Towards the optimization of optical properties of particulate products

Michael Stingl[*], Lukas Pflug[**], Nico Nees[*]

(+ colleagues from chemical engineering and physics in the CRC 1411: Design of Particulate Products)

FAU DCN-AvH Seminar, Erlangen (online), 13-10-2021

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From classical **unit operations** ….

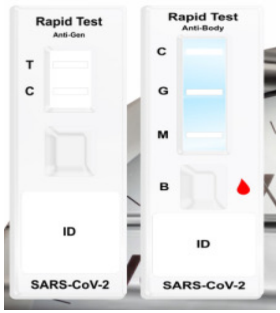
with focus on balance equations, thermodynamic equilibria and rates

…. to **product** and **property design**

Property	= F (dispersity, composition)	**property function**
Dispersity	= G (process variables)	**process function**

CRC 1411: Exemplary focus on design of optical properties of nanoparticles (NPs)

Antigen test



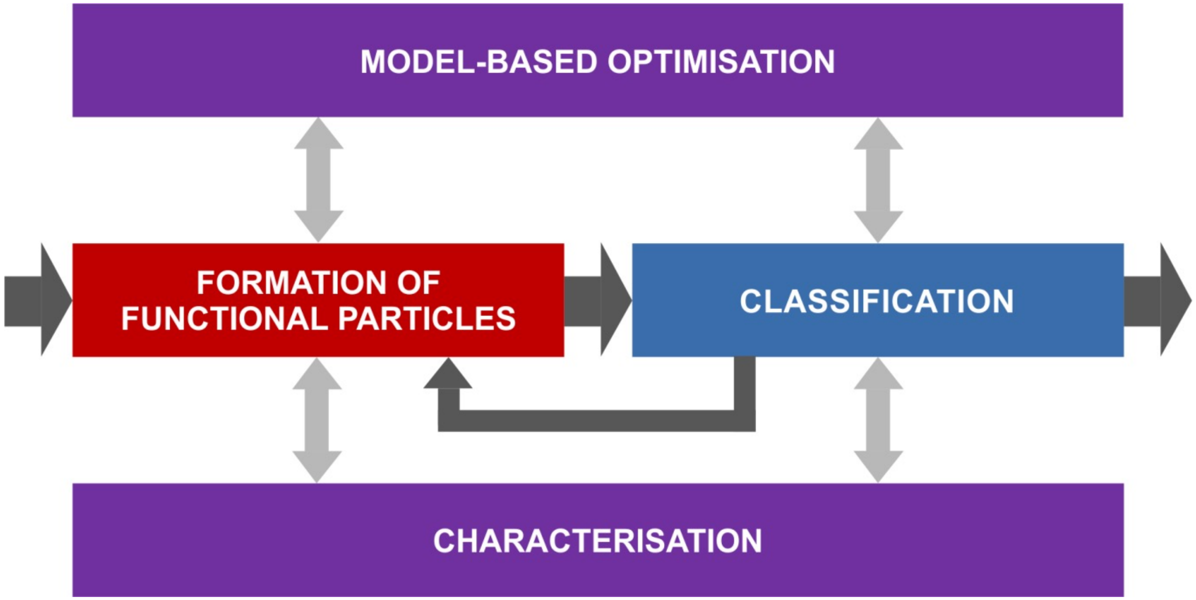
Quantum dot display

Structural colours

Challenges for the design of nanoparticulate products:
- Large gap between synthetic protocols and technical application
- Missing process technologies for NPs and their predictive design

the CRC 1411: structure and key challenges

Product design most important development in chemical engineering



Research Area A: Rigorous design of continuous particle formation processes

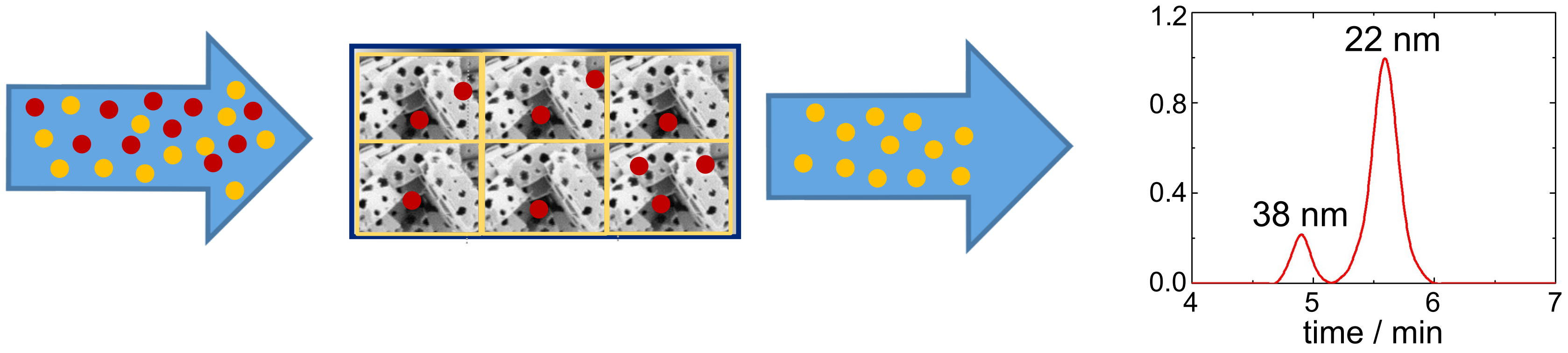
Research Area B: Preparative chromatography for classification of NPs

Research Area C: Characterisation: from single particles to NP ensembles

Research Area D: Multiscale modelling, simulation and optimisation

the CRC 1411: chromatographic separation

Product design most important development in chemical engineering



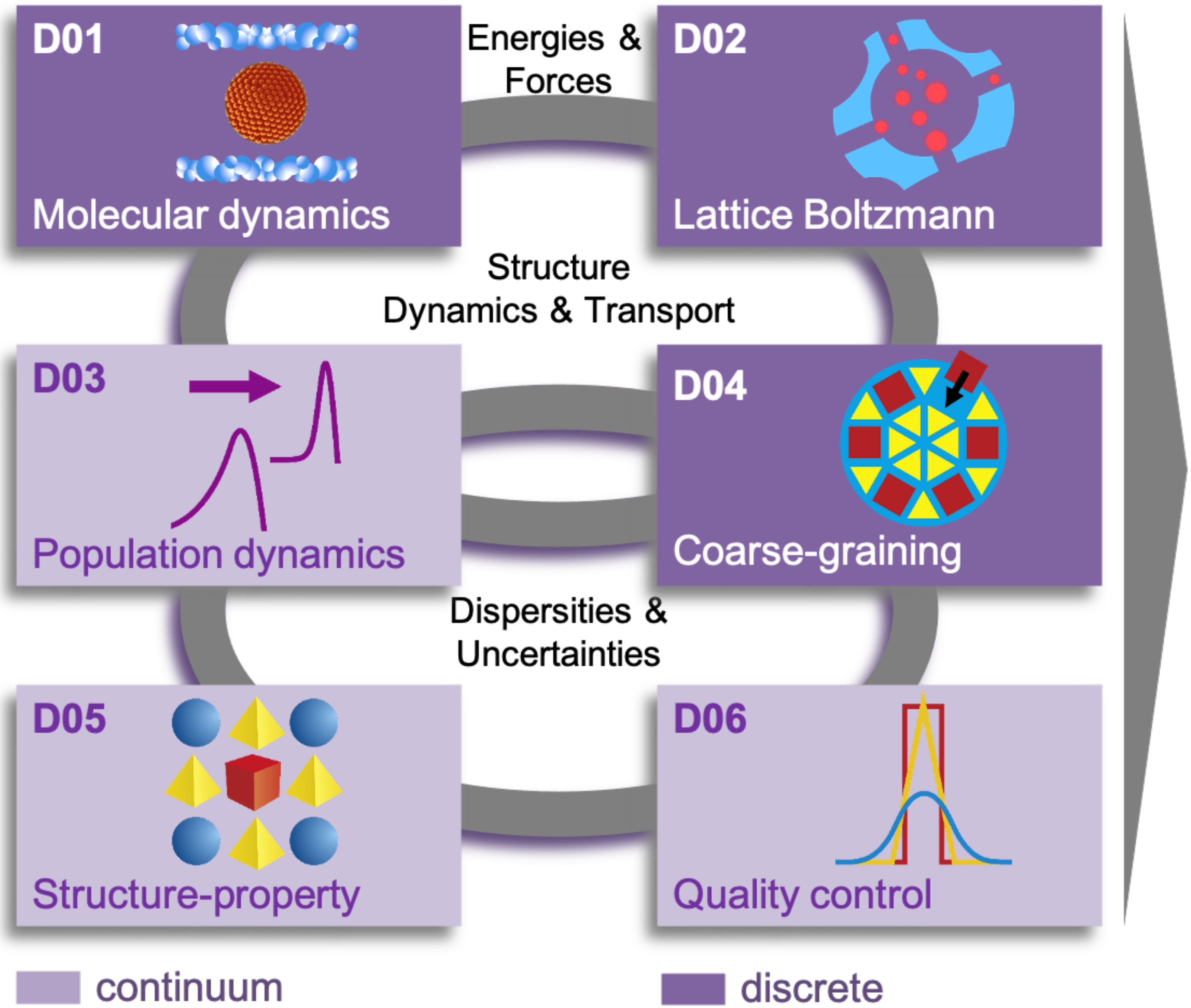
CRC1411: "distribution in – distribution out"

