Interparticle forces in Nanoparticle Agglomerates

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Due to the high surface energy of nanoparticles their tendency to form agglomerates is quite strong. Upon contact the primary particles of an agglomerate form bonds which can be of different nature. Sintering and monomer adsorption from the surrounding atmosphere can lead to solid state necks. Chemical bonds between the particle surfaces may also form and magnetic dipole forces can potentially contribute to the interparticle forces. As a baseline of bond energy van der Waals forces are always present. The strength of these interparticle bonds determines to a large part their physical properties and applicability in materials synthesis. However, there are indications for an effect of agglomerate strength on the toxicological properties of nanoparticles. If the interparticle forces are weak, deagglomeration of particles in biological fluids may occur. For particles deposited in the lung, a deagglomeration in the lung lining fluid leads to a change in the particle size and an increase in particle number. For nanoparticle aerosols, where agglomerate sizes of around 100 nm are common, this can result in a change in particle size by a factor of 10-20 and an increase in particle number by roughly two orders of magnitude.

To determine the bond energies of primary particles within agglomerates the method of impact fragmentation was adapted to the nanoscale and integrated into a novel device. Fragmentation patterns of agglomerates where imaged in a transmission electron microscope (TEM) and statistically analyzed. A variety of materials was tested, ranging from metal particles and oxides to polymer particles and diesel soot. Particle size effects were analyzed for the separate materials, revealing the different origins of the interparticle bonds. For some materials near van der Waals behavior was found. For Nickel the onset of additional magnetic forces were observed for larger particle sizes, when the super-paramagnetic behavior of particles smaller than ~12 nm transforms into permanent magnetic dipoles. Another strong effect on the magnitude of agglomerate strength seems to be surface purity, which is qualitatively determined from aerosol photoemission spectroscopic analysis.

As a major representative of engineered NP the agglomerate strength of fumed silica deserves special attention. For this material a limit of the dispersibility in liquid media is observed, where an increase of the energy input does not lead to further fragmentation. The particles remain at diameters of about 100 nm, while the primary particles are much smaller than this, in the range of 10-20 nm (e.g. Pohl et al. 2005; Wengeler et al. 2006). While electron micrographs show no signs of sintering there are obviously substructures of the agglomerates with high interparticle forces that can not be fragmented. It can be speculated that these substructures are aggregates, formed in regions of high temperature in the synthesis process where minute sintering in the contact regions was possible. These aggregates may then agglomerate in cooler regions to form weak agglomerates.

To investigate the question on the origin of the poor dispersibility of fumed silica, silica particles were generated and allowed to agglomerate at room temperature, forming low energy contacts. The formation of high energy bonds was then induced by controlled sintering at various temperatures between 1000 and 1500°C at a constant residence time of 30 ms. The bond energies of the primary particles within the agglomerates were determined using the method of impact fragmentation, which was adapted to the nanoscale (Seipenbusch et al., 2002; Seipenbusch et al., 2007). The method enables fragmentation of agglomerates under variation of the kinetic energy prior to impaction. Analysis of the fragmentation patterns at different initial kinetic energies then yields fragmentation curves that show the distribution of interparticle forces within the agglomerates. In parallel to the fragmentation experiments the evolution of solid state bridges was analyzed using electron microscopy.

The experiments with our synthesized SiO_2 showed that particles agglomerated at room temperature are indeed held together by relatively weak forces (van der Waals and possibly liquid bridges) and can be deagglomerated almost entirely. At temperatures higher than 1000°C however, the maximum degree of deagglomeration (fragmentability) obtainable in the applied energy range rapidly decreased. When sintering necks eventually became visible at temperatures above 1300°C the fragmentability had already dropped to about 50%. The fragmentation curve of Aerosil®200 was approximated for temperatures exceeding 1400°C. The interparticle contacts in fumed silica therefore appear to be dominated by solid state necks. The implications of this regarding the dispersibility are already known. It is possible to break the van der Waals contacts and liquid bridges between the aggregates but under application of energies within an economically reasonable range it is impossible to break the aggregates, thus a fragmentation down to the primary particle size can not be achieved. From the point of view of NP toxicology the implication of the experimental results is that the size of the aggregates rather than the size of the primary particles is a relevant metric for mechanisms depending on particle geometry such as transport and cell uptake, determining the fate of a particle in an organism.

As a representative of incidental nanoparticles the strength of Diesel soot was investigated by Rothenbacher et al. using the method described above. In analogy to silica agglomerates the existence of strong aggregates was found for these particles as well. The soot particles sampled directly from the exhaust of a VW TDI engine could not be fragmented. After aging of the aerosol however, agglomerates held together by van der Waals forces and liquid bridges were formed, which could be fragmented in the same energy range as the silica agglomerates (10^{-17}J per interparticle bond). The application of a denuder downstream of the aging chamber resulted in a decrease of the agglomerate strength, presumably by a reduction of the number and size of liquid bridge bonds between the particles.

References

Rothenbacher S., Messerer A., Kasper G. (2008) Fragmentation and bond strength of airborne diesel soot agglomerates. Particle Fibre Tox., 5:9

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Pohl M., Schubert H., Schuchmann H.P. (2005) Herstellung stabiler Dispersionen aus pyrogener Kieselsäure. Chem. Ing. Techn. 77:258-262

