# Poster Abstract

Name of Author: Lorenzo Isella…….
Co-Authors Yannis Drossinos…….
Affiliation: European Commission, Joint Research Centre…….
Mailing address: Joint Research Centre, IES, Transport and Air Quality Unit, TP 441, via Enrico Fermi, Ispra (VA), Italy, I-21027.
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Phone / Fax +39 0332 785335…….. E-mail lorenzo.isella@jrc.it

## Title: Nanoparticle Langevin dynamics

## Abstract: (min. 300 - max 500 words)

Combustion-generated solid nanoparticles are often fractal aggregates (clusters) of smaller units, monomers, taken to be spherical primary particles. We investigate the non-equilibrium Brownian dynamics of fractal aggregates by solving the Langevin equations of motion of a system of interacting monomers in three dimensions. The monomer-monomer interaction potential is taken to consist of a strongly repulsive part, to model the monomer hard-core, and a deep, short-range attractive part, to model the sticking forces that cause monomers to stick upon collision. Our objective is to study the static structure of the resulting aggregates as generated by their Brownian, diffusive, motion.

We solve the Langevin equations for a system of 5000 interacting monomers initially distributed uniformly in a box with periodic boundary conditions. The simulations were performed with the ESPResso package, Limbach *et al.* (2006). The cluster fractal dimension is determined from the dependence of the mean, cluster radius of gyration on the number of monomers in the cluster, namely $R_g \sim N_{\mathrm{mon}}^{1/d_f}$, where $N_{\mathrm{mon}}$ is the number of monomers in a cluster, $R_g$ is the mean radius of gyration averaged over all clusters with the same number of monomers, and $d_f$ is the aggregate fractal dimension.

The aggregate fractal dimension depends on the agglomeration mechanism, with monomer-cluster agglomeration leading to a higher fractal dimension than cluster-cluster. We argue that for an initial state consisting of monomers both agglomeration mechanisms arise during the evolution of the system. At early times, when the monomer density is high, most collisions are monomer-cluster, whereas as time progresses and agglomeration reduces the number of unbound monomers cluster-cluster agglomeration dominates. This is shown in Fig. 1 (left) where we present the time-evolution of the total number of clusters, along with the evolution of the number of small and large clusters. We identified the threshold between small and large clusters as $N_{mon} = 15$, by analyzing the results shown in Fig. 1 (right). Figure 1 (right) presents the mean cluster radius of gyration as a function of cluster size for all the clusters generated during our simulations. We notice different slopes for small and large clusters, leading to two distinct fractal dimensions. Hence, small clusters have different morphology from large clusters (they are more compact), suggesting that combustion-generated nanoparticles may be better described by at least two fractal dimensions, in the spirit of Kostoglou & Konstandopoulos (2001) who used a distribution of fractal dimensions.

Kostoglou, M., & Konstandopoulos. A. (2001). *J. Aerosol Sci.* 32, 1399-1420.
Limbach, H.J., Arnold, A., Mann, A.B., & Holm, C. (2006). *Comput. Phys. Commun.* 174, 704-727.