Research Area A: Rigorous design of continuous particle formation processes

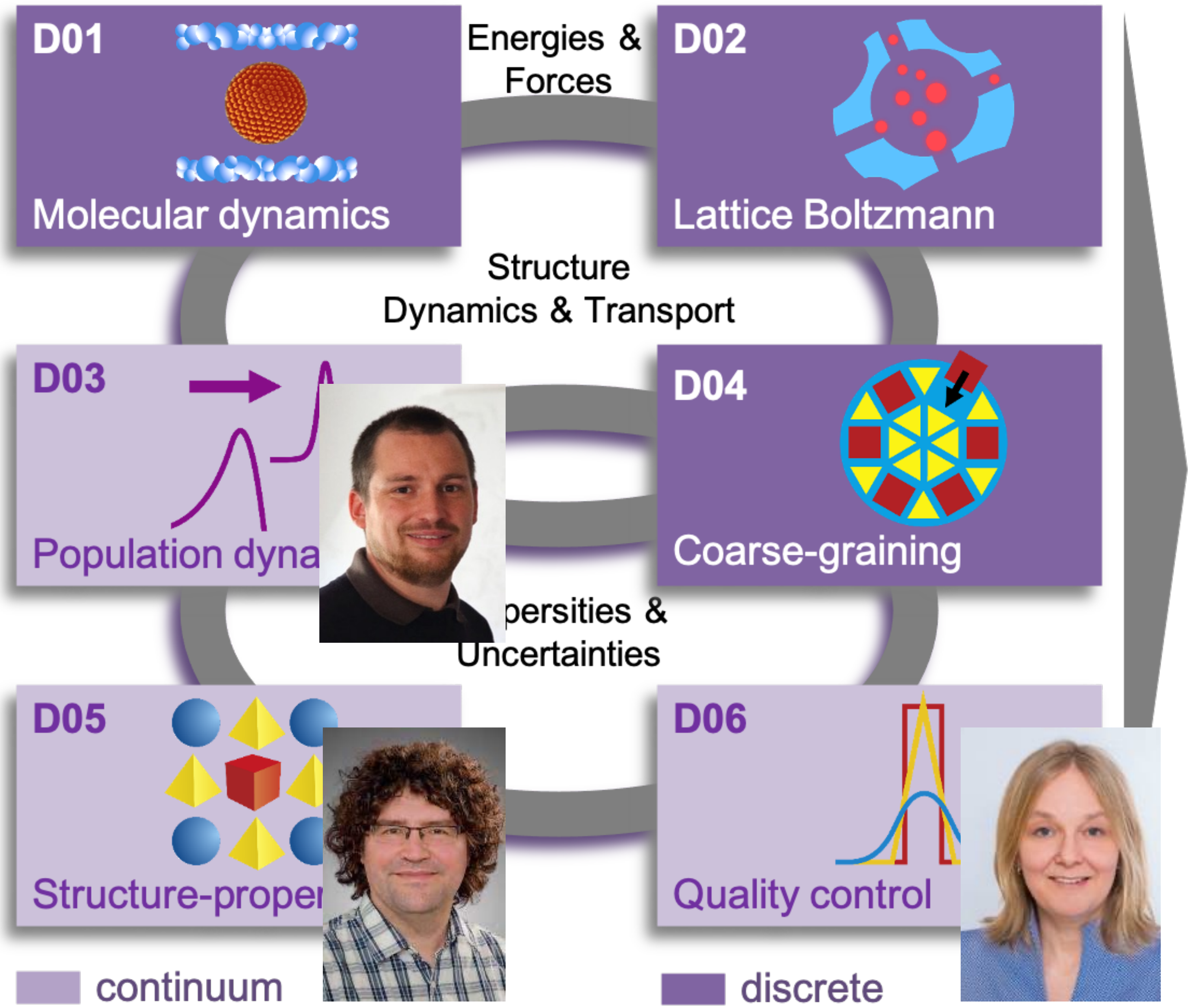
Research Area B: Preparative chromatography for classification of NPs

Research Area C: Characterisation: from single particles to NP ensembles

Research Area D: Multiscale modelling, simulation and optimisation

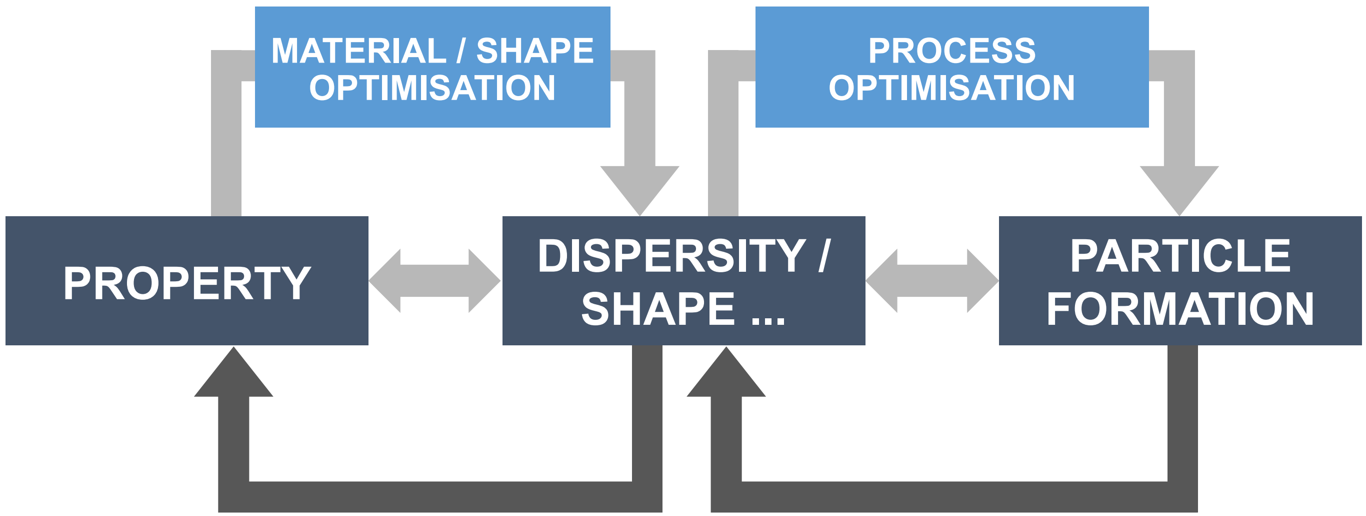


To address the challenge of knowledge-driven property and process design



To address the challenge of knowledge-driven property and process design

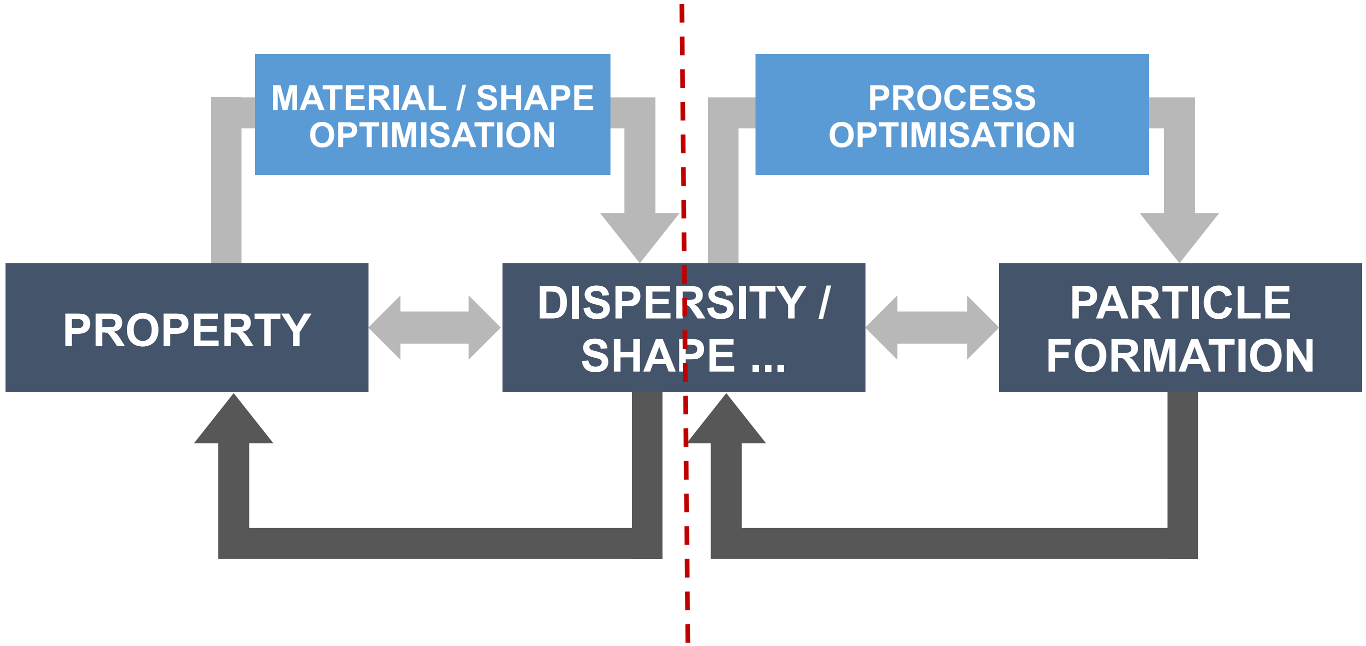
focus today: “individual particles”



Dispersity q **:** distribution of size / shape / composition / ... full information!

