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The roles of fracture and coagulation in determining a universal size distribution for light duty diesel particulate matter

The roles of fracture and coagulation in determining a universal size distribution for light duty diesel particulate matter

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Introduction

We have previously reported that the soot mode of particulate matter from light duty diesel vehicles is remarkably well described by the lognormal distribution [Harris, S.J. and Maricq, M.M; J. Aerosol Sci. **32**, 749 (2001)]. While the number of particles emitted and their mean size varies depending on the vehicle, the width of the distribution appears to be almost invariant. It is nearly independent of the vehicle tested, the fuel that is used, whether the emissions are made using an engine dynamometer or the full vehicle is tested, exhaust dilution conditions, and engine operating conditions. The measurement of mobility diameter is of sufficiently high quality to demonstrate that the data are not well fit by a self preserving distribution that is predicted from coagulation dynamics [Friedlander, S.K.; Wang, C.S. *J. Colloid Interface Sci.* **22**, 126 (1966)]. We show that including fragmentation in the particle dynamics model significantly improves the model predictions and conclude by commenting on the relevance to the current discussions concerning the measurement of diesel PM emissions.

Representative light duty diesel PM size distributions

Figure 1 illustrates particle mobility size distributions obtained from diesel vehicle and engine emission measurements.

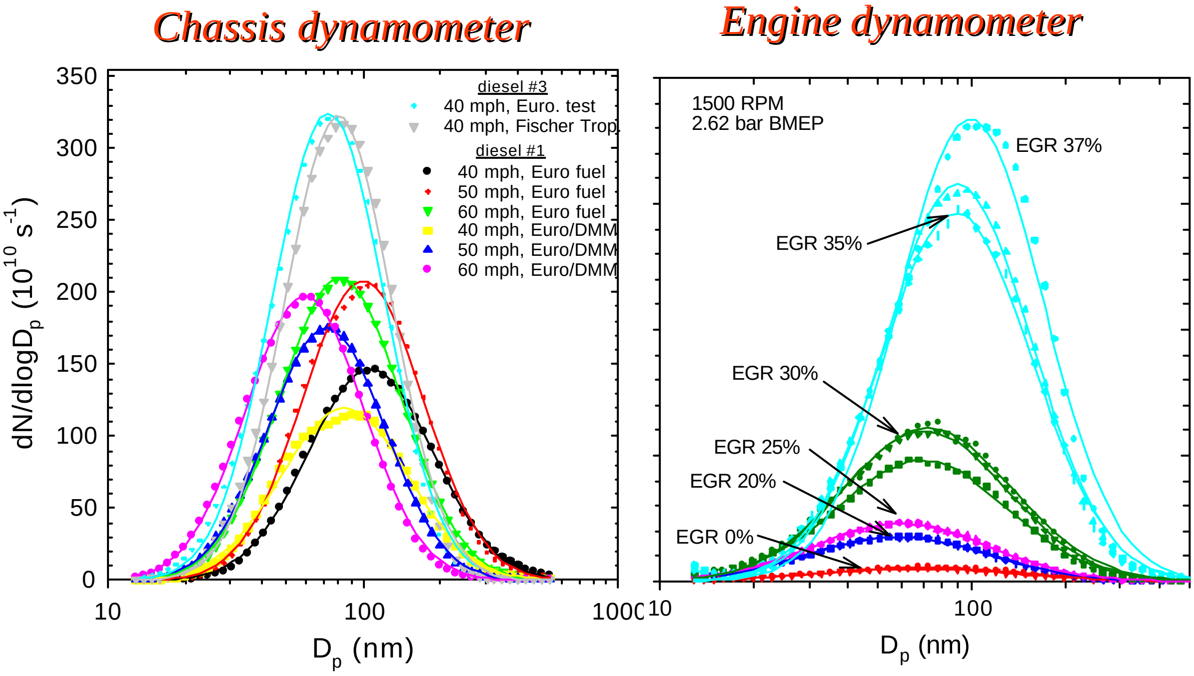

Figure 1. Diesel soot mobility distributions with various fuel and engine operating conditions.

The symbols display the data and the lines represent fits of the data to the lognormal distribution. By defining new coordinates, $\log(h) = \log(D_p) - \langle\log(D_p)\rangle$ and $m = N(D_p)/N_{tot}$, we find in Figure 2 that these data collapse onto essentially the same normalized distribution. Again the symbols represent data, whereas lines represent lognormal distributions with σ_g = 1.7 and 1.8 for the vehicle and engine data respectively. Other researchers obtain these same "reduced" distributions, as shown in Figure 3.

