VAN DER WAALS INTERACTION FORCES BETWEEN RASPBERRY-LIKE AGGLOMERATES OF NANOPARTICLES

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TITRE

Forces d'interaction de type Van der Waals se produisant entre agglomérats de nanoparticules de type « framboise »

RESUME

Les forces d'interaction de Van der Waals entre les agglomérats de nanoparticules sont déterminées à partir d'expressions analytiques dérivées d'une fonction de corrélation de paires simplifiée. Ces forces sont directement proportionnelles au taux de remplissage, un paramètre morphologique lié à l'empilement des particules primaires constitutives de l'agglomérat. Les expressions proposées sont en bon accord avec les calculs préliminaires basés sur des calculs détaillés de sphère-molécule.

ABSTRACT

Van der Waals interaction forces between agglomerates of nanoparticles are determined based on analytical expressions derived from a simplified pair correlation function. These forces are directly proportional to the packing factor, a morphological parameter related to the packing of the constituting primary particles inside an agglomerate. The proposed expressions are in good agreement with preliminary calculations based on detailed sphere-molecule calculations.

MOTS-CLÉS : van der Waals, agglomerat, nanoparticules, fractale / **KEYWORDS:** van der Waals, agglomerates, nanoparticles, fractal

1. INTRODUCTION

The Van der Waals (VdW) interaction forces between nanoparticles are electric forces even present for electrically neutral particles. Their origine is related to the permanent or induced dipolar interaction between electrons belonging to atoms. These forces play an important role in aerosol particles filtration, resuspension, and aggregation. Indeed, the probability of aggregation between nanoparticles upon collisions is directly related to both VdW and short-range repulsion forces. The latter becomes especially relevant in the <10 nm particle diameter range as observed for soot particles generated in flames (Morán *et al.*, 2021). VdW may considerably enhance the coagulation kinetics of nanoparticles.

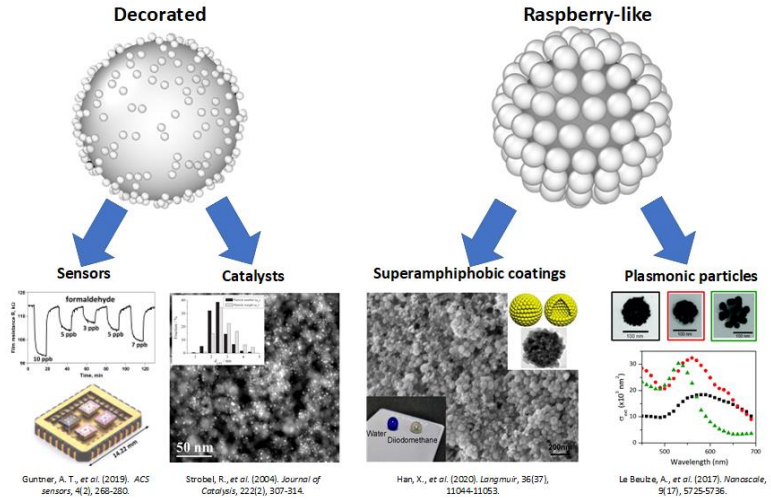

Figure 1: Decorated and raspberry-like agglomerates of nanoparticles and their applications.

On the other hand, tailoring nanoparticle surface properties may have remarkable consequences in their optical properties, catalytic performance, and aerosol particles stability. The surface of nanoparticles may be

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controlled by coating, decorating (see the left panel of Fig. 1), and producing the so-called raspberry-like agglomerates (see the right panel of Fig. 1). These particles may find important applications in nanotechnology due to their tunable surface rugosity, versatile chemical composition, and simpler geometry compared to other stochastic fractal-like agglomerates of nanoparticles. Raspberry-like agglomerates exhibit remarkable stability against agglomeration (Lan *et al*., 2018). Controlling the surface packing and size of raspberry-like particles allows to shift plasmonic extinction into near-infrared which is essential for their application as therapeutic or antimicrobial particles (Le Beulze *et al*., 2017; Merkl *et al*., 2021).