Property $J(q)$ **:** optical property, e. g. visibility, colour, ...

two different approaches



all at once: optimization variables are controls for synthesis process; requires full process-structure-property map J(q(T,c,...)) !

→ restricted design freedom; "synthesizability" clear

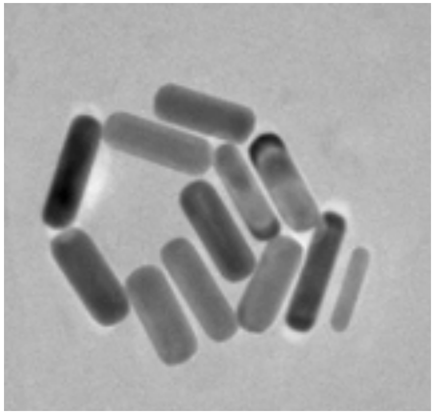
two stage: first ask for optimal shape / composition / ... (idealized) – and then design process taylored to this

→ large design freedom; synthesizability?

all at once

Assumption:

output of synthesis process can be represented as low-dimensional distribution



example: gold nanorods

- 2d distribution (length l and diameter d)
- idealized geometry
- geometry of hemispherical end caps given as function of length and diameter

Wawra S., Pflug L., Thajudeen T., Kryschi C., Stingl M., Peukert W., Nature Communications 9, **2018**

Optical property:

many interesting properties based on extinction cross section;
for fixed wavelength λ , l and d given as ...

$$\sigma_{\text{ext}}(d,l;\lambda) = \frac{1}{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} \hat{\sigma}_{\text{ext}}(d,l;\lambda,P(\theta,\phi,\psi),D(\phi,\psi))\sin(\phi)\mathrm{d}\theta\mathrm{d}\phi\mathrm{d}\psi$$

technical computation of extinction

time-harmonic Maxwell‘s equation (fixed wavelength, fixed orientation)

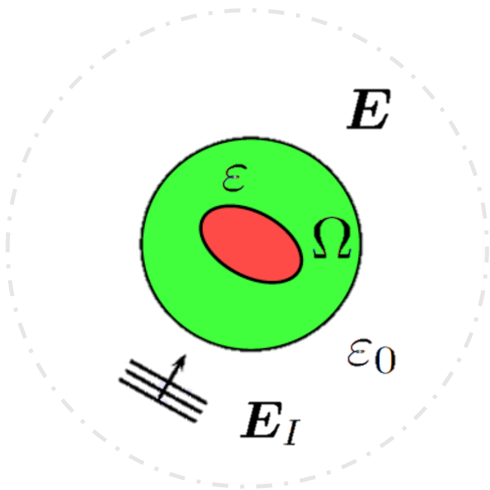
$$\operatorname{curl}\operatorname{curl}\boldsymbol{E}(\boldsymbol{x}) - \omega^2\varepsilon(\boldsymbol{x})\boldsymbol{E}(\boldsymbol{x}) = -\omega^2(\varepsilon(\boldsymbol{x}) - \varepsilon_0)\boldsymbol{E}_I(x) \quad \text{in } \Omega \subset \mathbb{R}^3$$

$$\operatorname{curl}\operatorname{curl}\boldsymbol{E}(\boldsymbol{x}) - \omega^2\varepsilon_0\boldsymbol{E}(\boldsymbol{x}) = 0 \quad \text{in } \mathbb{R}^3 \setminus \Omega$$

$$[\boldsymbol{E} \times n] = [\operatorname{curl}\boldsymbol{E} \times n] = 0 \quad \text{on } \partial\Omega$$

$$\lim_{||\boldsymbol{x}|| \to \infty} (\operatorname{curl}\boldsymbol{E} \times \hat{\boldsymbol{x}} - \imath\omega\boldsymbol{E}) = 0$$

$\boldsymbol{E}$ scattered electric field
$\boldsymbol{E}_I$ incident electric field
ω wave number
ε relative permitivity
ε_0 relative permitivity of matrix/background



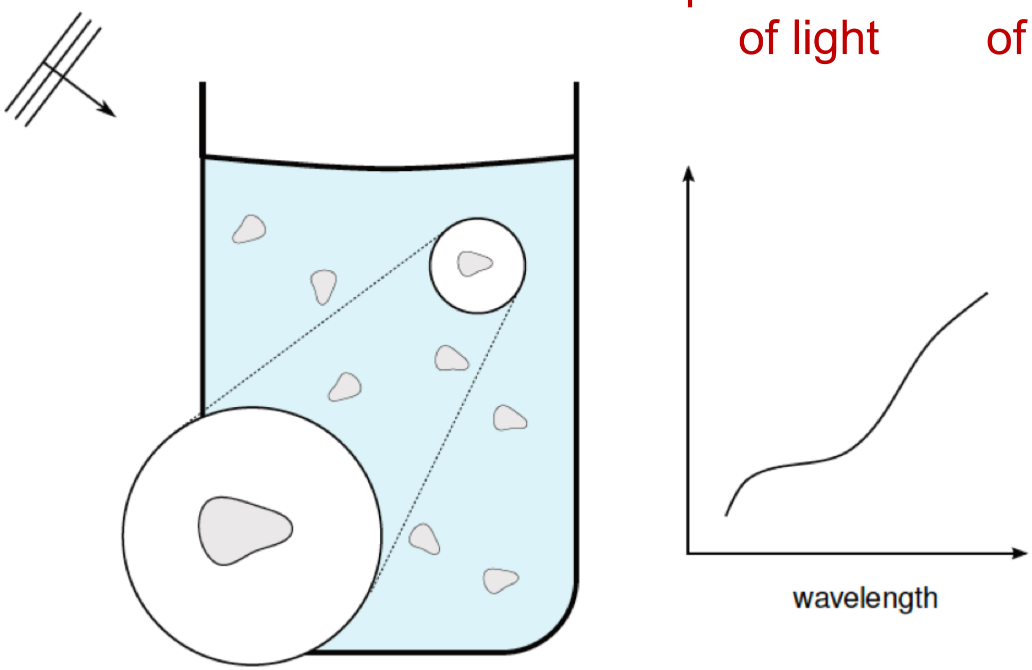
approximation/ solution, e.g. by FEM with edge elements, PML, adaptivity ...

extinction: integrate Poynting vector (linear function of ***E***,***H***) over observation sphere ...

Extinction cross section:

$$\sigma_{\text{ext}}(d,l;\lambda) = \frac{1}{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} \hat{\sigma}_{\text{ext}}(d,l;\lambda,P(\theta,\phi,\psi),D(\phi,\psi))\sin(\phi)\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}\psi$$

polarization & orientation
of light of particle



Extinction cross section:

