Determination of the dominating forces that influence the process of self-assembly of nanoparticles in the volume of an evaporating droplet.

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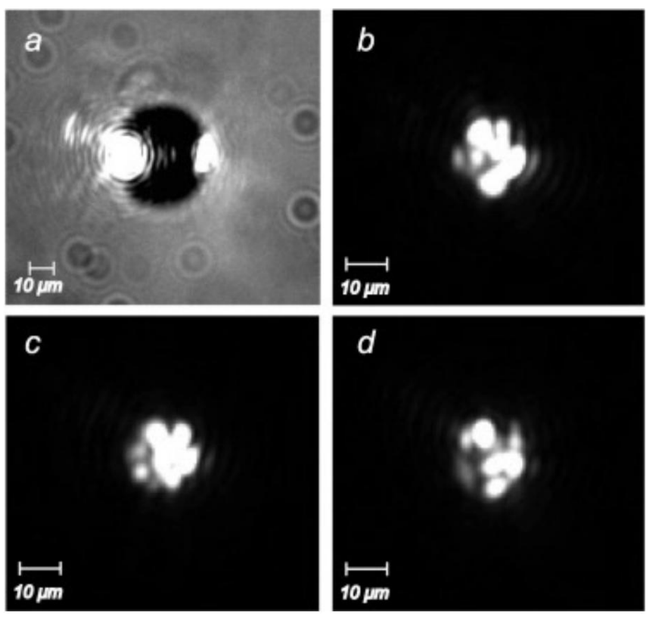
Abstract:

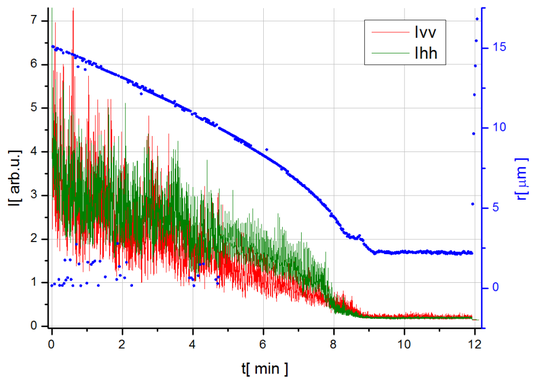
The development of models of light scattering by droplets of suspensions, together with the development of models describing the process of evolution of nanoparticles into an aggregate, makes it possible to determine the dominant forces influencing the process of self-assembly of nanoparticles. The properties of light scattered by the droplet of suspension depend not only on the optical properties of the droplet material but also on the geometric parameters (structure) of an aggregate that the droplets contain. In turn, the evolution of the geometry of an aggregate depends on the external forces acting on its prime particles, as well as the forces of interparticle interaction. The properties of nanoparticles differ from those of bulk material. The inter-particle interaction forces can be found either by using quantum chemistry methods (in principle, currently not available for nanometer-sized particles) or empirically. Observing the evolution of the macroscopic parameters of the aggregate, such as the fractal dimension or the density distribution function, one can draw a conclusion about the types of interactions acting at the nano level. The evolution of the fractal dimension and the density distribution function depend on the forces acting on the particles and simultaneously correlate with the intensity of light scattered by the droplet. Additionally, the evolution of the aggregate influences the speed of evaporation of the droplet which is reflected in the temporal evolution of the radius of the droplet. Comparison of the simulation results with the results obtained during the experiment makes it possible to determine the dominant forces acting during the process of self-assembly of nanoparticles. Furthermore, the type of dominant force acting during the process of self-assembly strongly influences the final shape of the aggregate. It can be used as an additional check of our hypothesis by comparing the shape of the final aggregate obtained during the simulation with the SEM image of the final state of the aggregate obtained during the experiment.

Experimental results:

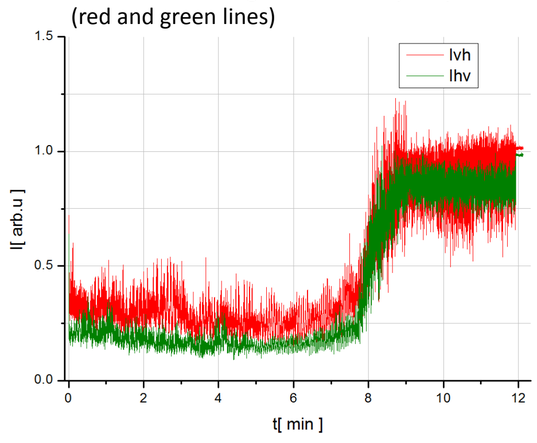


a) *Experimental in-focus image of a levitated, pure TetraEG, 40 µm droplet, obtained with additional back-illumination with unpolarised white light, in order to visualise the droplet boundaries.*

b,c,d) *Consecutive in-focus images of an aggregate - at the final stage of evolution - obtained from a water droplet containing ~300 TiO2 spheres of 250 nm diameter.*