Despite the importance of VdW forces, there are currently no equations to determine these forces for agglomerates of nanoparticles (Babick *et al*, 2011). In this France-Canada collaboration project we intend to propose new equations to approximate the VdW forces for agglomerates of nanoparticles with a particular emphasis on fractal-like agglomerates. In this work, raspberry-like agglomerates are studied.

2. METHODOLOGY

Let us consider the VdW interaction energy between identical atoms separated by a distance r having the form $w(r) = -C/r^n$ where $C > 0$ is a constant, and n is typically 6 for VdW attractive potentials.

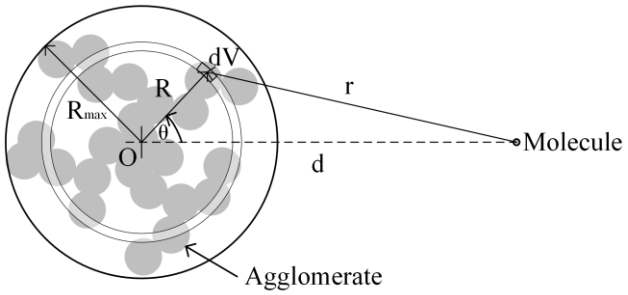

Figure 2: Agglomerate – molecule interaction geometrical properties.

The total interaction energy (W) between a molecule and a particle of volume V separated by a distance d as shown in Fig. 2, may be obtained based on the agglomerate's pair-correlation function $A(R)$,

$$W(d) = \int_V w(R)A(R)\,dV \tag{1}$$

For fractal-like agglomerates, when neglecting lower and larger scales limitations, the isotropic pair-correlation function is given as follows,

$$A(R) = \frac{\phi D_f}{3}\left(\frac{R}{a}\right)^{D_f-3}; \qquad a < R < R_{max} \tag{2}$$

Where ϕ is the packing factor, D_f is the fractal dimension, a and R_{max} are the primary particle's and agglomerate's characteristic radius, respectively. A generalized solution of this problem, combining Eq. (1) and Eq. (2), means solving the following equation,

$$W(d) = \frac{2\pi C\phi D_f}{3(n-2)da^{D_f-3}}\int_0^{R_{max}} R^{D_f-2}[(R+d)^{2-n} - (d-R)^{2-n}]dR \tag{3}$$

As observed by (Neumann and Bunz 1993), the integral of Eq. (3) has no analytical primitive for non-integer D_f values. In the particular case of a hollow raspberry-like agglomerate, considered a fractal object ($D_f = 2$), solving Eq. (3) for $n = 6$ leads to,

$$W_2(d) = \frac{a\pi C\phi}{9d^4}\left[2 - \frac{1}{(1-R_{max}/d)^3} - \frac{1}{(1+R_{max}/d)^3}\right] \tag{4a}$$

In addition, for a filled raspberry-like agglomerate, considered a fractal object ($D_f = 3$), we obtain,

$$W_3(d) = -\frac{\pi C\phi}{12d^3}\left[\frac{1-3R_{max}/d}{(1-R_{max}/d)^3} - \frac{1+3R_{max}/d}{(1+R_{max}/d)^3}\right] \tag{4b}$$

When considering a solid sphere for which $\phi = 1$, Eq. (4b) leads to the same results derived by (Hamaker 1937) based on a different approach. Finally, the accuracy of Eq. (4a) and Eq. (4b) to describe the VdW interaction energy between raspberry-like agglomerates and isolated molecules is tested. To this end, the code FracVAL (Morán *et al*., 2019) has been modified to generate both filled and hollow raspberry-like agglomerates. Once the desired agglomerates of nanoparticles have been generated, the interaction energy calculations are carried out.