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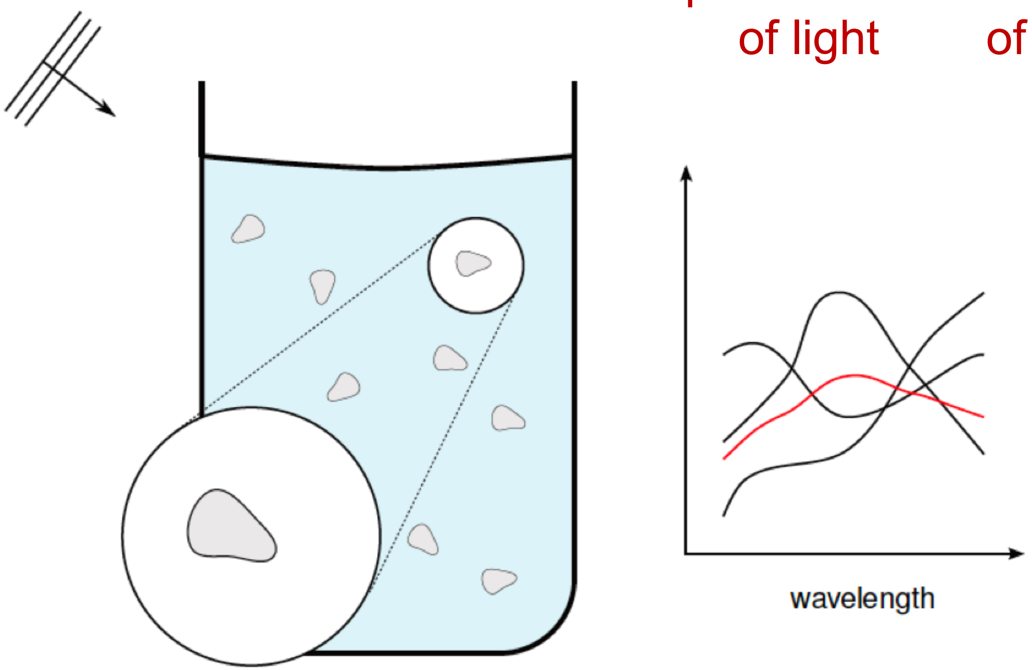
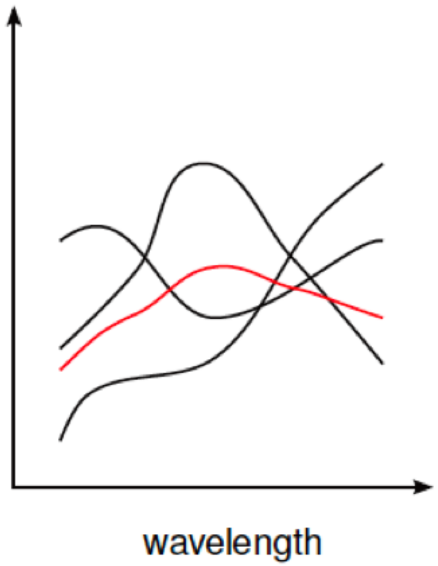


expected extinction:

2d integral ...

$$\overline{\sigma_{ext}}(\lambda) = \iint_{d,l} \sigma_{ext}(d,l;\lambda)\,\mathrm{d}q(d,l)$$



Finally:

observed property requires further weighted integration of $\sigma_{\text{ext}}(d, l; \lambda)$ over d, l

→ every evaluation of J requires (approximate) solution of 4d integral for many λ

tractability of cost function evalution

Brute force approach:

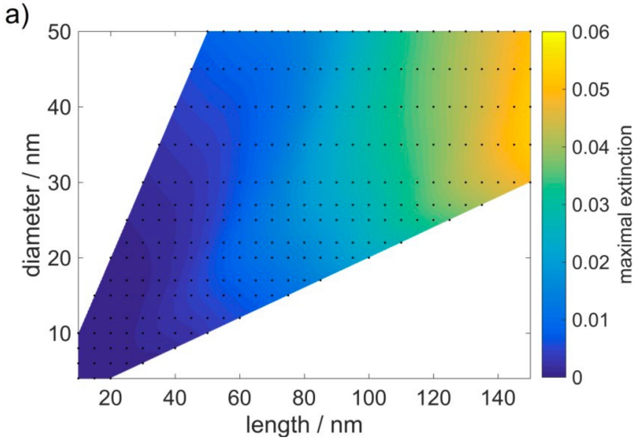
(too) coarse discretization of 10 x 10 x 10 x 10 for 10 wavelengths would mean solving 3d time-harmonic Maxwell's equation 100k times for every optimization iteration!

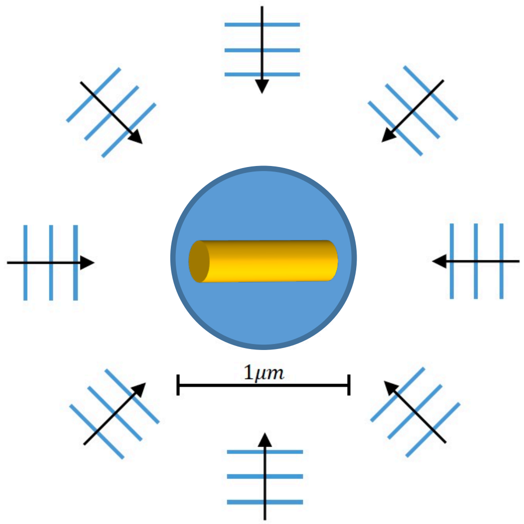
Remedy:

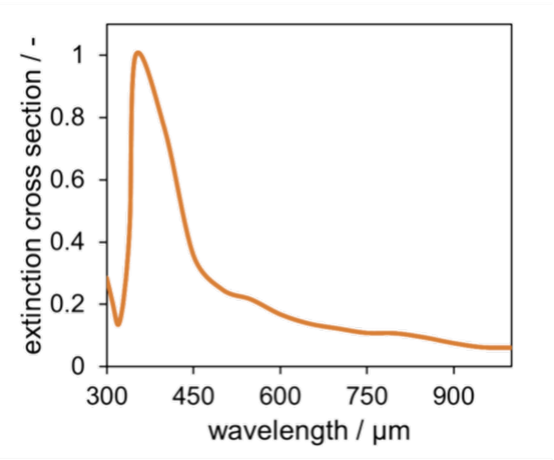
- use offline / online approach
- offline: computations, which only require information about the particle system (refractive indices, shape parametrization, and bounds on d, l and λ)
- online: use highly taylored interpolation schemes, to evaluate particular property J

Offline:

- use "coarse" grid for length l and diameter d
- for every "node" (l, d) repeatedly solve time harmonic Maxwell's equation for sufficiently many orientations with adaptive step size for λ



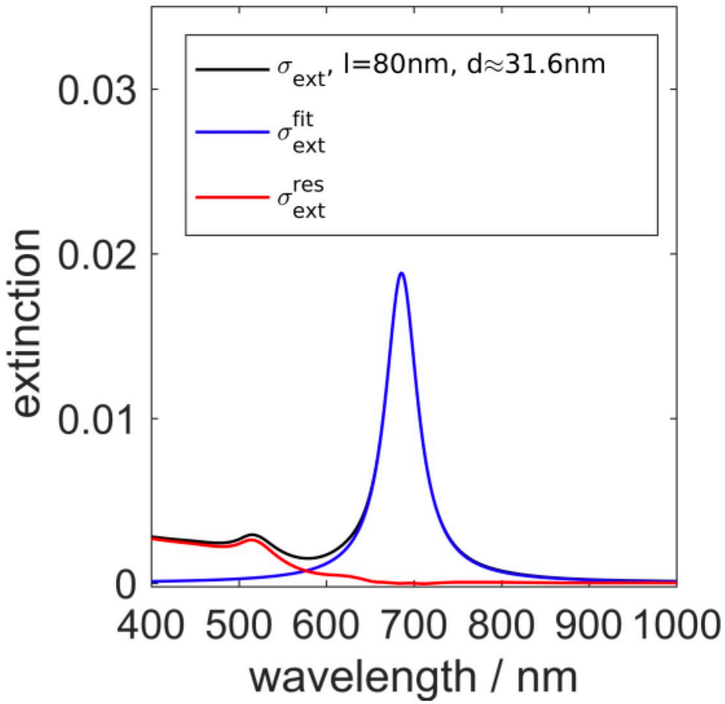




Tool: FEM due to exact representation of geometry, adaptive meshes, rotation of direction of light rather than particle orientation, ...

Offline:

- represent spectrum using by physics-based Ansatz function parametrized by
  - height (a), width (b) and position (c) of peak (a,b,c determined by fitting)
  - plus remainder term r to compensate the error



$$\sigma_{ext}(d,l;\lambda) = \sigma^{fit}_{ext}(d,l;\lambda) + \sigma^{res}_{ext}(d,l;\lambda)$$

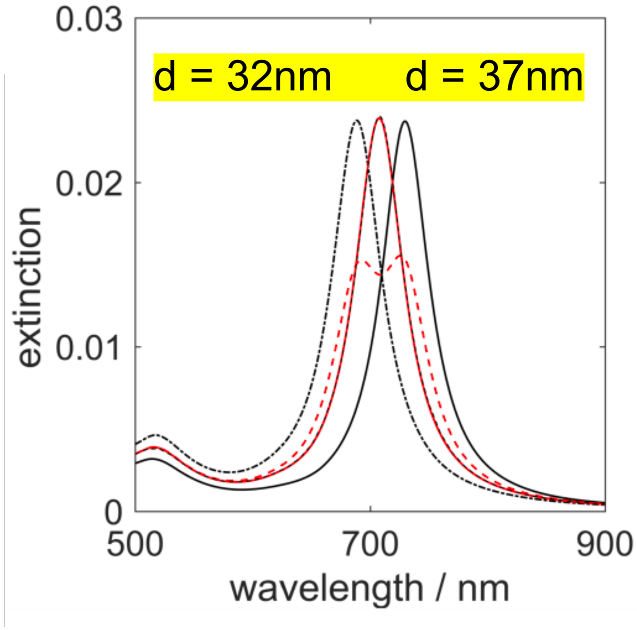
$$\sigma^{fit}_{ext}(d,l;\lambda) := \frac{a(d,l)}{b(d,l)\left(\lambda.-c(d,l)\right)^2+1}$$