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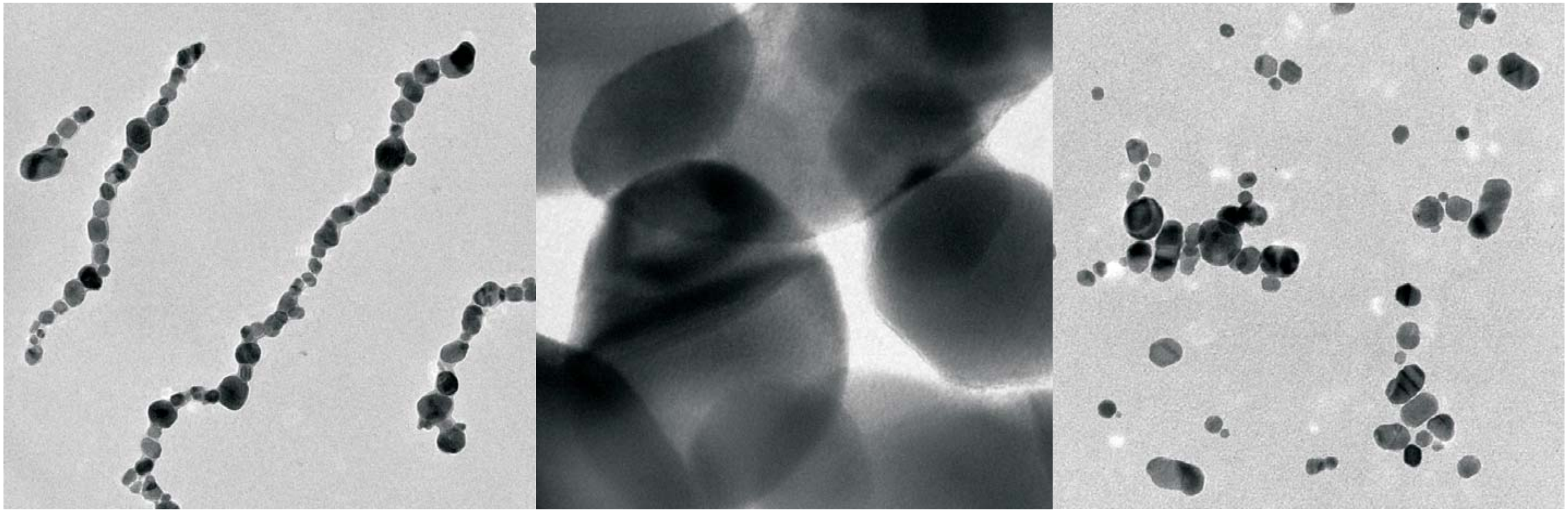


Outline

- Introduction
- Impact fragmentation for the determination of interparticle forces
- Two examples for applications:
    - Agglomerates vs. aggregates in silica nanoagglomerates
    - Interparticle forces in diesel soot agglomerates
- Summary

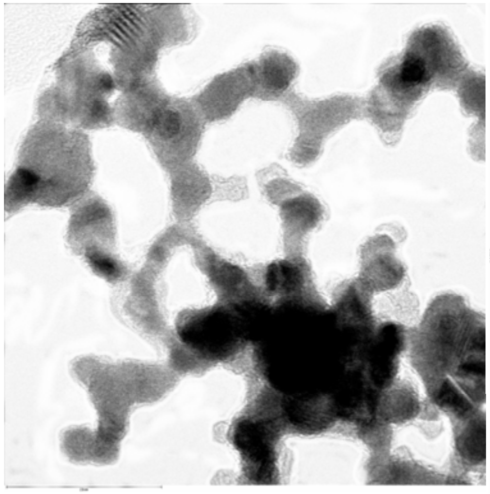
Introduction

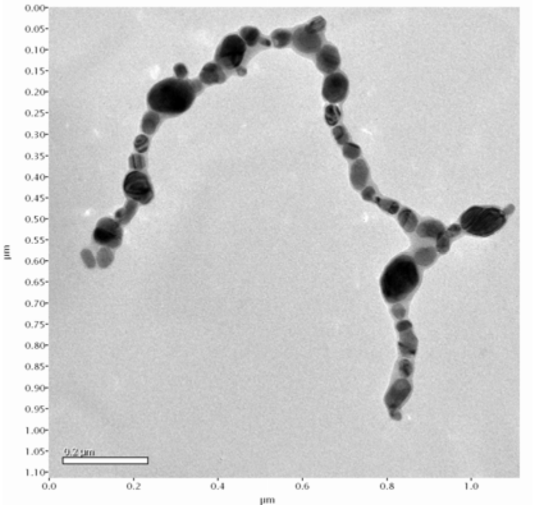
Interparticle forces in agglomerates decide over product properties

- Fillers in elastomers
- Dispersibility
- Possibility of deagglomeration in biological systems

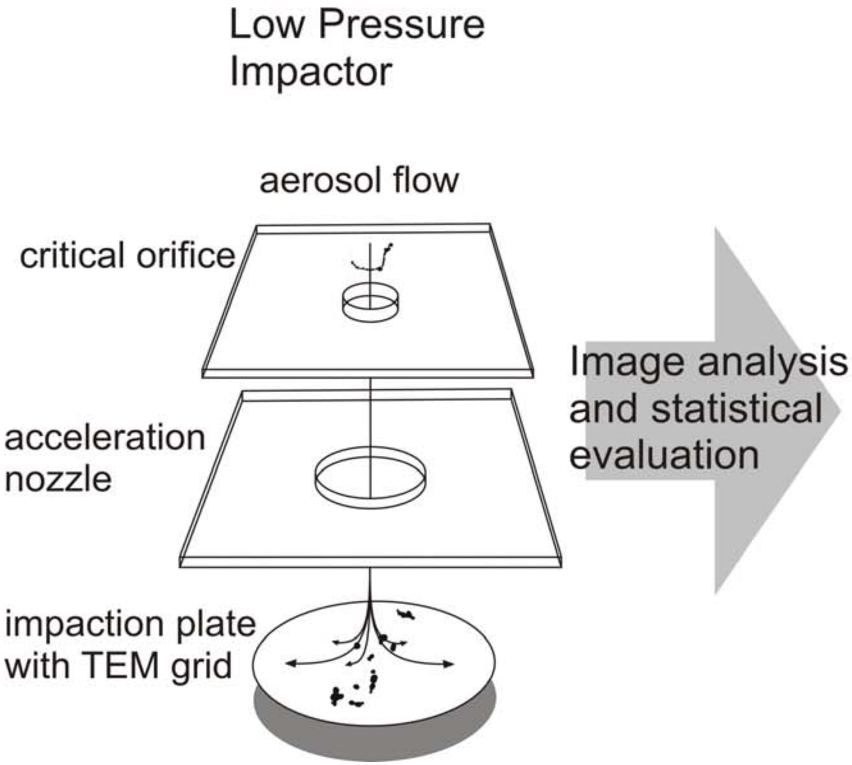
Relevant mechanisms:

