Supplemental Information

Mixing state evolution of agglomerating particles in an aerosol chamber: Comparison of measurements and particle-resolved simulations

1 Fractal formalism

The fractal structure can be expressed by a power law between the number of primary particles, N, and a characteristic radius R (m) (Friedlander, 2000), with

$$N \sim R^{d_\mathrm{f}}, \tag{S-1}$$

where the exponent d_f is the fractal (or Hausdorff) dimension. In the approach proposed by Naumann (2003), R is expressed by the geometric radius R_geo (m) of a fractal particle, which is defined as the radius of the particle's closest convex envelope. Let $m(R_\mathrm{geo})$ (kg) be the particle mass, so R_geo can be related to $m(R_\mathrm{geo})$ by

$$R_\mathrm{geo} = R_0 \left(\frac{3fm(R_\mathrm{geo})}{4\pi\rho R_0^3} \right)^{\frac{1}{d_\mathrm{f}}}, \tag{S-2}$$

where R_0 is the radius of the primary particles. To obtain the diffusion coefficient D needed to calculate the Brownian coagulation rate, R_geo is first converted to a mobility equivalent radius in the continuum regime $R_\mathrm{me,c}$ (m) using a convenient mathematical form based on the Kirkwood-Riseman (KR) theory (Kirkwood and Riseman, 1948):

$$R_\mathrm{me,c} = h_\mathrm{KR} R_\mathrm{geo} = (-0.06483 d_\mathrm{f}^2 + 0.6353 d_\mathrm{f} - 0.4898) R_\mathrm{geo}, \tag{S-3}$$

where h_KR is the Kirkwood-Riseman ratio. The mobility equivalent radius R_me that covers the entire dynamic regime can then be obtained by

$$R_\mathrm{me} = R_\mathrm{me,c} \frac{C(R_\mathrm{me})}{C(R_\mathrm{eff})}. \tag{S-4}$$

Eq. (S-4) is solved iteratively to obtain R_me. Eqs. (S-2), (S-3), and(S-4) allow the conversion between the measured mobility size distribution (e.g., from a differential mobility analyzer or scanning mobility particle sizer) and the corresponding mass distribution. In Eq. (S-4), R_eff is the effective radius, and C is a correction function considering the transition from the continuum to the free molecular regime. R_eff is given by

$$R_\mathrm{eff} = \frac{S_\mathrm{acc}}{4\pi R_\mathrm{me,c}} \tag{S-5}$$

$$S_\mathrm{acc} = 4\pi R_0^2 N^{d_\mathrm{s}/3} \left[(d_\mathrm{s} - 2) \left(\frac{z}{N} \right)^{1-\gamma} - d_\mathrm{s} + 3 \right], \tag{S-6}$$

where d_s is the surface fractal dimension, which has the value of 3 when $d_\mathrm{f} \leq 2$, and $6/d_\mathrm{f}$ when $2 \leq d_\mathrm{f} \leq 3$. The symbols z and γ are the scaling factor and exponent with values of 1 and 0.86, respectively.

The correction function C in Eq. (S-4) has the form

$$C(R) = 1 + A\frac{l}{R} + Q\frac{l}{R}\exp\left(-b\frac{R}{l}\right), \tag{S-7}$$

where $A = 1.142$, $Q = 0.588$, and $b = 0.999$ are constant parameters with values determined empirically (Allen and Raabe, 1985; Cheng et al., 1988), and l is the mean free path of carrier gas molecules.

After obtaining R_{me} from Eq. (S-4), the diffusion coefficient D of fractal particles is calculated as

$$D = \frac{kTC(R_{\mathrm{me}})}{6\pi\eta R_{\mathrm{me}}}, \tag{S-8}$$

where k (J K^{-1}) is the Boltzmann constant, T (K) is the temperature, and η (kg m^{-1} s^{-1}) is the gas viscosity. Then the Brownian coagulation kernel $K(\mu,\nu)$ can be written as

$$K(\mu,\nu) = \frac{4\pi\left(D(R_{\mathrm{me},\mu}) + D(R_{\mathrm{me},\nu})\right)\left(R_{\mathrm{geo},\mu} + R_{\mathrm{geo},\nu}\right)}{1 + G_{\mu\nu}} \tag{S-9}$$

$$G_{\mu\nu} = \frac{4\left(D(R_{\mathrm{me},\mu}) + D(R_{\mathrm{me},\nu})\right)}{R_{\mathrm{geo},\mu} + R_{\mathrm{geo},\nu}}\sqrt{\frac{\pi m_\mu m_\nu}{8kT(m_\mu + m_\nu)}}. \tag{S-10}$$

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