Poster - Extended Abstract

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Title: On the relation between aerodynamic and mobility diameter distributions for aggregates consisting of few monomers.

Introduction

Combined measurements of electrical-mobility-radius-based (measured by Scanning Mobility Particle Sizer, SMPS) and aerodynamic-radius-based (measured by Electrical Low Pressure Impactor, ELPI) distributions are typically employed to study the morphology of soot aggregates produced by diesel engines. This approach is used to calculate the aggregate's effective density, ρ_{eff} (Virtanen *et al*., 2004). The effective density can be correlated to particle morphology assuming specific morphology descriptors. For well-defined random isotropic fractal-like aggregates the appropriate descriptor is the fractal dimension. In this way the size-dependence of the fractal dimension can be estimated (Konstandopoulos *et al*., 2004, Baltzopoulou *et al*., 2012).

In some cases, such as diesel soot and flame soot (Di Stasio *et al*., 2002), the aggregates consist of a relatively small number of monomers or exhibit specific (non-random) anisotropic structures. In these cases the concept of effective density is under question and the exploitation of the aerodynamic and the mobility radius distributions cannot be made without incorporating knowledge on the structure of the aggregates.

From a fundamental point of view, ELPI gives the aggregate distribution with respect to the quantity m/f (where f, m are the friction factor and the mass of the aggregate, respectively). The mobility analyzer (SMPS) gives the distribution with respect to f. The inverse problem of determining the structure of the aggregates for these distributions is difficult to solve. Therefore, the direct problem of determining the two distributions for given structures is evaluated. In particular, the cases of linear aggregates and of oligomers (3-4mers) are studied.

Calculation method

In the momentum transfer continuum regime, where the primary particle radius (R_1) is much more larger from the mean free path of the gas (λ), the mobility radius (R_m) of a structure can be calculated by the Stokes equation,

$$f = 6\pi\mu R_m, \qquad (1)$$

where μ is the gas viscosity.

The friction factor of the examined structures is calculated with the “collision-rate method” as suggested by Isella and Drossinos (2011). According to this method the ratio of the friction factors of two aggregates (herein taken to be a monomer and an aggregate composed of N monomers) can be related to the corresponding ratio of collision rates and by the Stokes equation also to the mobility radius,

$$\frac{f_N(0)}{f_1(0)} = \frac{K_N(0)}{K_1(0)} = R_m. \qquad (2)$$

The collision rate can be calculated by integrating the diffusive flux on the particle surface. The diffusive flux is obtained from the diffusion equation, since it is related to the gradient of the molecular density, $J = -D\nabla\rho$, with D the molecular diffusion coefficient and ρ the gas density. The appropriate boundary conditions are Dirichlet conditions and the gas density is 1 on the particle surface and 0 far away from it.

The aerodynamic radius is related to the mobility via the dynamic shape factor (χ_N), which is a factor that shows the effect of the shape of a structure on particle motion (Kasper, 1982)

$$\chi_N = \frac{R_m}{R_1} N^{-1/3} = \left(\frac{\varrho_p}{\varrho_1}\right)^{1/3} \left[\frac{R_m}{R_{ae}}\right]^{2/3} \qquad (3)$$

$$R_{ae}{}^2 = \frac{\varrho_\rho}{\varrho_0} N R_1{}^3 \frac{1}{R_m}, \qquad (4)$$

where ϱ_0 is the unit density (1g/cm^3), ϱ_ρ the particle density (~2 g/cm^3 for soot aggregates) and N the number of primary particles of the structure under examination.

All our results refer to creeping flow (particle Reynolds number << 1) and to continuum regime.

Results

We calculated the mobility and the aerodynamic radii of well-characterized oligomers. Figure 1 presents the mobility and the aerodynamic radii of 3-mers in the continuum regime against the 3-mer angle, a morphological descriptor of the spatial arrangement of the three monomers. The 3-mer angle (θ_{213}) is specified by two intersecting lines passing through the center of the central monomer (2) and the center of the two (1, 3) monomers pairwise touching it.