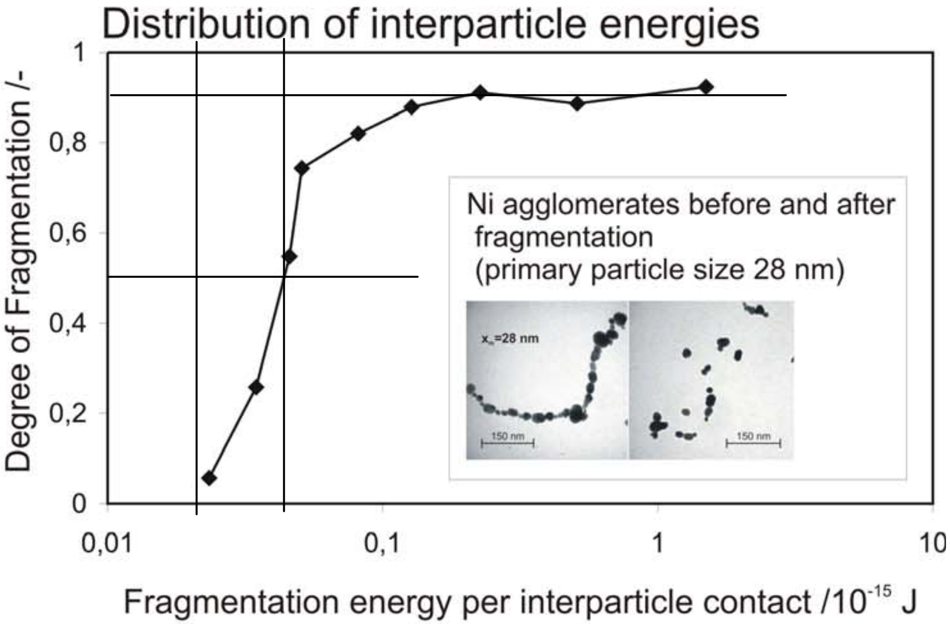
- Van der Waals energy
- Magnetic dipole forces
- Chemical bonds
- Liquid bridges
- Solid state necking





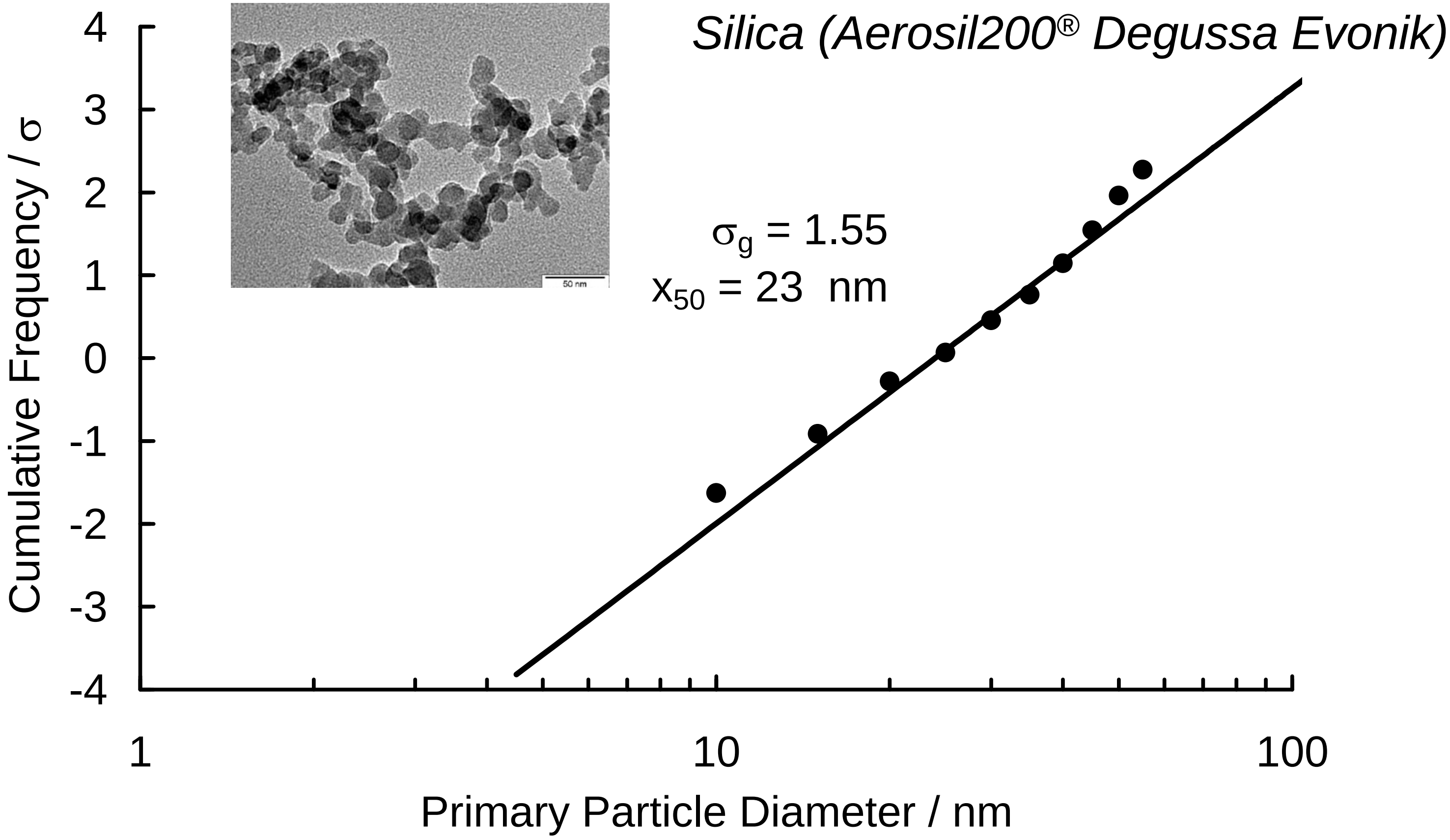
Impact fragmentation for the determination of interparticle forces





- Threshold energy
- Energy for 50% fragmentation
- Maximum fragmentation

Example I: poor dispersability of flame made Silica Agglomerates or Aggregates?