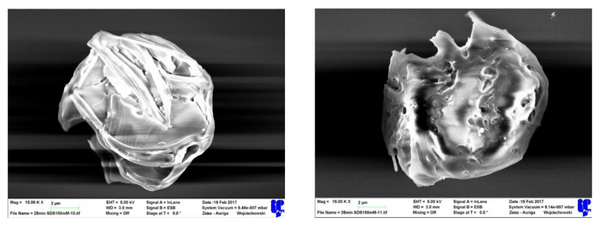


The time evolution of the radius of an evaporating droplet (blue line); The time evolution of the light scattered by droplet (red and green lines)

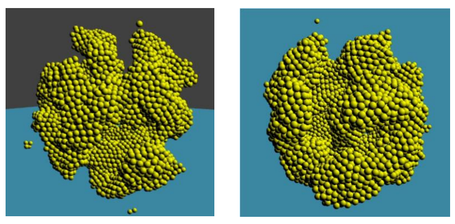


The time evolution of the intensity of cross-polarized light

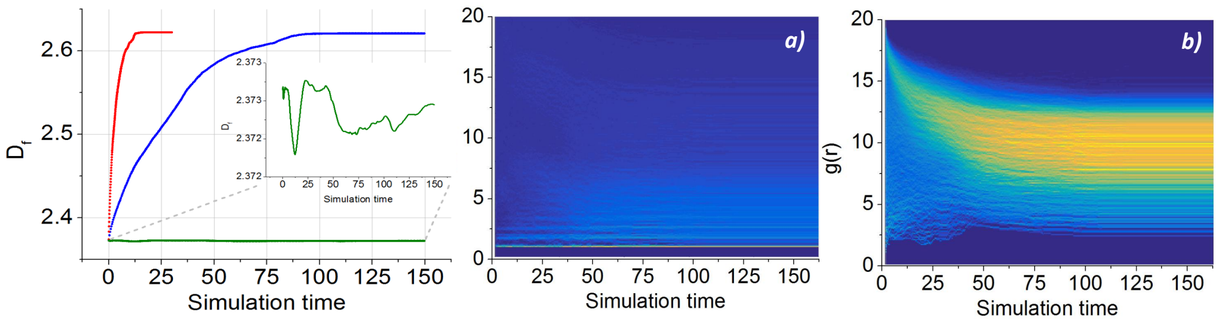
Results of the MD-like simulation



The SEM image of the final state of the aggregate that was produced by an evaporating ethylene glycol droplet containing SiO2 particles stabilized by SDS



The result of the molecular dynamics simulation of the evolution of the system comprising 10 thousand particles that interacts by means of the Lennard Jones potential



Left side: Possible temporal evolutions of the fractal dimension of an aggregate forming in a microdroplet for different model parameters. In all three cases, 10^4 NPs were considered. The droplet was neither rotating nor evaporating. The red line – the NP-NP interaction modelled with Lennard-Jones potential only. The blue line – apart from L-J interaction, half of the NPs were charged positively and another half – negatively. The green line – all the NPs had the same charge.

Right side: Radial distribution function (RDF) functions' evolution obtained for parameters corresponding to the red line in (neither evaporation nor rotation of the microdroplet, only L-J interactions between NPs): panel ***a)*** – standard RDF, panel ***b)*** – RDF calculated from the center of the sphere.

Definitions:

The fractal parameters are standard mathematical constructs for describing self-similar objects. When real-world aggregates are concerned, we encounter concepts of a mass-fractal and a surface-fractal. For a mass-fractal we can estimate the mass (or a number of elementary building blocks – primary particles) of the aggregate, knowing the size of its bounding box and the space dimensionality. For example, in Euclidean geometry, we have the relationship between the mass and size of a solid in the form of $m \sim d_p^3$, where d_p is the mean diameter of primary particles. In the case of a mass-fractal, the relation becomes $m \sim d_p^{D_f}$, where D_f is the fractal dimension. In detail, the relation takes the form:

$$m = k_f \left(\frac{R_g}{d_p} \right)^{D_f} \qquad R_g = \left(\frac{1}{N} \sum_{i=1}^{N} (r_0 - r_i)^2 \right)^{1/2}$$

where R_g is the gyration radius, measured from the centre of mass of a given axis and k_f is the fractal prefactor. When the formation of an aggregate with a compact hexagonal structure is allowed in the system/experiment, the value of k_f can be determined as 1.593