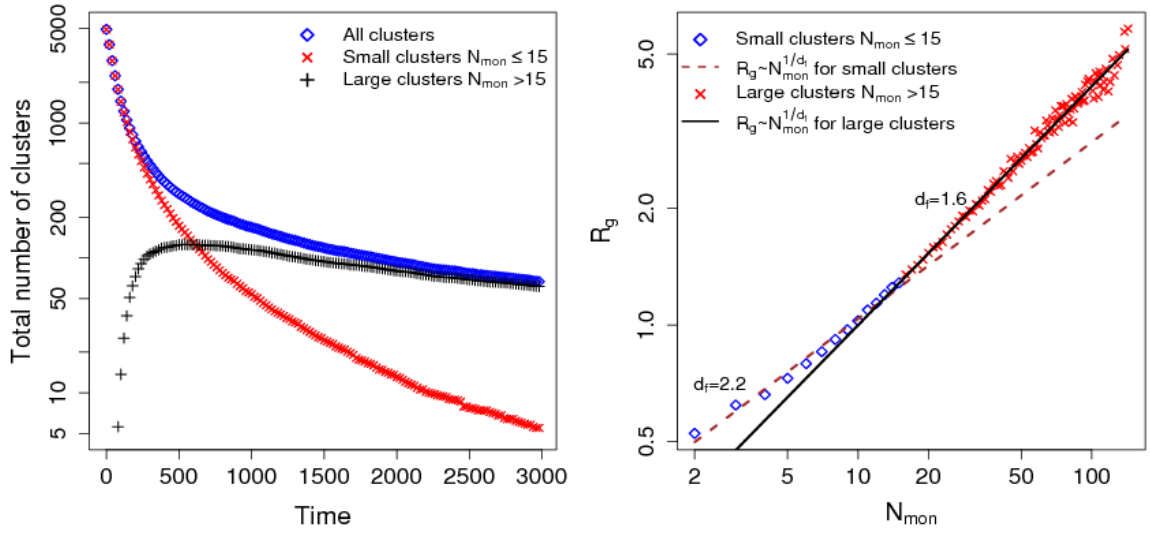



Fig.1: Left: Time evolution of the number of small, large, and all clusters. Right: Mean cluster radius dependence on the number of monomers in a cluster, and fractal dimensions for small and large clusters.

# Langevin Nanoparticle Dynamics

## Model

•Combustion-generated solid nanoparticles are aggregates (clusters) of smaller spherical units [monomers].

• Langevin equations for a 3D system of interacting monomers

$$m\ddot{\mathbf{r}}_i = -\frac{1}{2}\nabla_{\mathbf{r}_i}\sum_{j\neq i}u(r_{ij}) - \beta m\dot{\mathbf{r}}_i + \boldsymbol{W}_i$$

•Monomer-monomer interaction potential $u(r_{ij})$ strongly repulsive at short separations (monomer "hard-core") and attractive on a short range to model monomers sticking upon collision.

•Effect of collisions between aggregates and fluid molecules modelled by drag and noise terms; $\boldsymbol{W}_i$ Gaussian white noise.

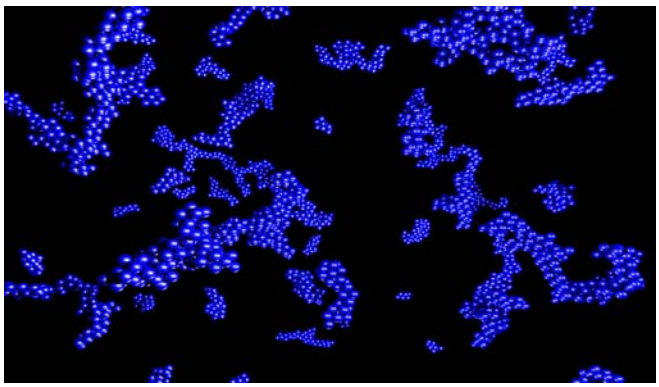
## Simulations

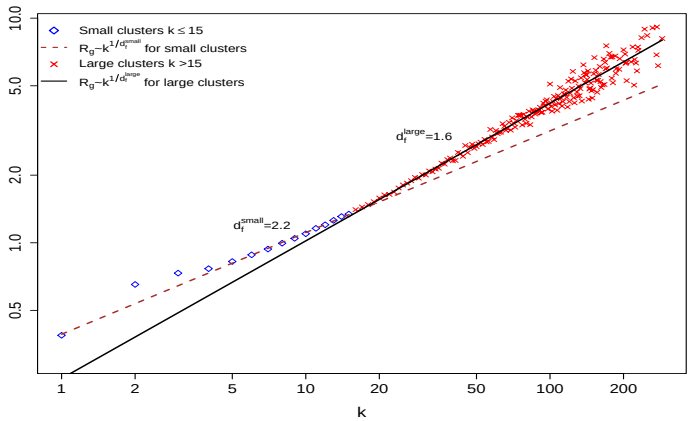
•Langevin equations for 5000 interacting monomers initially distributed uniformly in a box with periodic boundary conditions.

• Simulations performed with the molecular dynamics ESPResso package.

•Results obtained by averaging 10 simulations with different initial conditions.