3. PREELIMINARY FINDINGS

In Fig. 3 the VdW interaction energy between a molecule approaching to a hollow raspberry-like agglomerate (having a total of 54 primary spheres and $\phi = 2.15$) as calculated based on different methods, are shown. All calculations are based on the sphere-molecule model proposed by (Hamaker 1937), excepting the solid red curves that are determined based on Eq. (4a). In Fig. 3a the calculated minimum (yellow line) and maximum

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(green line) values considering all the raspberry primary spheres to interact with the molecule are shown. At very short distances, namely $d/R_{max} < 1.25$, the minimum and maximum values are just explained by the raspberry agglomerate's primary spheres configuration (see the insert in Fig. 3a). The proposed model is closer to the maximum value because Eq. (2) is orientationally averaged and assumes $A(r) > 0$ up to a radial position $r = R_{max}$ which is only an approximation. For larger radial positions, Eq. (4a) is in excellent agreement with the calculated values.

As shown in Fig. 3b, the proposed model is in excellent agreement with an average raspberry-molecule interaction (blue dots). In addition, solid cyan line represents the interaction to be approximated as only the closest sphere belonging to the agglomerate. Solid black line neglects the morphology of the agglomerate and consider it as a volume equivalent sphere. At short distances $d/R_{max} \to 1$, the interaction forces can be simplified by only considering the closest primary sphere. At large distances $d/R_{max} \gg 1$, the morphology of the agglomerate can be neglected and all the interactions are just determined by the volume of the agglomerate. Note that these asymptotic behaviors are consistent with the findings of (Babick *et al*, 2011) who studied a different type of agglomerates. It is very remarkable how Eq. (4a) shows good agreement at both asymptotic limits and also with the all-spheres calculation. The latter is only useful when the morphology of the raspberry-like agglomerate is known and is very time-consuming. On the contrary, Eq. (4a) only requires the maximum radius of the agglomerate, the radius of its primary particles, and their packing factor to be known.

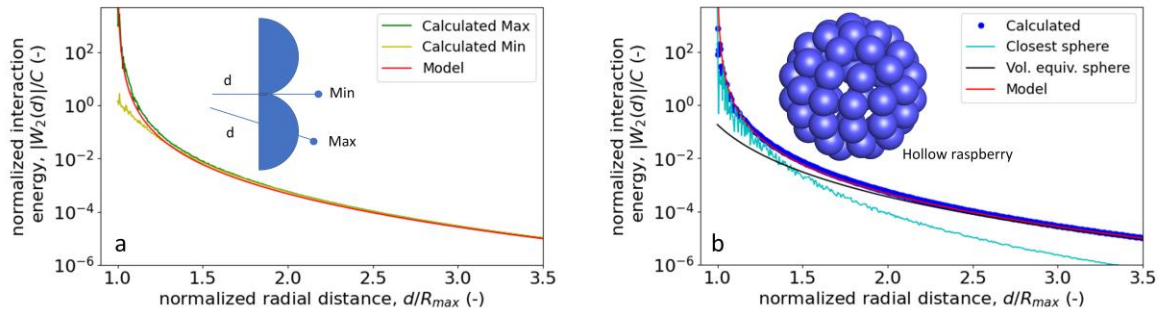

Figure 3: Comparison of the particle-molecule VdW interaction energy of a hollow agglomerate of nanoparticles (having a total of 54 primary spheres and $\phi = 2.15$). The model corresponds to Eq. (4a).

4. CONCLUSIONS

In this work, a simplified pair correlation function describing the spatial distribution of volume for fractal-like agglomerates of nanoparticles is used to explicitly predict the Van der Waals particle-molecule interaction energies. The preliminary results show good agreement between the theoretical calculations and the numerical simulations for raspberry-like agglomerates. Future work will focus on the particle-particle VdW interaction energy for raspberry-like and propose approximations for other fractal like agglomerates of nanoparticles.

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