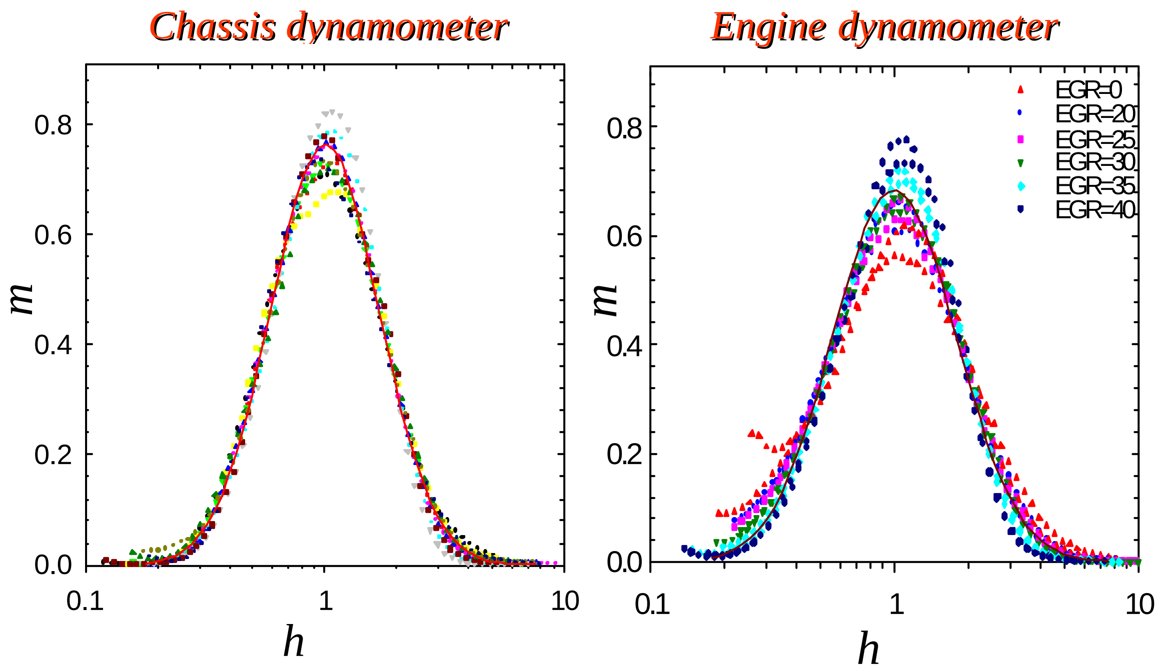

Figure 2. Reduced "m-h" plots of the data in Figure 1.

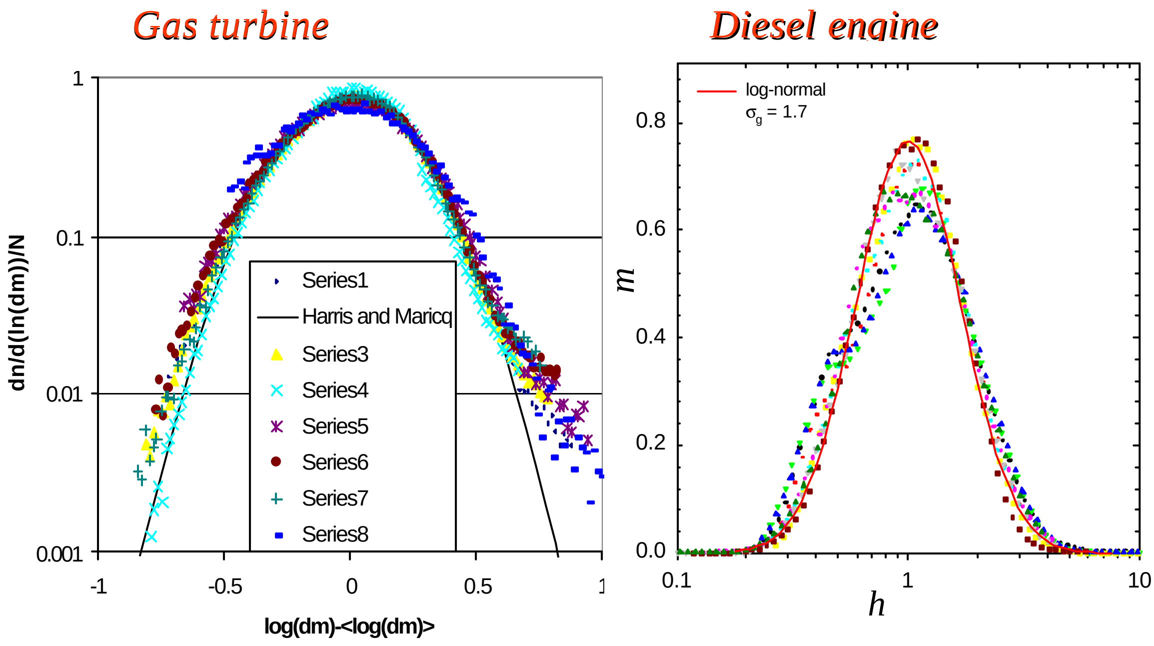

Figure 3. Reduced "m-h" plots from Colket et al. and Chen et al. [private communication].