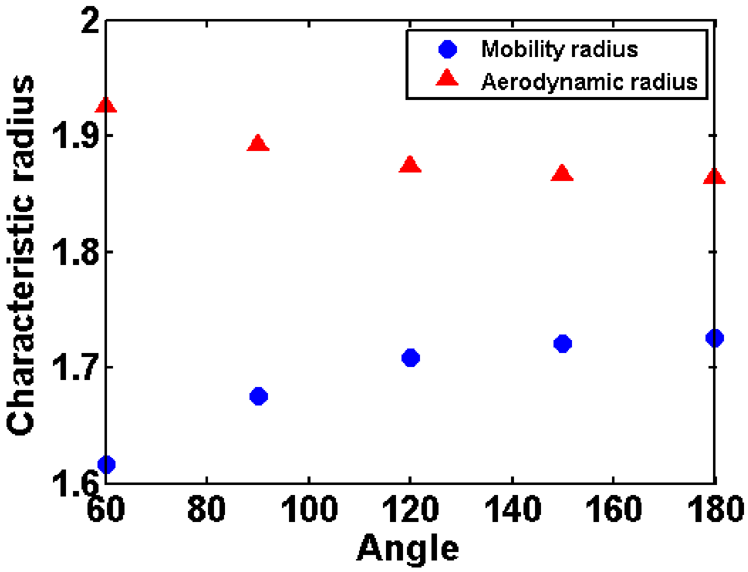

Figure 1. The mobility and aerodynamic radius of 3-mers against the angle they form

The examined 4-mers are formed by two 2-mers that form angles in two dimensions that take values from 0 (rectangle) to 180 (straight chain). Figure 2 presents our results.

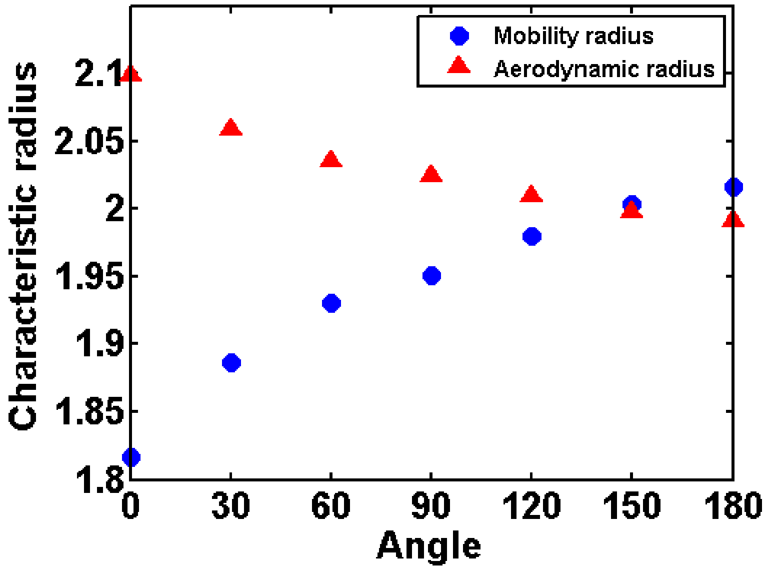

Figure 2. The mobility and aerodynamic radius of 4-mers against the angle they form

Finally, we examined straight chains that had primary particles from two to five. In Figure 3 we plot again the two characteristic radii against the number of primary particles of straight chains.