## Results and Discussion



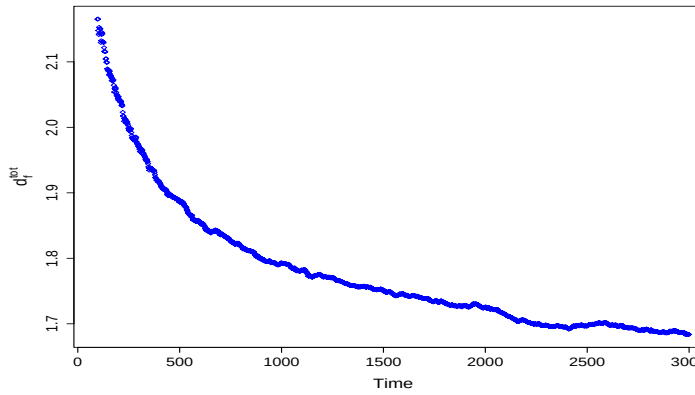


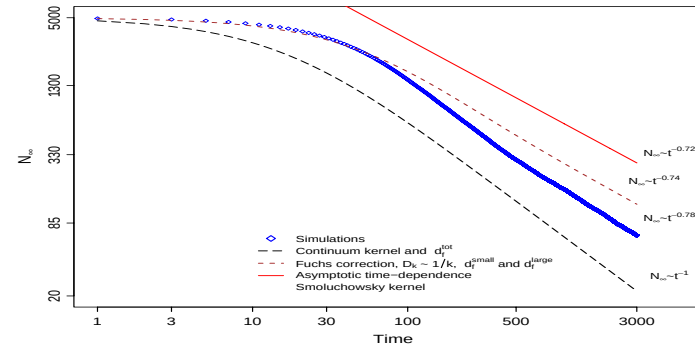

•Aggregate radius of gyration scales with the number of monomers $k$ in a cluster: $R_g \sim k^{1/d_f}$ , where $R_g^2 = k^{-1}\sum_i (\mathbf{r}_i - \mathbf{r}_{cm})^2 + a_0^2$.

•Two aggregate populations with different time-independent power-law exponents, $d_f^{large} = 1.6$ , and $d_f^{small} = 2.2$. Cluster threshold $k_* = 15$.

•Two populations arise from different aggregation mechanisms: monomer-cluster $(d_f \simeq 2.4)$ and cluster-cluster $(d_f \simeq 1.7)$ collisions, respectively→ different fractal dimensions.

•Time-dependent average fractal dimension $d_f^{tot}$ due to interplay between the two populations and depletion of small clusters.




•Cluster diffusion coefficient scales as $D_k \sim 1/k$ : aggregates are transparent→ reasonable approximation for open clusters with $d_f \leq 2$.

• $D_k \sim 1/k$ modifies the degree of homogeneity of the standard continuum Smoluchowski kernel. Smoluchowski kernel $\lambda = 0$ and $\lambda = -1 + 1/d_f$ for $D_k \sim 1/k$. Asymptotically $N_\infty \sim t^{-z}$ with $z = 1/(1-\lambda)$, leading to $N_\infty \sim t^{-1}$ and $N_\infty \sim t^{-0.72}$, respectively.

•Numerical solution of the agglomeration equation: the standard continuum kernel with the time-independent $d_f^{tot}$ does not reproduce the simulations at short times. The theoretical asymptotic limit is confirmed but it is significantly different from Langevin simulations.

Improve agreement with simulations by :

•Explicit introduction of $D_k \sim 1/k$ in the kernel.

• Use $d_f^{small} = 2.2$ and $d_f^{large} = 1.6$ depending on $k$ of the colliding aggregates.

•At early times, the aggregate mean-free path is comparable to the radius of gyration: Fuchs correction to account for aggregate-aggregate non-continuum effects.

As a result:

• improved agreement between agglomeration equation and the Langevin simulations at early times.

• the asymptotic decay is not reached during the time of the simulations, but

• the scaling exponents of the decay of the total cluster concentration, -0.74 (agglomeration equation) and -0.78 (simulations), differ by less than 6%.

**Contact**

**Lorenzo Isella and Yannis Drossinos**
European Commission • Joint Research Centre
Institute for Environment and Sustainability
Tel. +39 0332 785335 • Fax +39 0332 786499
E-mail: lorenzo.isella@jrc.it



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