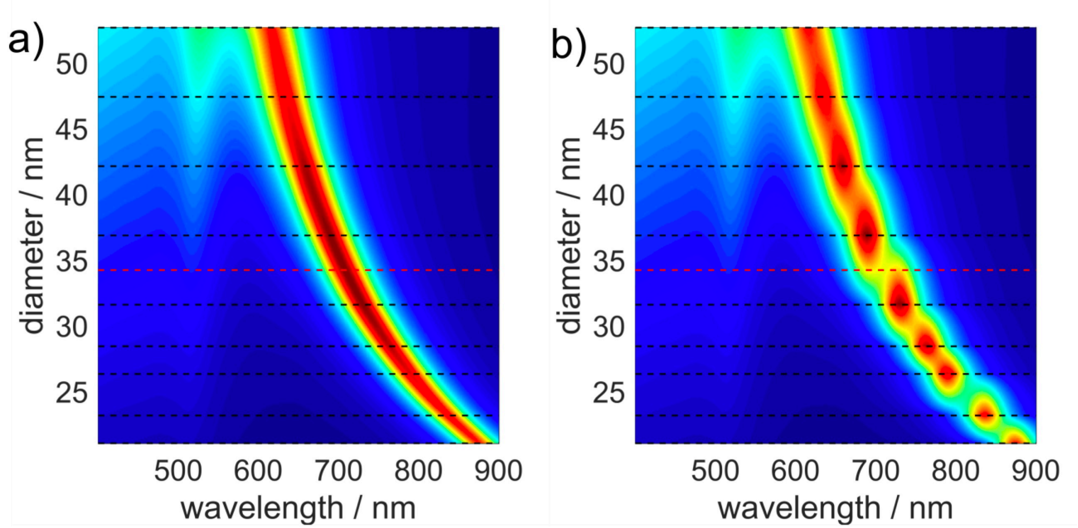
$$\sigma^{res}_{ext}(d,l;\lambda) := \sigma_{ext}(d,l;\lambda) - \sigma^{fit}_{ext}(d,l;\lambda).$$

- storage: # wavelengths + 3 values for every (l,d)

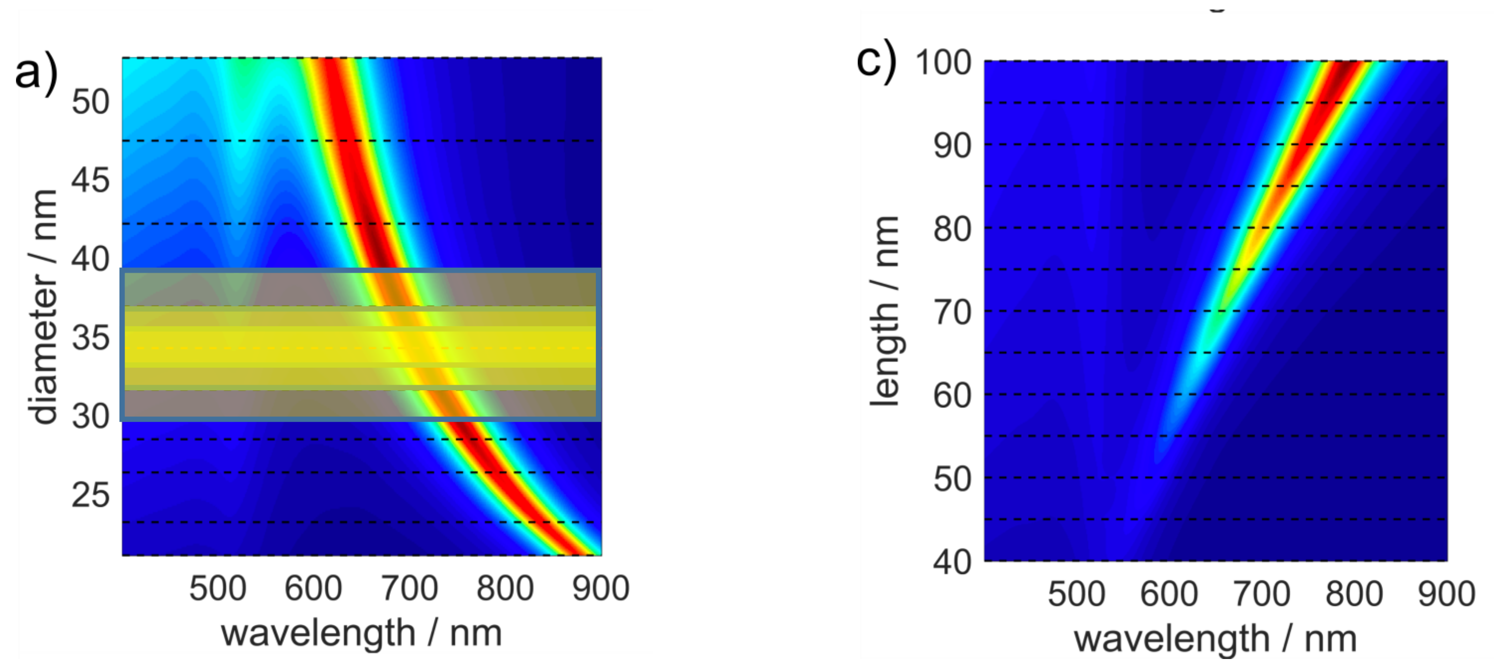
Online:

- evaluation of $\sigma_{\text{ext}}(d, l; \lambda)$ requires 'standard' interpolation of a, b, c and r plus evaluation of cheap analytic formula (previous slide; no PDE to solve!)





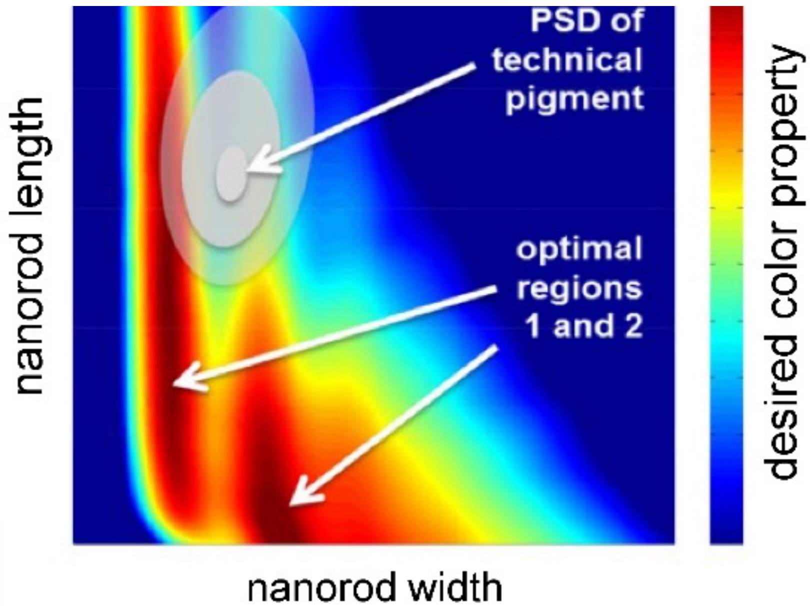
High-quality-interpolation despite rather coarse discretization of shape space

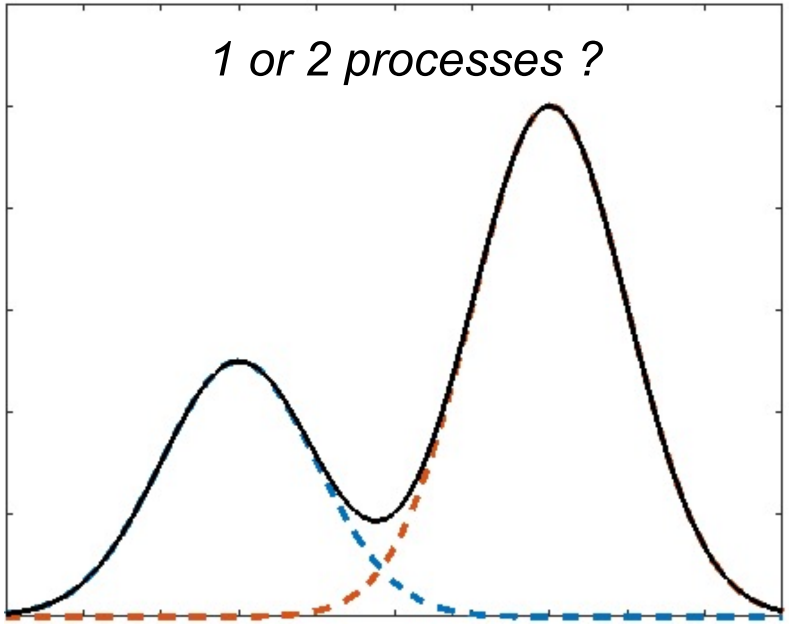


Now we can ...