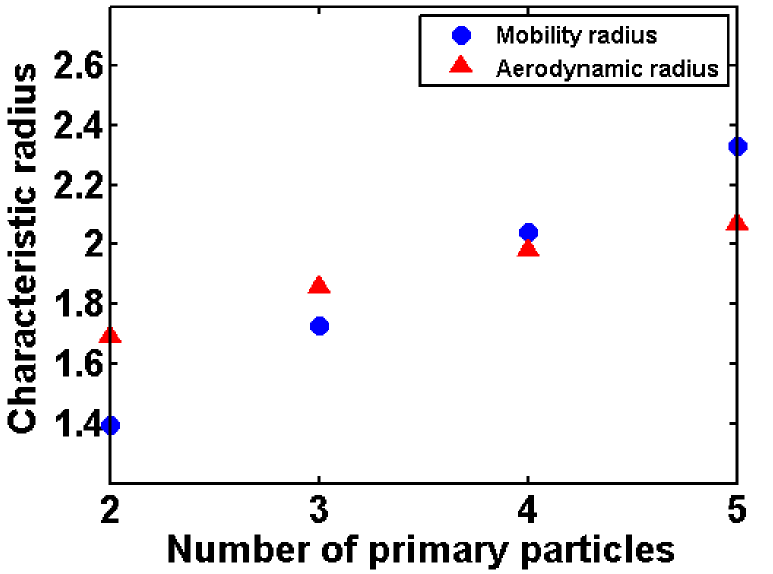

Figure 3. The mobility and aerodynamic radius of straight chains

Conclusions

Figures 1-3 suggest that the mobility radius depends on both morphology (herein angle θ) and number of primary particles, as expected (Melas *et al.*, 2013). From Figs. 1,2 we note that the distribution of the mobility and the aerodynamic radii are anti-correlated, for a constant number of primary particles. This can be extracted from the definitions of the two radii and also from Eq. 4, $R_{ae} \sim {R_m}^{-1/2}$. This difference for oligomers shows that for fractals that consist of larger number of primary particles the distributions will vary even more. Consequently there is no linearity between the mobility and the aerodynamic radius and their relation problem is not a one-to-one definition. When the number of primary particles increases (Fig. 3) both radii increase but again differently. In conclusion, the effect of the aggregate structure on the aggregate radii for oligomers sets under question the concept of the effective density even for large anisotropic fractal aggregates.

References

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On the relation between aerodynamic and mobility diameter distributions for aggregates consisting of few monomers.

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INTRODUCTION

Combined measurements of electrical-mobility-radius-based (measured by Scanning Mobility Particle Sizer, SMPS) and aerodynamic-radius-based (measured by Electrical Low Pressure Impactor, ELPI) distributions are typically employed to study the morphology of soot aggregates produced by diesel engines. This approach is used to calculate the aggregate's effective density, ρ_{eff}[1] which can be correlated to particle morphology assuming specific morphology descriptors. For well-defined random isotropic fractal-like aggregates the appropriate descriptor is the fractal dimension. In this way the size-dependence of the fractal dimension can be estimated[2,3].

ELPI: Gives the aggregate distribution with respect to the quantity m/f.
SMPS: Gives the distribution with respect to f.
where f is the friction factor
and m the mass of the aggregate.

In some cases, such as diesel soot and flame soot[4], the aggregates consist of a relatively small number of monomers or exhibit specific (non-random) anisotropic structures. In these cases the concept of effective density is under question and the exploitation of the aerodynamic and the mobility radius distributions cannot be made without incorporating knowledge on the structure of the aggregates. Herein, we determine the two radii distributions for given structures; straight chains and oligomers (3-mers, 4-mers).

CALCULATION METHOD

Mobility radius

In the momentum transfer continuum regime, where the primary particle radius (R_1) is much larger than the mean free path of the gas (λ), the mobility radius (R_m) of a structure can be calculated by the Stokes equation, $f = 6\pi\mu R_m$, where μ is the gas viscosity.

The friction factor of the examined structures is calculated with the "collision-rate method"[5]. According to this method the ratio of the friction factors of two aggregates (herein taken to be a monomer and an aggregate composed of N monomers) can be related to the corresponding ratio of collision rates and by the Stokes equation also to the mobility radius,

$$\frac{f_N(0)}{f_1(0)} = \frac{K_N(0)}{K_1(0)} = R_m. \quad (1)$$

The collision rate can be calculated by integrating the diffusive flux on the particle surface. The diffusive flux is obtained from the diffusion equation, since it is related to the gradient of the molecular density, $J = -D\nabla\rho$, with D the molecular diffusion coefficient and ρ the gas density. The appropriate boundary conditions are Dirichlet conditions and the gas density is 1 on the particle surface and 0 far away from it. Figure 1 shows the diffusive flux on the surface of a 3-mer that forms an angle $\theta = 120$ (left) and on a 4-mer linear aggregate (right).