Model of the particle dynamics in soot growth

Our original particle dynamics model was based on the assumption that once the incipient soot particles are formed, then the growth of the particles is dominated by coagulation. Thus, following Friedlander and Wang, we solved the Smoluchowski equation using both continuum and free molecule kernels to describe particle collisions. Because soot particles are not spherical, the collision kernels are calculated assuming, as done by Mountain et al. [*J. Colloid Interface Sci.* **114**, 67 (1986)], Mulholland et al. *Energy and Fuels* **2**, 481(1988)], and others, that particle volume scales as $V_i \sim V_1 (D_{p,i}/D_{p,1})^{DF}$, where D_F is the fractal dimension and i denotes the number of primary particles in the cluster.

Coagulation dynamics

$$\frac{dn_i}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} b(j,i-j)\, n_j n_{i-j} - \sum_{j=1}^{\infty} b(i,j)\, n_i n_j$$

Collision kernels for fractal particles

$$b(i,j) = \left(\frac{6kTr_0}{r}\right)^{1/2}\left(\frac{1}{i}+\frac{1}{j}\right)^{1/2}\left(i^{1/D_F}+j^{1/D_F}\right)^2$$

$$b(i,j) = \frac{2kT}{3m}\left(\frac{1}{i^{1/D_F}}+\frac{1}{j^{1/D_F}}\right)\left(i^{1/D_F}+j^{1/D_F}\right)$$

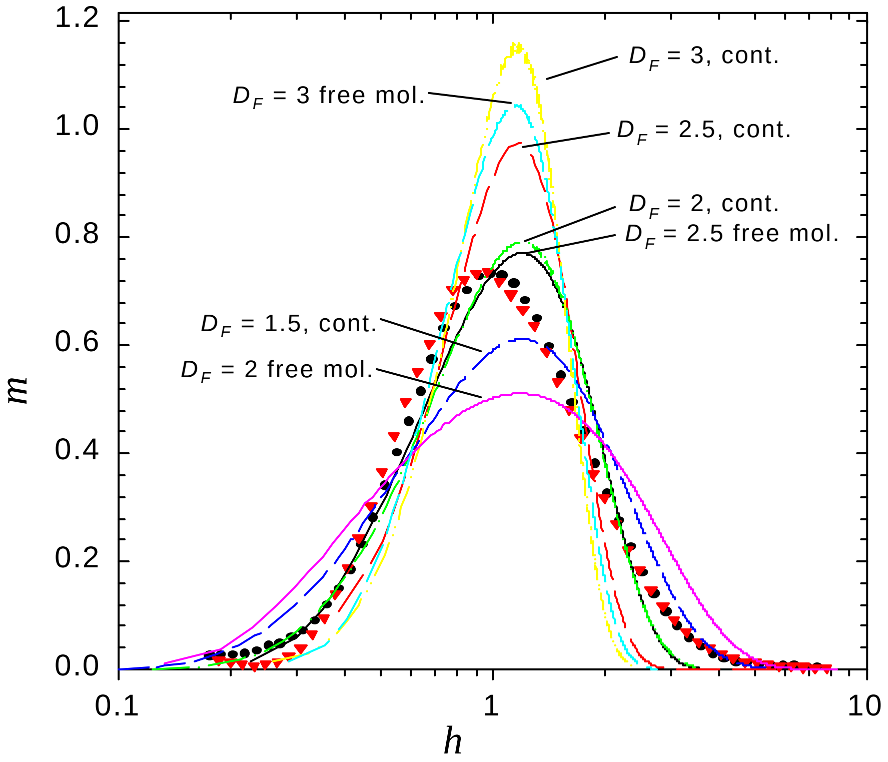

Figure 4. Comparison of diesel PM size with coagulation model predictions

The best fit to the data in Figure 4 is with a fractal dimension between 1.5 and 2, as expected for soot; however, there is a consistent asymmetry apparent in the predictions that is absent in the data. To overcome this problem, we add to the model the possibility that the particles also fragment. This assumption is motivated by the following phenomenological considerations; namely, if a particle executes a random walk, at each step of which it has a probability of becoming a certain fraction larger or a fraction smaller, then the size distribution at long time approaches a lognormal distribution. To test this, we reformulated our model by adding terms describing fragmentation, where the fragmentation rate has a power law dependence on particle size., Here i denotes the number of primary particles, and $\gamma_{i,j}$ describe the fragmentation pattern. Figure 5 illustrates the improvement obtained using the modified model.