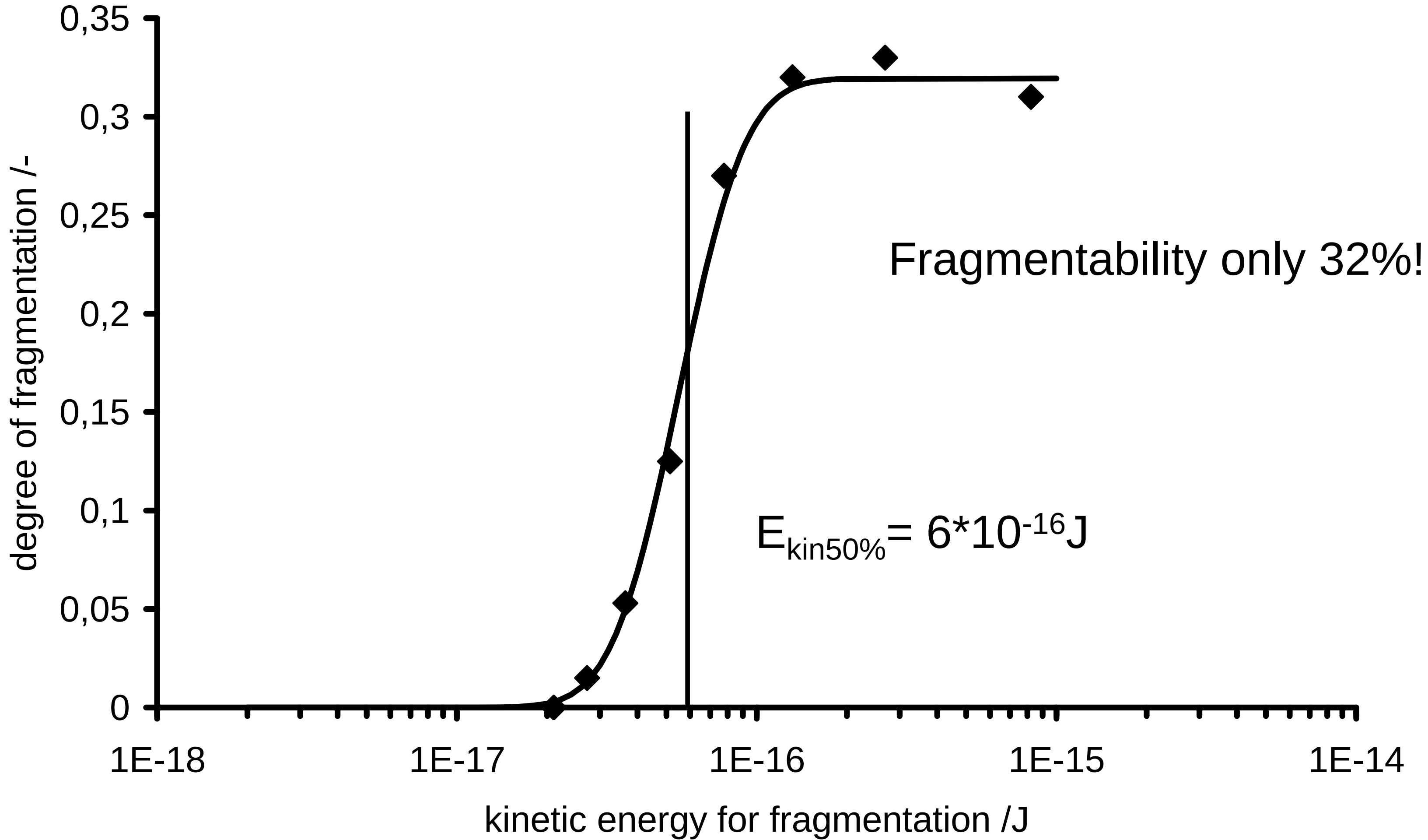


Silica (Aerosil200® Degussa Evonik)