- integrate over size / shape / ... distribution in a cheap way → expected (wave-length dependent) extinction → evaluate more objectives like "colour"
- formulate an optimization problem in q (shape distribution)
- note: projections of 3d landscapes are shown for the gold nanorod example

Cooperation with industrial partner



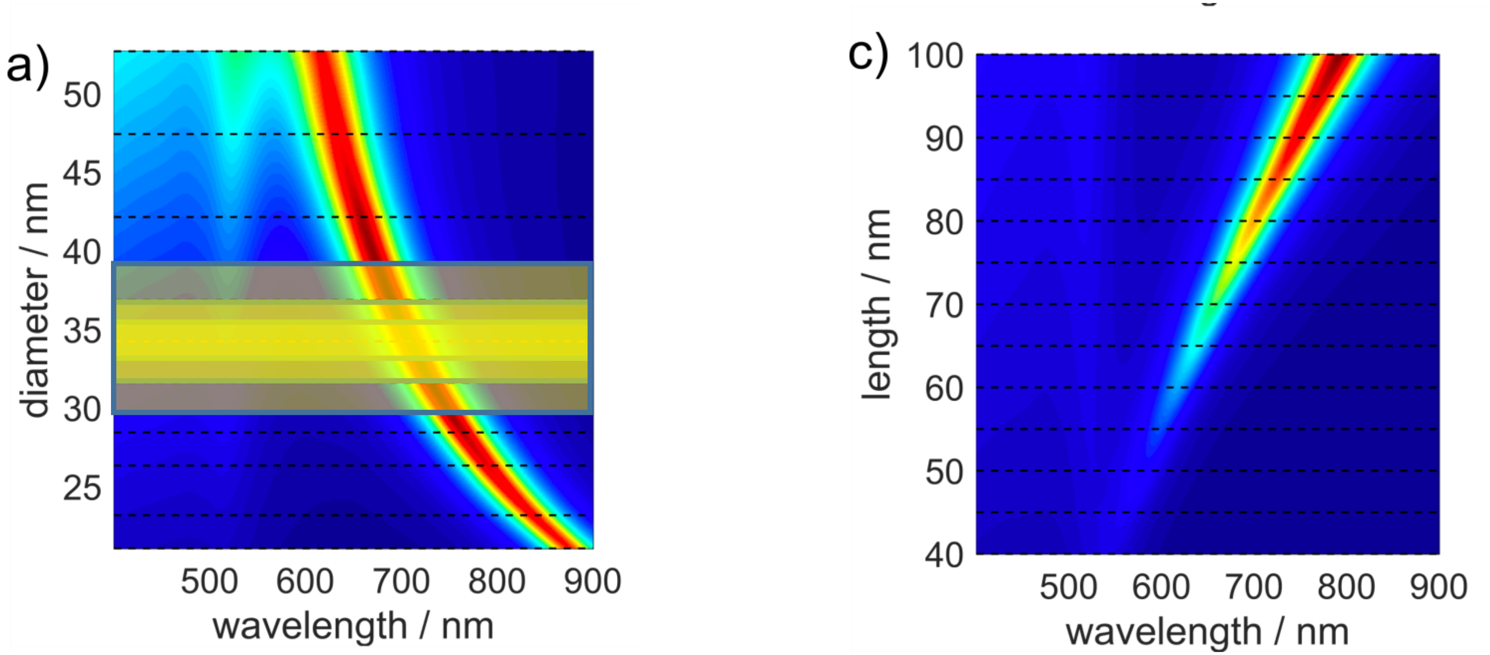


here: given distribution (uncertainty!)

example: bimodal distribution

- formulate an optimization problem in q (shape distribution)
- use fast continuous optimization methods (access to derivatives easy)
- in certain cases, even global optimization not out of scope

cheap access to property landscapes



Now we can ...

- ...
- or formulate optimization problem directly in process parameters: J(q(T,c,...)) ...
- requires control-to-dispersity function!

about the control-to-dispersity function

$$\frac{\partial}{\partial_t} \boldsymbol{q} + \frac{\partial}{\partial_x}\left(\boldsymbol{R_q q}\right) + \frac{\partial}{\partial_z}\left(\boldsymbol{T_q q}\right) = \frac{\partial}{\partial_z}\left(\boldsymbol{D_q} \frac{\partial}{\partial_z} \boldsymbol{q}\right) + \boldsymbol{Q_q}$$

PSD to product — **growth/ ripening** — **convection** — **diffusion** — **source/sink-terms**

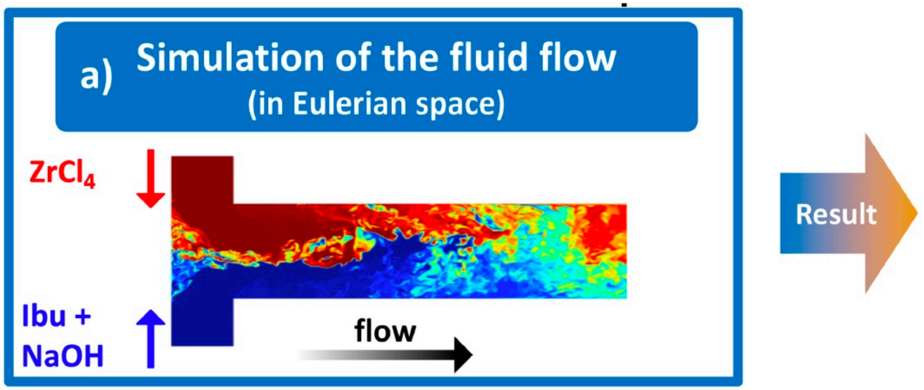
- framework of nonlocal population balance equations (PBEs)
- accurate and efficient numerical solution schemes using semianalytical solutions
- EMOM (exact method of moments) method delivers full particle shape distribution

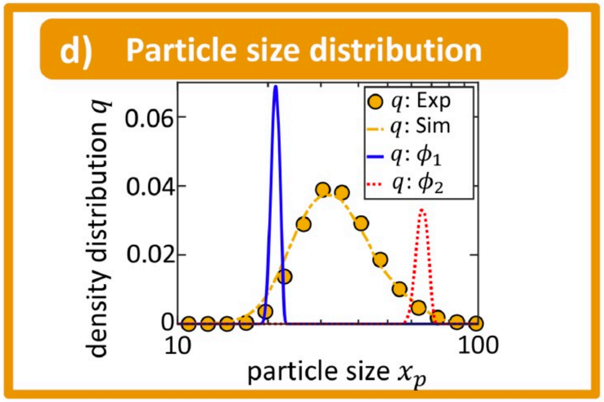
Pflug L., Schikarski T., Keimer A., Peukert W., Stingl M., Computers & Chemical Engineering 136, **2020**

- project D03 in CRC 1411 (lead by L. Pflug, FAU): derivative-based optimisation of time-dependent process conditions (using adjoint PBE, ...)

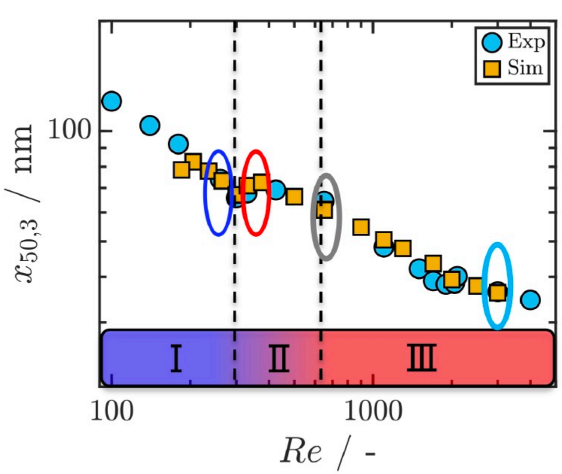
q: particle property distribution, **t**: process time, **x**: disperse properties, **z**: spatial coordinates, $\mathbf{R_q}$: growth/ripening, $\mathbf{T_q}$: spatial transport, $\mathbf{D_q}$: spatial diffusion, $\mathbf{Q_q}$: nucleation/agglomeration/,,,