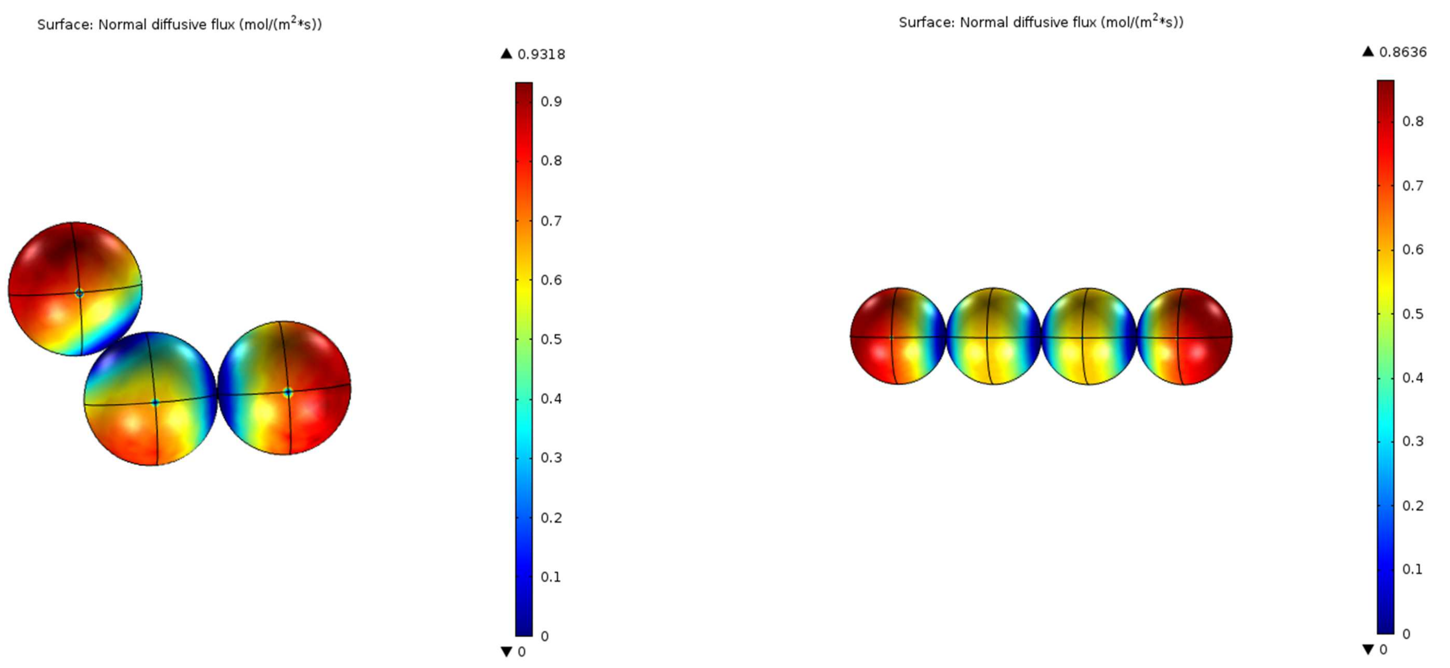

Fig 1. The diffusive flux on the surface of a 3-mer that forms an angle $\theta = 120$ (left) and of a 4-mer linear aggregate (right).

Aerodynamic radius

The aerodynamic radius is related to the mobility via the dynamic shape factor (χ_N), which is a factor that accounts on the effect of the shape on particle motion[6]

$$\chi_N = \frac{R_m}{R_1} N^{-1/3} = \left(\frac{\varrho_p}{\varrho_1}\right)^{1/3} \left[\frac{R_m}{R_{ae}}\right]^{2/3} \quad (2)$$

$$R_{ae}^{\ 2} = \frac{\varrho_\rho}{\varrho_0} N R_1^{\ 3} \frac{1}{R_m}, \quad (3)$$

where ϱ_0 is the unit density (1 g/cm^3), ϱ_ρ the particle density (~2 g/cm^3 for soot aggregates) and N the number of primary particles of the structure under examination.