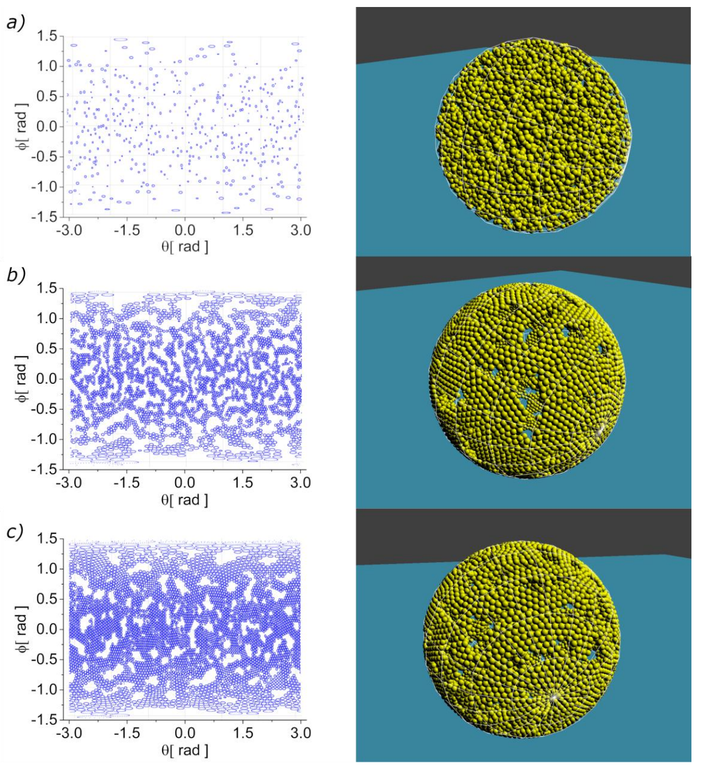
Obviously, if an aggregate consists of N identical spheres of the diameter d_p, we can link the number of particles to the radius of gyration. When we know the number and position of participating NPs, we can solve the fractal equation with respect to D_f

$$N = k_f \left(\frac{2R_g}{d_p} \right)^{D_f}$$

Information provided by Df (evolution) alone can be ambiguous. Thus, the other parameter that we considered – RDF – describes how the NPs concentration varies as the function of distance from the chosen particle. It can be perceived as the probability of finding a particle pair separated by a distance r, normalised to a probability corresponding to randomly distribution:

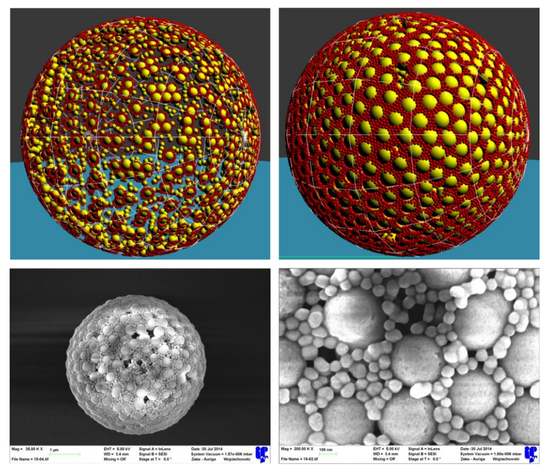
$$g(r) = \sum_{i=1}^{N} \frac{\varphi(r)_i / N}{(N-1)\delta V_r / V}$$

where ψ(r)i/N is the relative number of particles at a distance r from an i-th 'trial particle' and δVr /V is the ratio of an 'infinitesimal' volume at a distance r (i.e. a spherical shell of thickness δr) to the total sample volume.

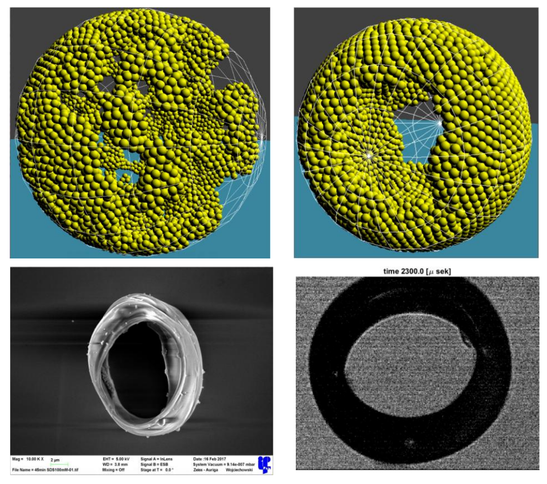


Visualisation of the temporal evolution of a microdroplet of suspension for specific model parameters: 10^4 NPs with the radius of 500 nm and the radius of the microdroplet of 20 µm. The droplet wasn't evaporating but underwent random Brownian rotations generating an effective centrifugal force in all directions, characterised by the effective angular velocity ω = 1 rad/s. The particles were electrically neutral and the NP-NP interaction was described by the Lennard-Jones potential. *Right panel* – perspective view;

left panel – distribution of NPs on the droplet surface presented in spherical coordinates.
Rows: a) early, b) intermediate, c) late stage of the evolution.



Visualisation of the temporal evolution of a microdroplet of suspension for specific model parameters: 500 NPs with the radius of 500 nm and 35500 NPs with the radius 50 nm, the radius of the microdroplet of 30 µm. The particles were electrically neutral and the NP-NP interaction was described by the Lennard-Jones potential.



Visualisation of the temporal evolution of a rotating microdroplet along Oz axes.