$\sigma_g = 1.55$

$x_{50} = 23$ nm

Aerosil200®: Fragmentation results

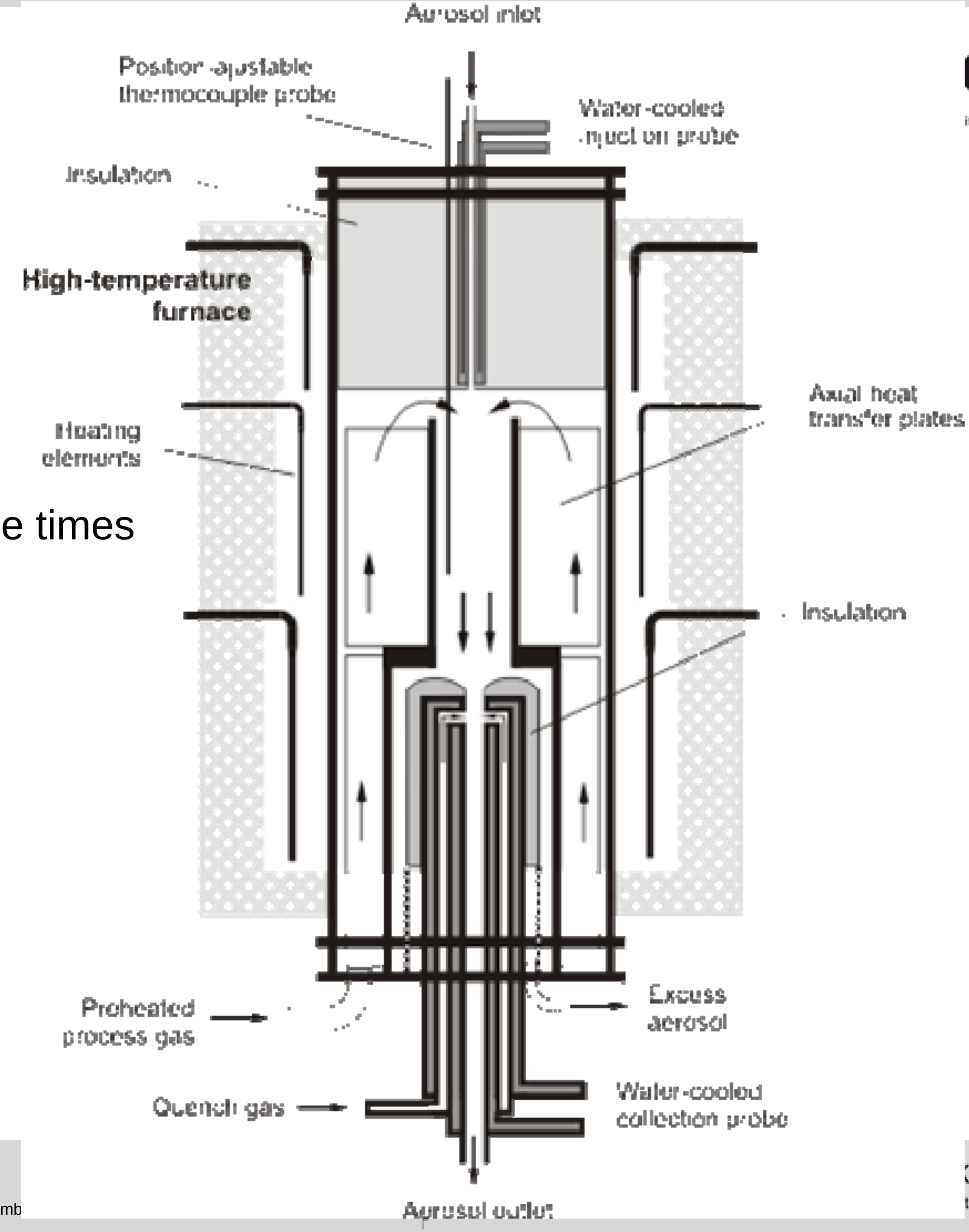


Fragmentability only 32%!

$E_{kin50\%} = 6*10^{-16} J$

Seipenbusch et al. J. Nanopart. Res.12 (2010) 2037

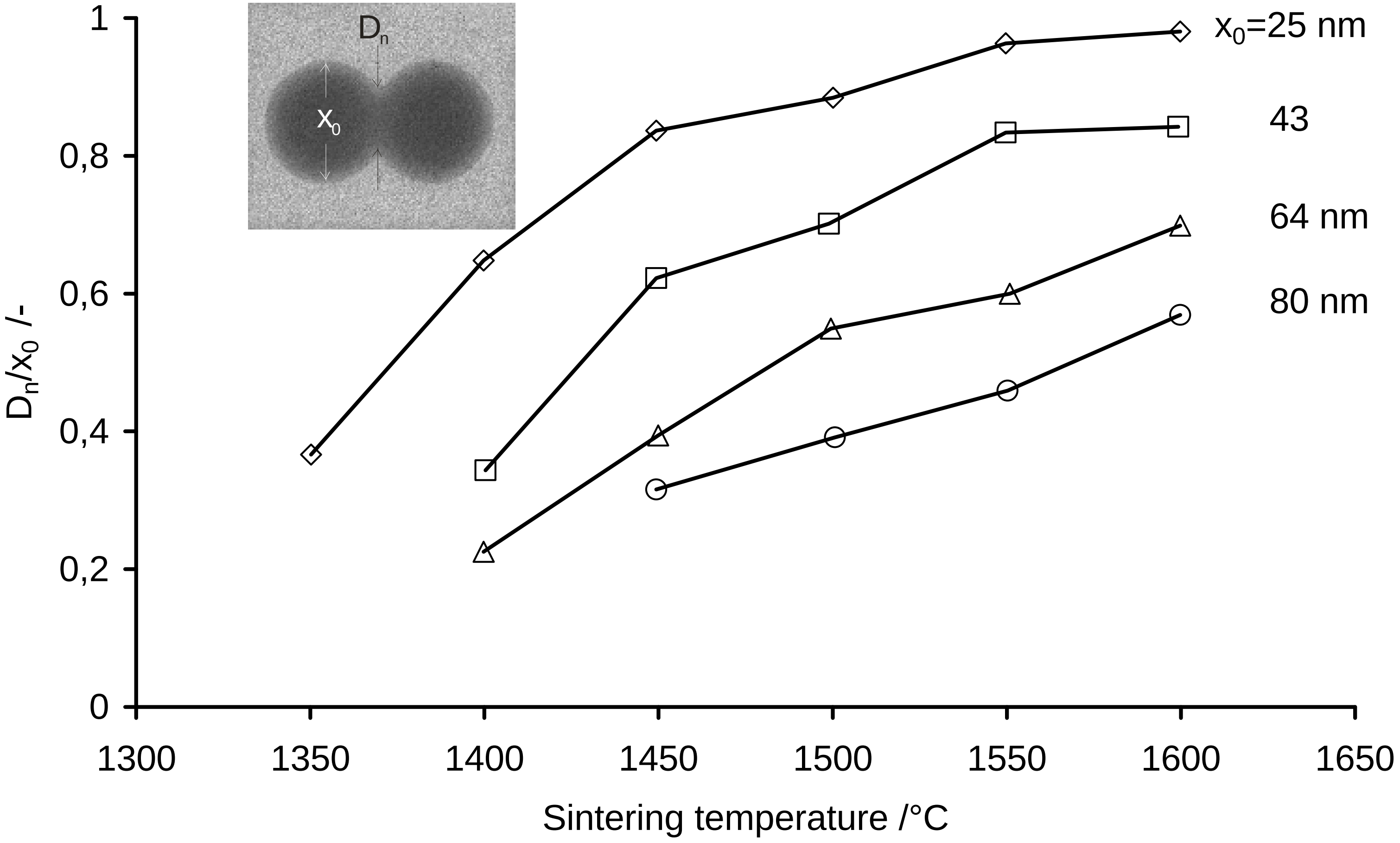
Agglomerates or Aggregates? Controlled sintering of silica dublets



