If it is assumed that a given entity can be surrounded by other 26 entities and that every one of them is located within its own cube then the scenario can be as that shown in Fig. 1b. As it will be shown below, notwithstanding this simplification it seems to be that the approach of a cubic lattice is enough for describing the behavior of the experimental data

The central cube corresponds to the one of the particle which we are interested in describing its collision rate with any of the 26 surrounding entities; hence the total volume v associated to the collision process corresponds to the volume of the 27 cubes,

$$v = 27v' \tag{7}$$

In order to estimate the collision probability $\gamma_{i,j}'$ between an entity i and an entity j, the following assumptions were made: (a) entity i has to diffuse in the direction towards the cube where entity j is contained, that is, within the tetrahedron shown in Fig. 1c; (b) entity j has to diffuse in the correct path to intercept particle i just at some point on the shared face of the two contiguous cubes. For sake of simplicity, the center of the shared surface is considered as the mean collision region, so that for the collision to occur, it is necessary that entity j follows a path within the imaginary cone-like region illustrated in Fig. 1c.

The probability γ_i for scenario a, can be calculated by dividing the volume of the tetrahedron v_{tetr} by the volume of cube v_{cube},

$$\gamma_i = \frac{v_{tetr}}{v_{cube}} = \frac{1}{6} \tag{8}$$

Analogously, the probability γ_j for scenario b, can be calculated by dividing the volume of the cone v_{cone} by the volume of imaginary sphere v_{sphere}, indicated with a dashed line on Fig. 1c.

$$\gamma_j = \frac{v_{cone}}{v_{sphere\,A}} = \frac{r_j^2}{\delta^2} \tag{9}$$

Therefore, the collision probability $\gamma_{i,j}'$ between a entity i and an entity j, is given by

$$\gamma_{i,j}' = \gamma_i \gamma_j = \left(\frac{1}{6}\right)\frac{r_j^2}{\delta^2} \tag{10}$$

Hence the collision probability $\gamma_{i,j}$ between a entity i with any of the 26 surrounding entities is given by

$$\gamma_{i,j} = 26\gamma_{ij}' \tag{11}$$

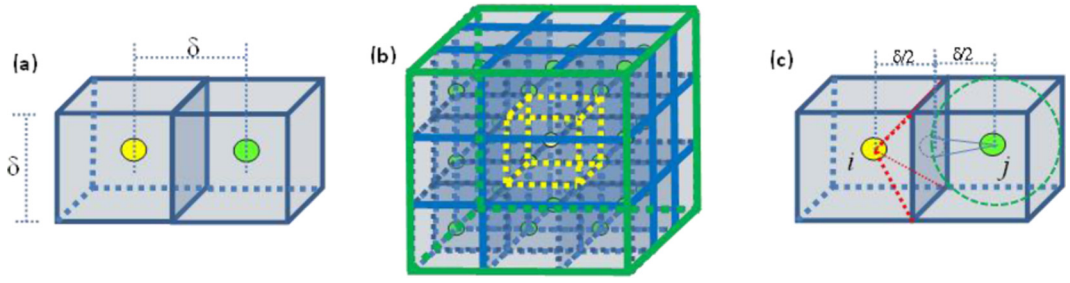

Fig. 1. Geometrical considerations for the proposed mathematical model: (a) Distance between two contiguous entities and their associated volume assuming cubic geometry; (b) representation of 27 entities and their associated volume; the central particle can collide with any of the 26 surrounding entities; (c) geometrical considerations for the collision probability between entity i and j; entity i has to diffuse within the tetrahedron toward the adjacent cube and, particle j has to diffuse within the cone-like region.