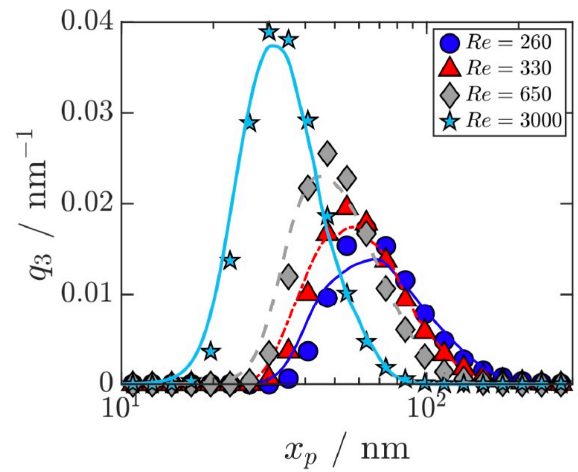
example: control-to-dispersity function

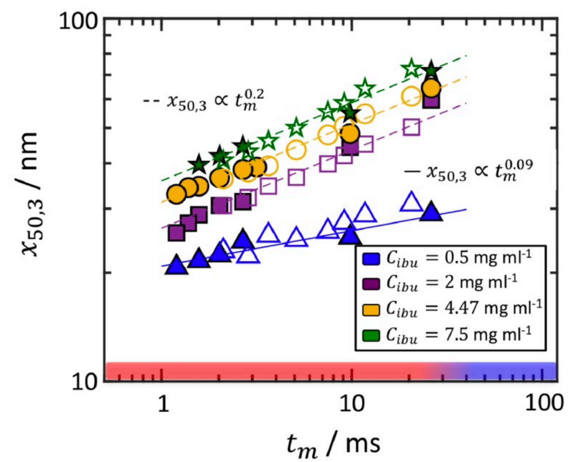




PSD (total and for individual trajectories)







effect of changing Reynold's number and concentrations (control variables!)

all-at-once?

- we can evaluate optical properties for disperse systems accurate and fast ✓
- we have a mathematical framework for a quick and accurate solution of PBEs ✓
- we have access to derivatives through interpolation framework (dispersity-to property) and through adjoint calculus for control-to-dispersity-functions ✓

- we do not yet have access to accurate growth kinetics in multi-dimensional setting!

scenarios to fix this

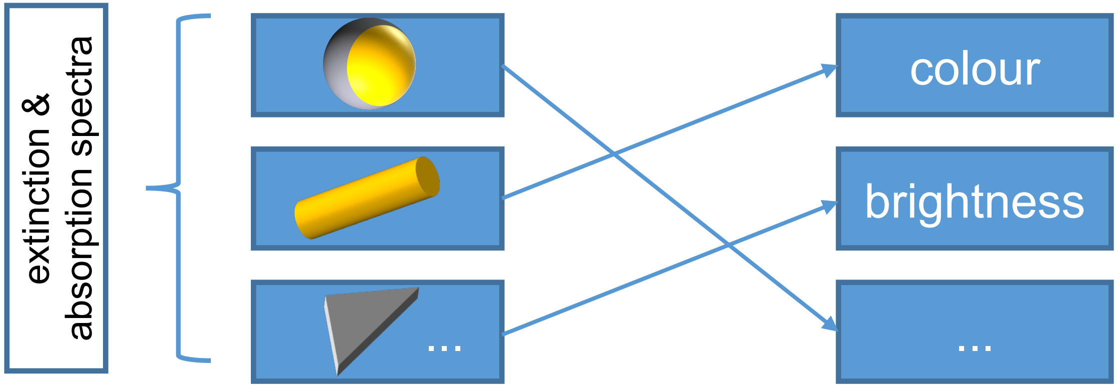
- first principle modelling → white box model
- fit a model based on experiments ... works well if you know the “general form” and just need to fit a couple of parameters → gray box model
- if nothing like this is available → use black box model, e. g. NN (?)
- challenge for the engineers: how to generate sufficiently rich data?

Added value of offline database ...

- (re)usable for different types optimization problems and parameter studies

  ... all this obtained for the cost of solving 1 optimization problem!

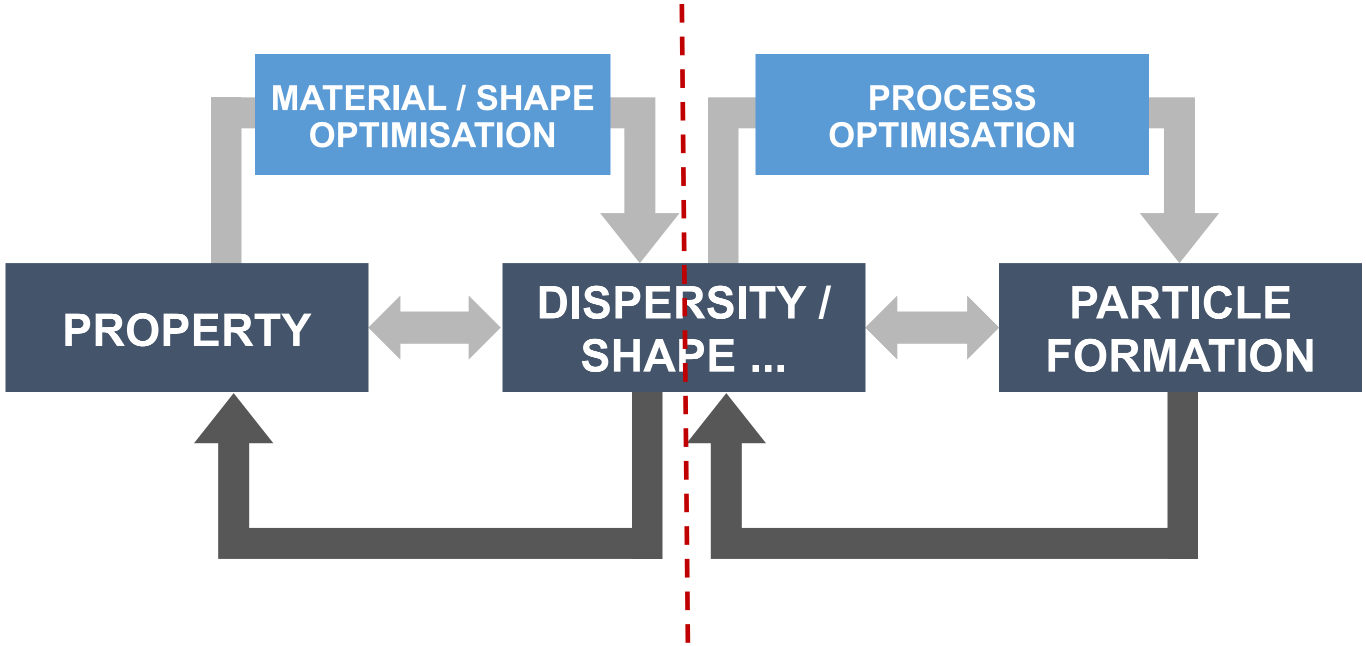
- useful for measurements / characterization, see (*)
- parameter fitting (previous slide) often done with optical measurements
  → use tracking with process-dispersity-property function!
- serves as basis for library of optical objective functions



separate data project in the CRC!

(*) Wawra S., Pflug L., Thajudeen T., Kryschi C., Stingl M., Peukert W., Nature Communications 9, **2018**

Recall: two different approaches



all at once: optimization variables are controls for synthesis process; requires full process-structure-property map J(q(T,c,...)) !

→ restricted design freedom; "synthesizability" clear

two stage: first ask for optimal shape / composition / ... (idealized) – and then design process taylored to this

→ large design freedom; synthesizability?

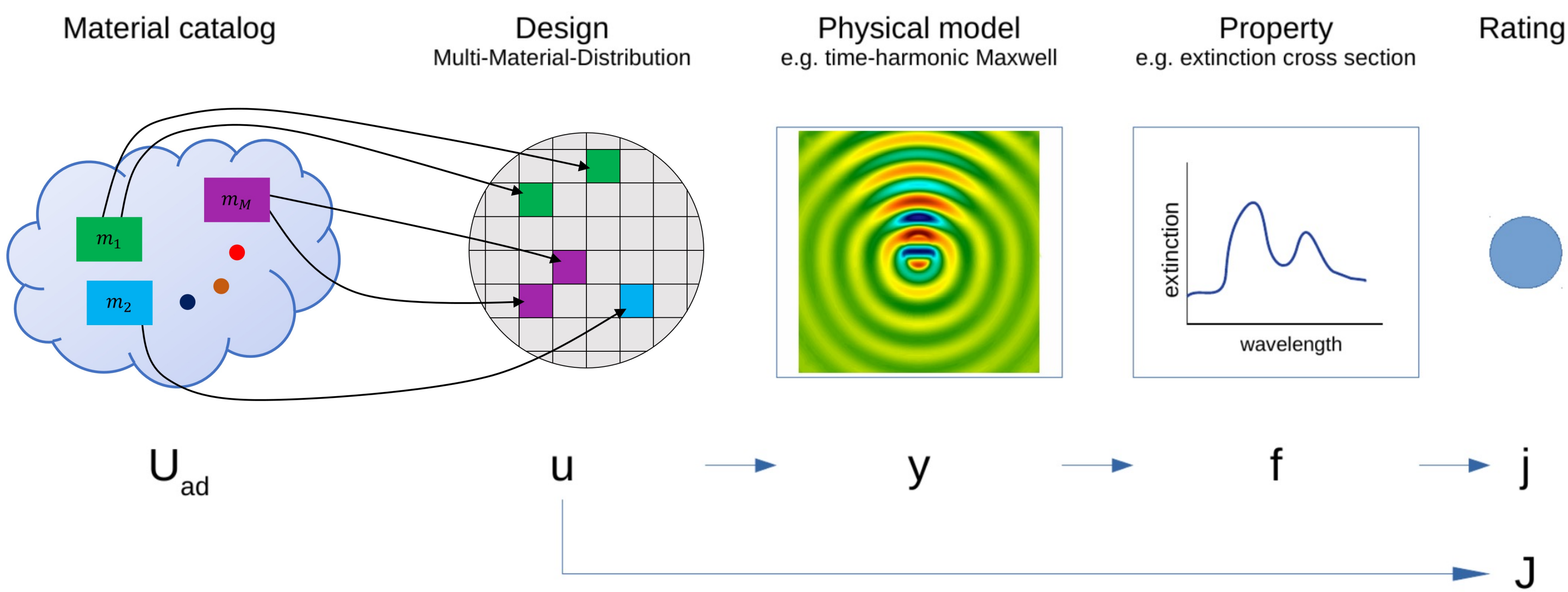
two stage approach (only geometry optimization)