Extremely short residence times (30 ms) and rectangular temperature profile

LMU Munich

Development of the neck size with increasing temperature



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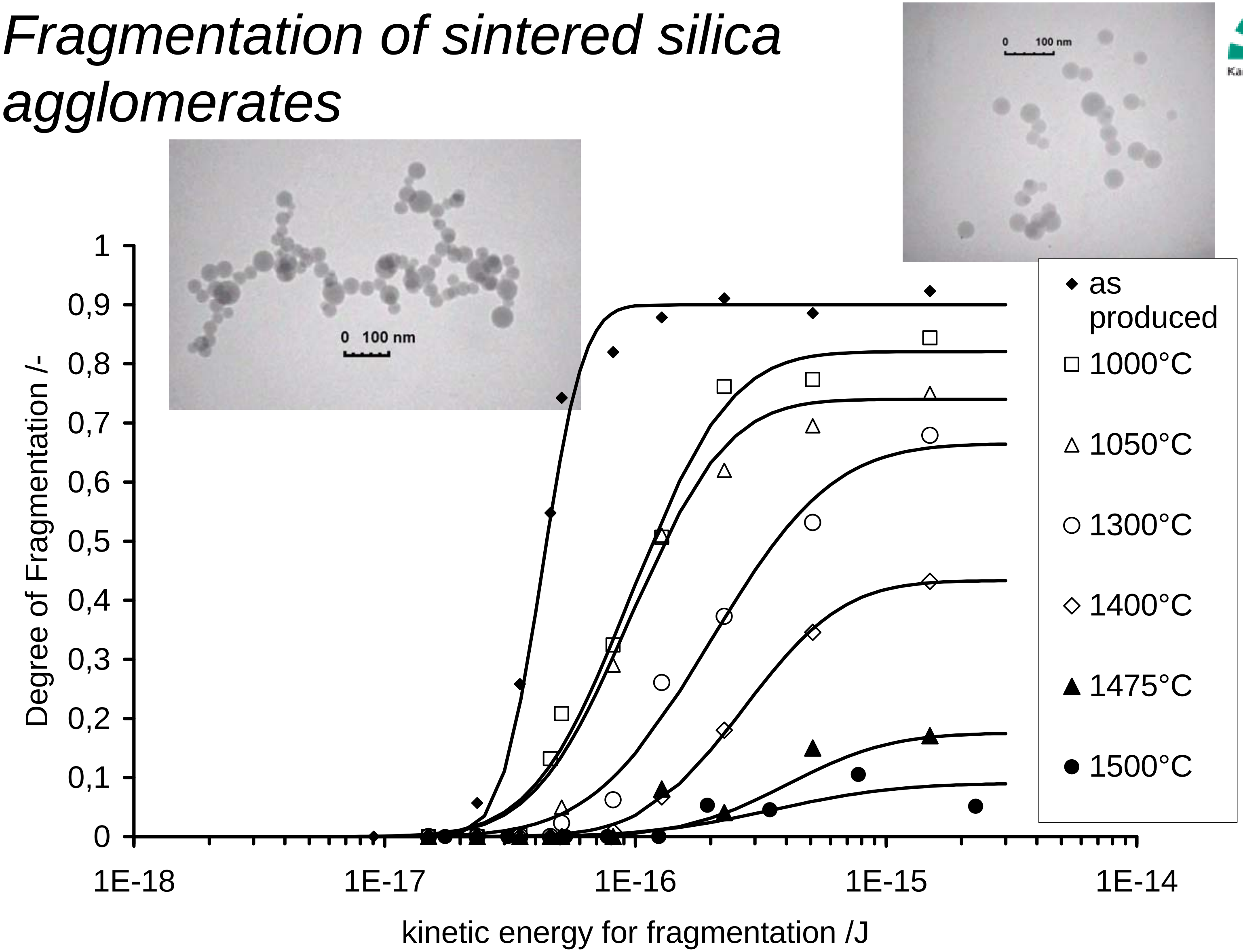
Fragmentation of sintered silica agglomerates



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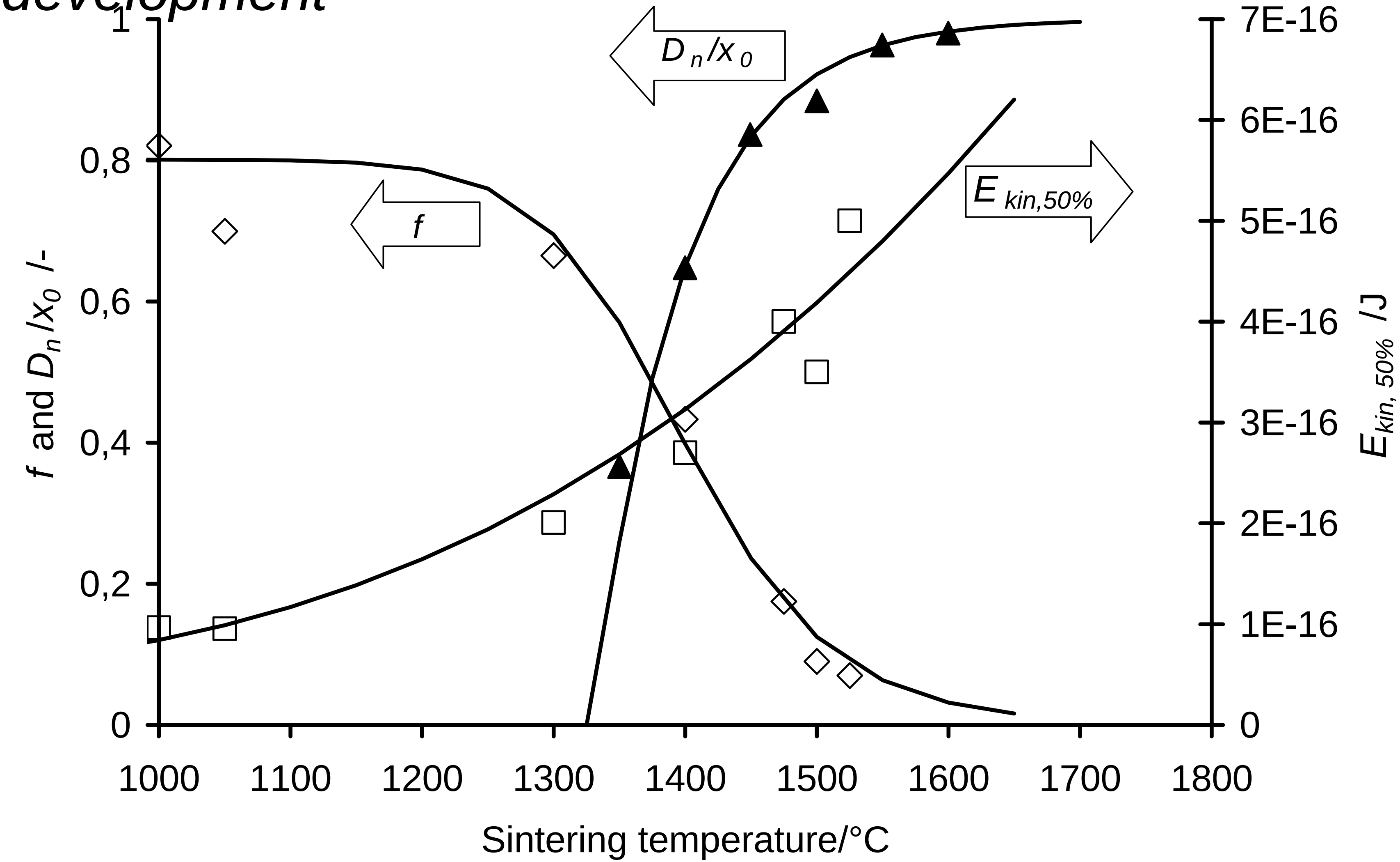
Fragmentability $E_{kin50\%}$ and neck size development