All our results refer to creeping flow (particle Reynolds number << 1) and to continuum regime.

RESULTS

3-mers

We calculated the mobility and the aerodynamic radii of well-characterized oligomers. Figure 2 presents the mobility and the aerodynamic radii of 3-mers in the continuum regime against the 3-mer angle, a morphological descriptor of the spatial arrangement of the three monomers. The 3-mer angle (θ_{213}) is specified by two intersecting lines passing through the center of the central monomer (2) and the center of the two (1, 3) monomers pairwise touching it.

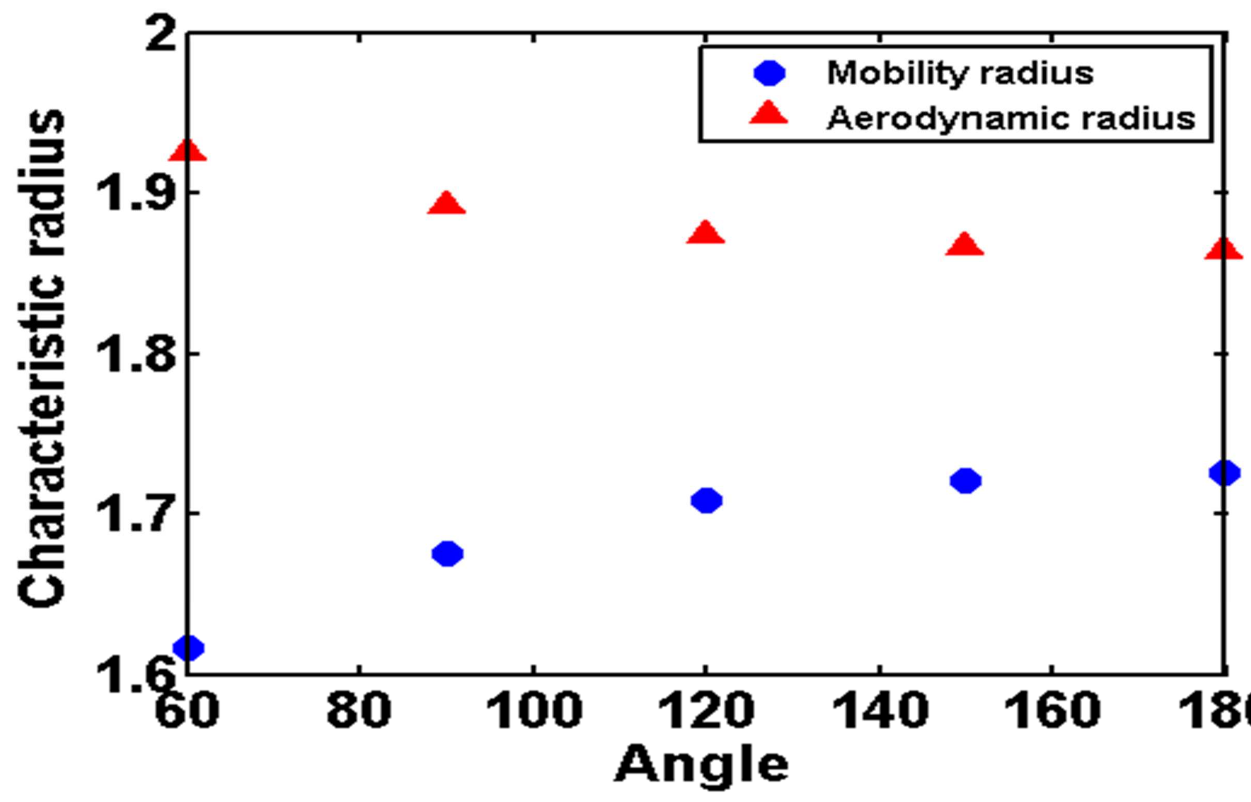

Fig 2. The mobility and aerodynamic radii of 3-mers against the angle they form.