Kinetic model – Coagulation & fragmentation dynamics

$$\frac{dn_i}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} b(j,i-j)n_j n_{i-j} - \sum_{j=1}^{\max} b(i,j)n_i n_j + \sum_{j=1}^{\max} g_{i,j} S_j n_j - S_i n_i \,.$$

Fragmentation of fractal particles –
a power law dependence on particle size (Tontrup et al. Colloid Inter. Sci. ***229*****, *****511 2000)***

$$S_i = A i^x$$

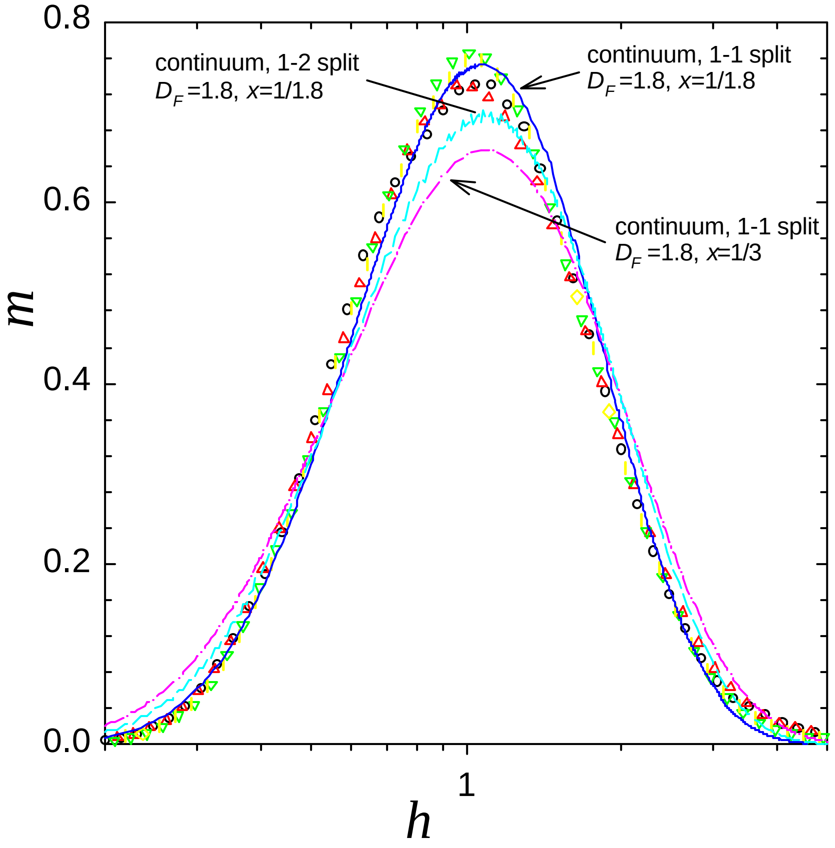

Figure 5. Predicted "signature" size distributions from the model including fragmentation.

Allowing that soot does not grow monotonically via coagulation, but that it also experiences fragmentation, yields a significantly superior fit of the soot mobility size distribution. The predictions are independent of the overall rate scale factor A. In addition, the exponent and the fragmentation pattern both have only modest effects on the predictions. As evident in Figure 5, an exponent based on the fractal dimension gives the best fit; however, changing x to 1/3 instead of $1/D_F$ has only a small effect. Likewise, very similar predictions are obtained whether the particles fragment into two equal pieces, or into pieces with a 2:1 mass ratio. Thus, the model predictions in Figure 5 are essentially obtained without any adjustable parameters; i.e., the quality of fit is not a result of some favorable set of model adjustments.

Discussion and Conclusions

While lognormal distributions are often used in aerosol science to approximate recorded size distributions, the present work shows that light duty diesel engine PM from a wide variety of sources, using different fuels, and measured in different laboratories is remarkably well described by a lognormal distribution with a geometric standard deviation of about 1.7. Current measurement techniques have grown sufficiently sophisticated to show that the self preserving size distribution expected for coagulation dominated aerosol does not adequately describe the data. Adding particle fragmentation to the model significantly improves the agreement between model predictions and the data. That the particles might also fragment is consistent with the general understanding that a large portion of the soot generated in cylinder is oxidized during the exhaust stroke and does not reach the tailpipe.

The current efforts to understanding and measuring diesel exhaust PM might benefit from the work presented here. Knowing that there is a signature distribution for the soot component of diesel PM (at least for light duty vehicles) could help interpret measurements that include nucleation mode particles. Thus, one can subtract out the soot mode from the data. Knowing that the soot mode is characterized by two parameters, number and mean size, can lead to the development of simplified, yet advanced and reliable, PM instrumentation that might be useful for engine testing and vehicle certification.