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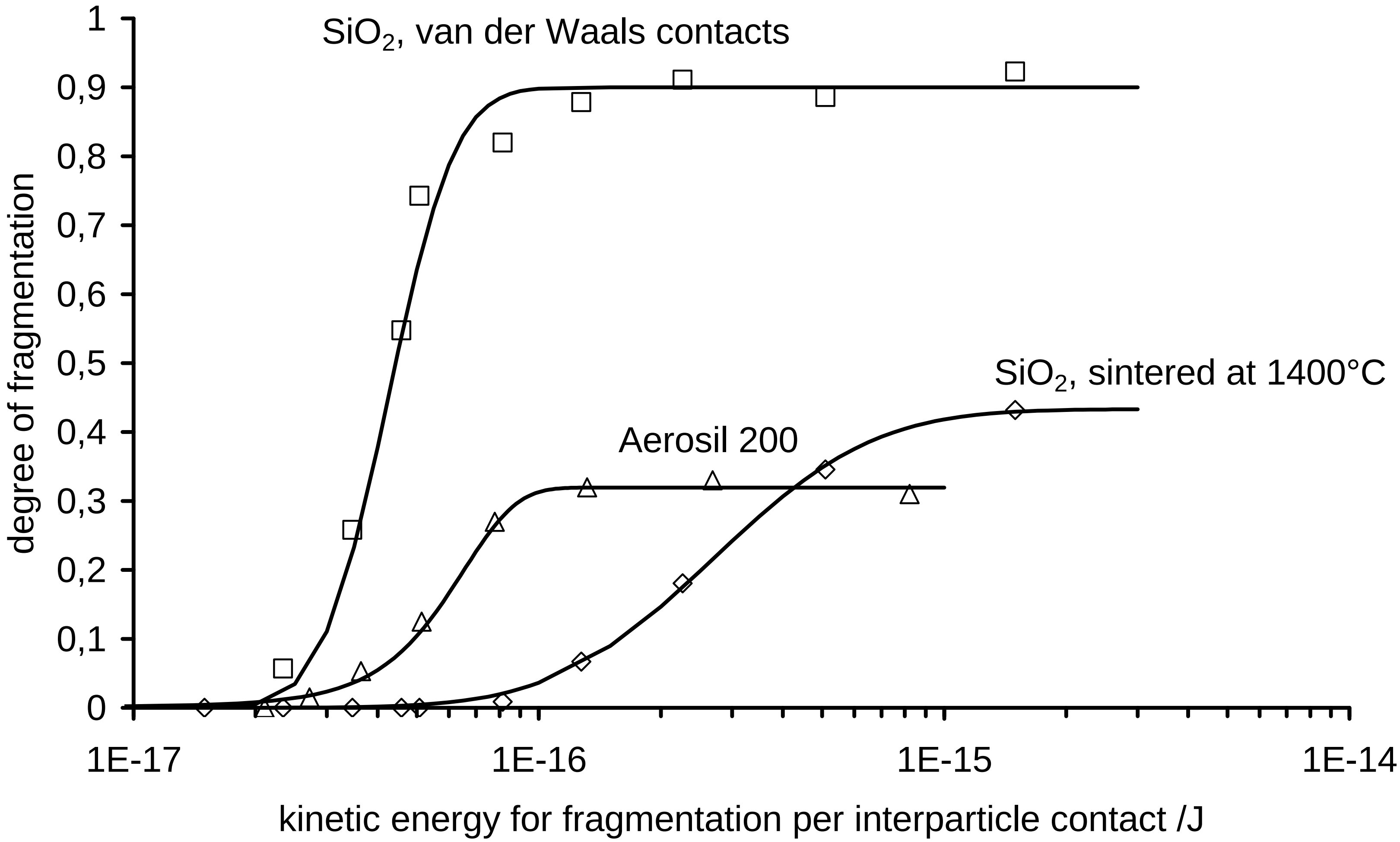
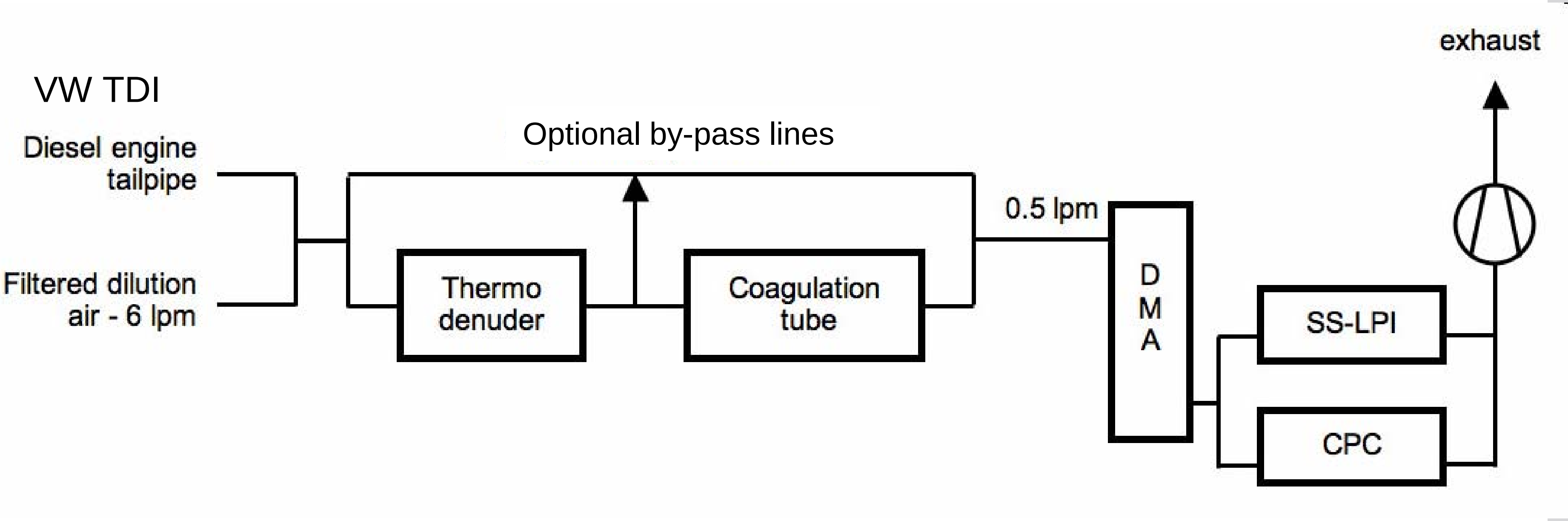
Comparison Aerosil200® - sintered silica