4-mers

The examined 4-mers are generated by two 2-mers that form angles in two dimensions that take values from 0 (rectangle) to 180 (straight chain). Figure 3 presents our results.

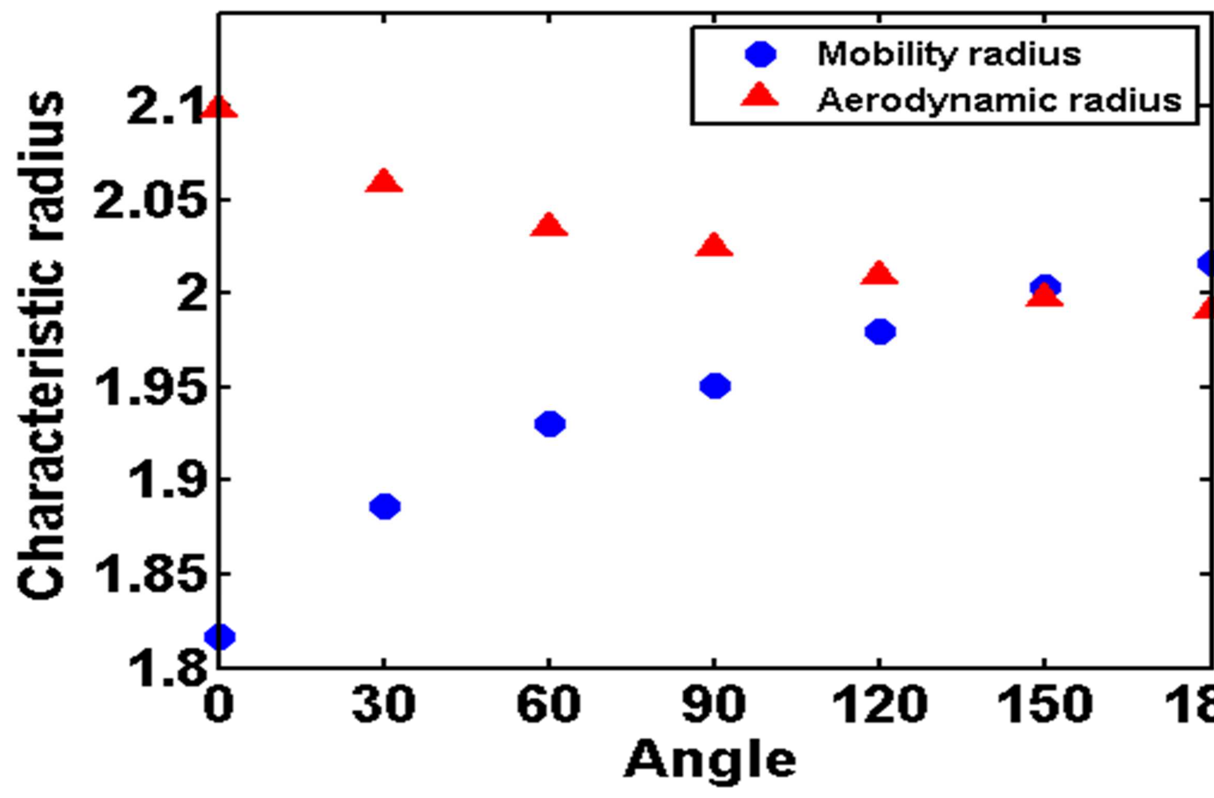

Fig 3. The mobility and aerodynamic radii of 4-mers against the angle they form.

Linear aggregates

Lastly, we examined straight chains that had primary particles from two to five. In Fig. 4 we plot again the two characteristic radii against the number of primary particles of straight chains.

