Challenges in nanoparticle technology – New prospects in flow syntheses and property classification

Wolfgang Peukert
Institute of Particle Technology, Center of Functional Particle Systems
Friedrich-Alexander University Erlangen-Nürnberg (FAU)
Erlangen, Germany
Email: wolfgang.peukert@fau.de

Abstract

A long-term vision in nanoparticle science and technology is the targeted design of particulate products by rigorous optimization based on predictive structure-property and process-structure functions. Particulate products consist in the simplest case of dispersed single particles and in more complex cases of hierarchically organized assemblies of particles in the form functional thin films or other formulated products, e.g. for pharmaceutical applications. We target scientific breakthroughs in the product engineering of nanoparticles (NPs) with optimized properties produced by continuous synthesis. A major challenge is the property classification of fine particles with respect to size or shape. These challenges will be addressed from different perspectives and will be underpinned by developments in synthesis, classification, characterization as well as modelling and simulation.

CV

Wolfgang Peukert is a chemical engineer who worked 7 years in industry, two of which he spent in Japan with Hosokawa Micron. He is professor at the university Erlangen and director of the interdisciplinary center of Functional Particle Systems. His research interests focus on product design and formulation. He is seeking for unifying principles in the design of particulate products in combination with modelling and optimization strategies. His activities include particle formation via bottom-up and top down techniques both in the gas and liquid phase. He uses methods from interface science for tailoring particle interactions, colloidal stabilization and ultimately particle properties. Recent activities include comprehensive particle characterization for size, shape and surface properties. He likes to work in interdisciplinary teams, his motto is: Innovation occurs at the interfaces.

Unifying principles of product design

Product design is the formation, formulation, handling, manufacturing, and characterization of complex multiphase products with specific properties. The applications define the required product properties which cover both classical fields of process technology in the chemical industry as well as new emerging fields of electronics, energy and environmental technologies, life sciences, materials science and engineering, nanotechnology, and photonic technologies highlighting the broad relevance of mesoscale science. The following five unifying principles of particulate product design are proposed which are widely applicable to many different kinds of products including solid, liquid, and even gaseous particles [1]: i) Particle formation by top-down and bottom-up approaches, ii) interactions between the building blocks, iii) structure formation by self-organization and by transport processes, iv) characterization along the process chain, v) multiscale modelling and simulation. A particular important aspect in the hierarchical design of advanced materials made from (nano-)particles is the multidimensional characterization of particle systems [2] including particle surfaces and particle interactions which are highly relevant for colloidal stabilization, self-assembly and formulation. In particular, solid-liquid interfaces of particles are poorly understood. We present examples for multidimensional particle characterization based on linear and nonlinear optical spectroscopy, analytical ultracentrifugation and related SAXS/SANS studies. Other important challenges are related to continuous formation of nanoparticles and their size classification which will be briefly addressed in the following sections.

Nanoparticle Precipitation

Precipitation of nanoparticles is used in various fields with a rising interest in the continuous formation and formulation of poorly soluble drugs. We analyze the impact of fluid mixing on the precipitation of organic nanoparticles in a T-Mixer. Direct numerical simulations are applied to determine the spatio-temporal evolution of the liquid phase composition and to estimate the particle evolution along Lagrangian trajectories. The simulation results are compared with experiments of mixing and particle size evolution, which use a recently developed approach to rapidly stabilize the precipitated nanoparticles. We reveal the impact of mixing on precipitation, thereby enabling a parameter-free estimation of the mean particle sizes and the particle size distributions. The distributions of residence time, supersaturation time and particle size are self-similar for Reynolds numbers in the turbulent regime and allow the derivation of scale-up rules [3].