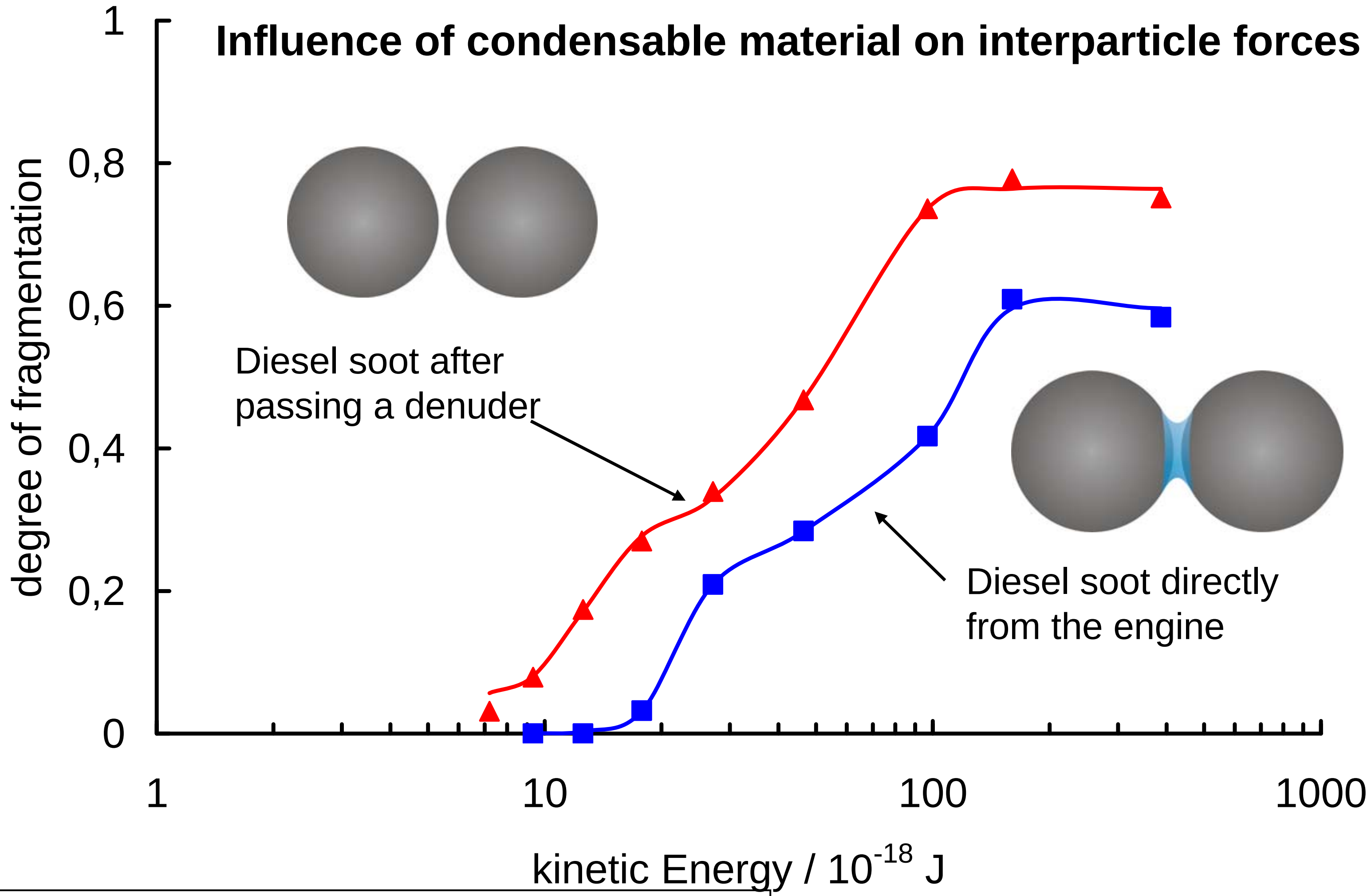


Example II: Diesel soot



Rothenbacher et al. Part. Fibre Tox. 2008 5:9

Example II: Diesel soot



Rothenbacher et al. Part. Fibre Tox. 2008 5:9

Summary

Impact fragmentation delivers a wealth of information about interparticle energies:

- **nature/origin of the interparticle force**
- **energy distribution: possible discrimination between individual contributions**
- **ratio of soft to hard bonds in agglomerates:**

  aggregates vs. agglomerates
- **overall magnitude (upper limit)**