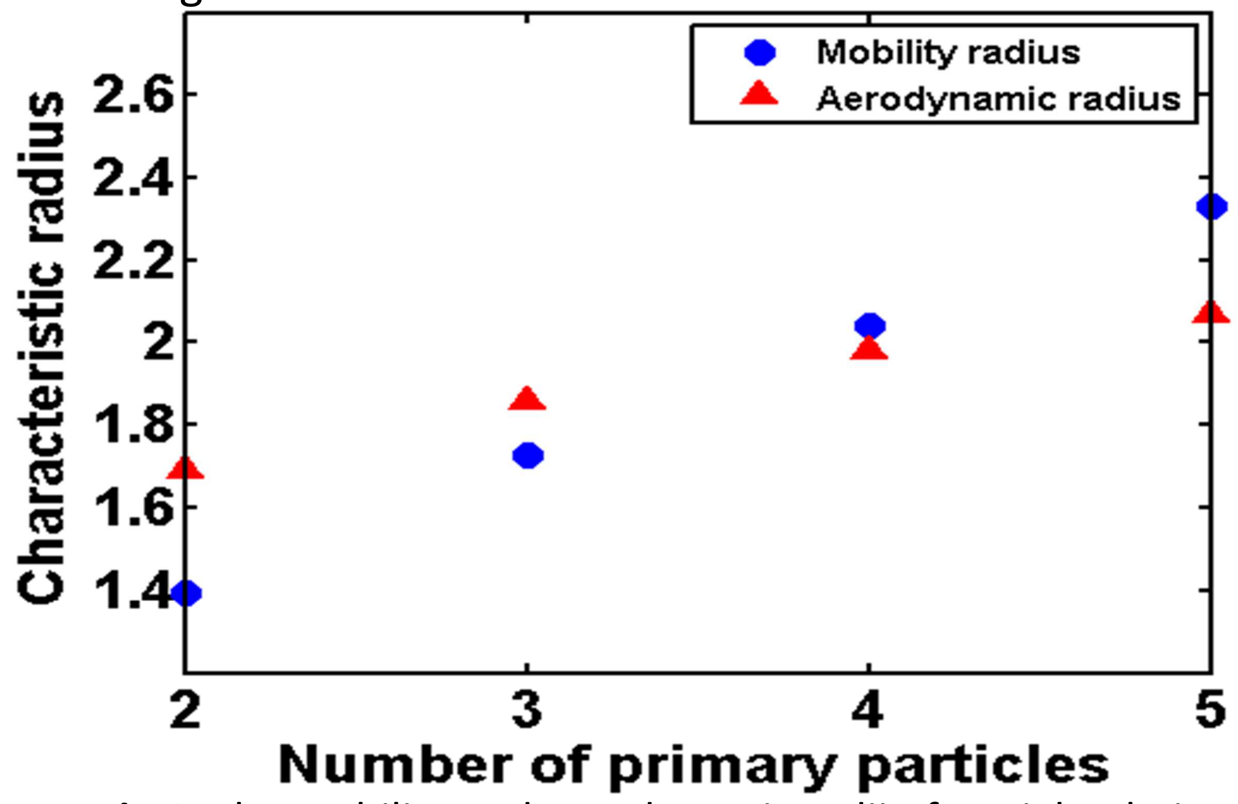

Fig 4. The mobility and aerodynamic radii of straight chains.

CONCLUSIONS

- The distribution of mobility and aerodynamic radii for oligomers depends on both aggregate morphology (herein angle θ) and the number of primary particles, as shown in Figs. 2-4 and argued in the literature[7].
- The distribution of the mobility and the aerodynamic radii are inversely related (Figs. 2, 3), for a constant number of primary particles. This can be extracted from the definitions of the two radii and also from Eq. 3, $R_{ae} \sim R_m^{\ -1/2}$. This difference for oligomers shows that for fractals that consist of larger number of primary particles the distributions will vary even more. Consequently there is no linearity between the mobility and the aerodynamic radius and their relation problem is not a one-to-one definition.
- The effect of aggregate structure, not necessarily quantifiable by the fractal dimension, on aggregate mobility radii of oligomers questions the concept of the effective density for large anisotropic fractal-like aggregates.

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