Nanoparticle chromatogaphy

For high-quality particulate products, a defined and narrow particle size distribution (PSD) is desired, since a small change in PSD can have a large impact on their properties, for instance the interaction of nanoparticles (NPs) with light is strongly size- and shape-dependent. Most of the techniques to produce NPs lead to size distributions and despite the remarkable progress in liquid phase syntheses of well-defined NPs of controlled size and shape. Therefore, a classification step is mandatory to adjust or modify the obtained PSD according to the needs of the later product. Specific targets for the classification are: Separation of a broader feed into two or more fractions, the removal of fine or coarse tail fractions, shape separation as many NP syntheses lead to shape distributions, or the separation of by-products when several phases are formed. For instance, narrowing of the initial PSD or exclusion of an unwanted particle fraction might already significantly improve the NP performance of the later application.

Currently, no technical solution for nanoparticle property classification is known. We propose chromatography as promising and scalable method for classification of NPs. We study the classification of different NPs in the size range from 1 nm up to 50 nm by separating C_{60} from C_{70} fullerenes roughly 1 nm in diameter [4], carbon nanodots of similar size as highly lumincent NPs [5], high precision classification of semiconducting ZnS quantum dots with sizes between 1.5 and 3 nm and plasmonic gold NPs below 50 nm [6], see Figure 1.

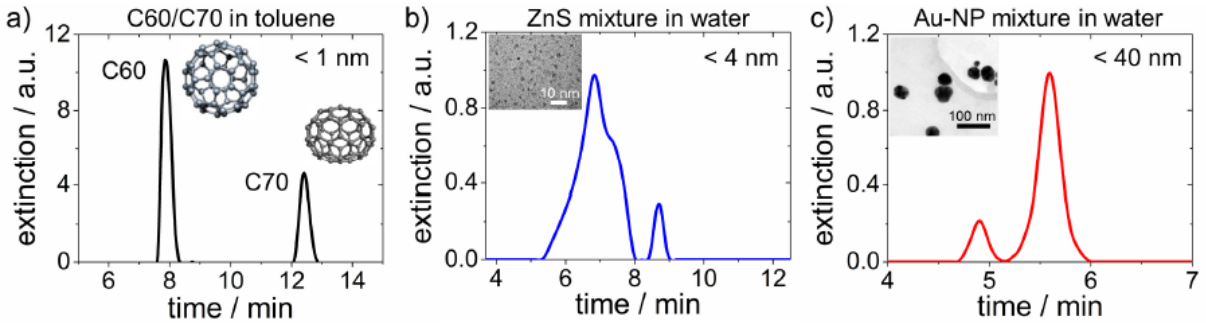

Figure 1. Examples of realized size-selective separations as function of retention time for (a) C_{60}/C_{70} fullerenes, (b) semiconducting ZnS quantum dots, and c.) plasmonic Au NPs.

C60 fullerenes are perfectly round, chemically well-defined and of uniform size of around 1 nm. Thus, they are perfect probe molecules to study particle interactions. We show how to measure Hamaker constants via adsorption equilibria obtained during their chromatographic separation. ZnS and Au NPs are classified by size-exclusion chromatography (SEC). First, we investigated the interactions of the NPs with potential stationary phases in order to identify a suitable material

for the chromatographic process where irreversible NP adhesion is excluded. Then, we demonstrate the high reproducibility of our SEC experiments by multiple sample injections that lead to constant peak areas. In particular, we show the size-dependent elution behavior of NP mixtures resulting in baseline-separated elution peaks, where size separation was confirmed by inline measured UV/Vis spectra. Finally, NP classification results by using a fraction collector are characterized by retention time, mass balances and size-dependent separation efficiencies. The fine-tuning of the PSDs is demonstrated by changing the switching time of the fraction collector.

Our study provides fundamentals of preparative chromatographic separation of NPs. We demonstrate the high effectivity and reproducibility of size-selected separation for varying particle types, particle concentrations and particle sizes < 50 nm. The huge potential of NP chromatography is demonstrated together with the strength of theoretical concepts for the quantitative analysis and the prediction of nanoparticle classification.

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