Assumptions:

idealized geometry → no dispersity taken into account for the moment

no specific assumption on expected shape / no a priori parametrization

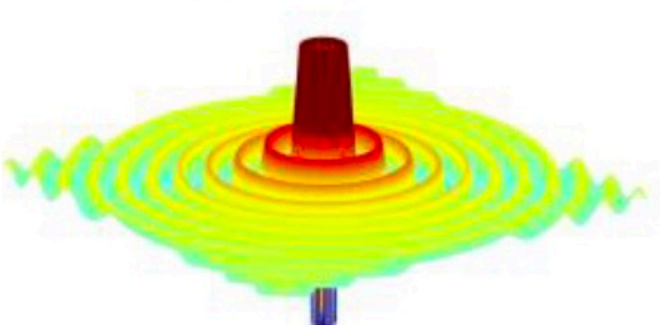
The material optimization approach:



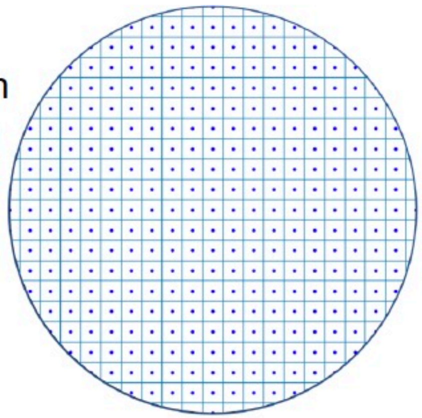
“free” material optimization & DDA

- Discrete Dipole Approximation (DDA) (*)

Electromagnetic field of an oscillating dipole:



Discretization of the design domain in dipoles:

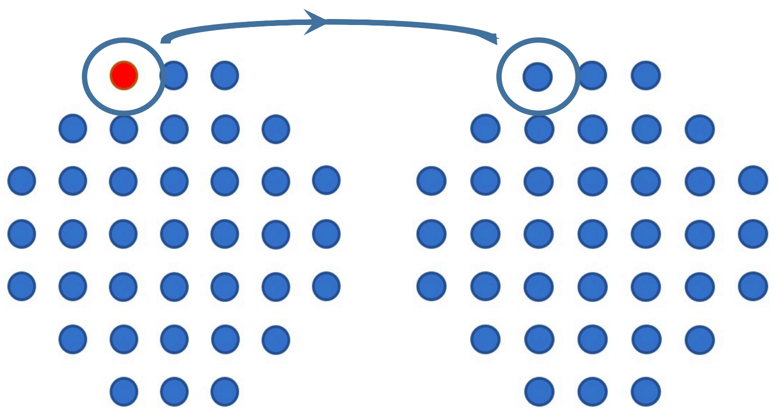


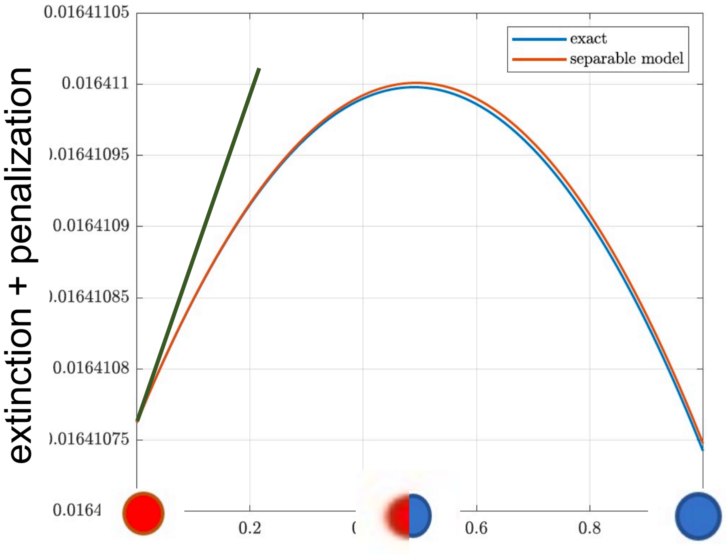
- high resolution: for NPs we can go down to a dipole distance of a very few atoms
- bi-material optimization:
    - 2 materials A and B
    - each dipole can be assigned either material A or B → large design freedom
- assignment problem: of combinatorial nature ... too hard to be solved direcly

(*) B. T. Draine, P. J. Flatau, Journal of the Optical Society of America A 11, **1994**

the SGP algorithm & DDA

- assignment problem: relaxation, penalization and sequential approximation techniques allow to find good local solutions, e.g. by the SGP method (*,**)
- idea of separable exact model





- very tight and tractable approximations
- separability of model → global optimization for non-convex model
- avoid “poor” local minima
- another advantage: easily parallelized (due to separability)

(*) J. Semmler, L. Pflug, M. Stingl, SIAM J. Sc. Comp., **2018**

(**) L. Pflug, M. Stingl, Proceedings of the Bremen Workshop on Light Scattering, **2018**

a better notion of (local) optimality

- on convergence Nash equilibrium points (NE points) are obtained, i.e. solutions which can not be improved by changing an individual design element (= dipole)
- any such point is a local optimum (and thus stationary)
- the other way round: there may be many more stationary points then NE points

... note close relation to topologigal derivative based setting!

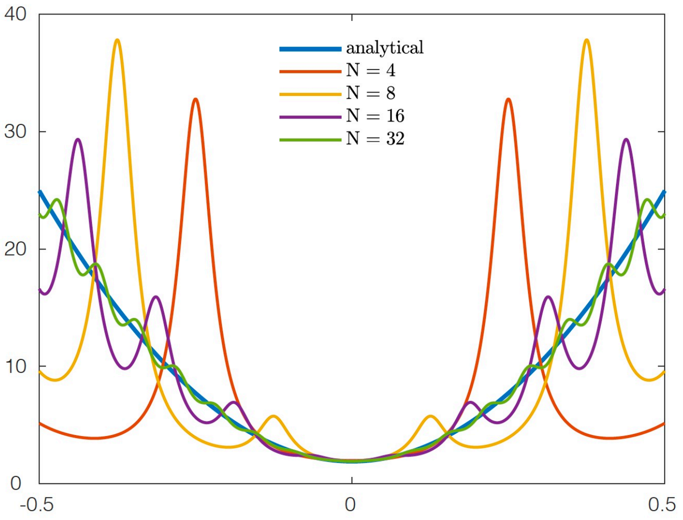
about the (random) orientation

$$J(\rho) = \overline{\sigma_{ext}}(\rho;\lambda), \qquad \overline{\sigma_{ext}}(\rho;\lambda) = \int_{S^2} \sigma_{ext}(\rho; d, \lambda)\, \mathrm{d}d,$$

- S^2: unit sphere in $\mathbb{R}^3$ for incident directions (equivalent to particle orientations)
- λ: wavelength (fixed or multiple wavelengths to approximate spectrum)
- ρ: design variable (high dimensional; 1 entry per dipole ...)

- Approach 1: SGP ... discretize and optimize

$$\overline{\sigma_{ext}}(\rho;\lambda) \approx \frac{1}{8\pi^2} \sum_k \sigma_{ext}(\rho; d_k, \lambda)$$



- particularly useful for oriented particles
- a priori discretization can be dangerous ...

(*) L. Pflug, N. Bernhardt, M. Grieshammer, M. Stingl, *CSG: A new stochastic gradient method for the efficient solution of structural optimization problems with infinitely many states*, Struct. Multidiscip. Optim., **2020**

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- ρ: design variable (high dimensional; 1 entry per dipole ...)

Approach 2: CSG = continuous stochastic gradient method

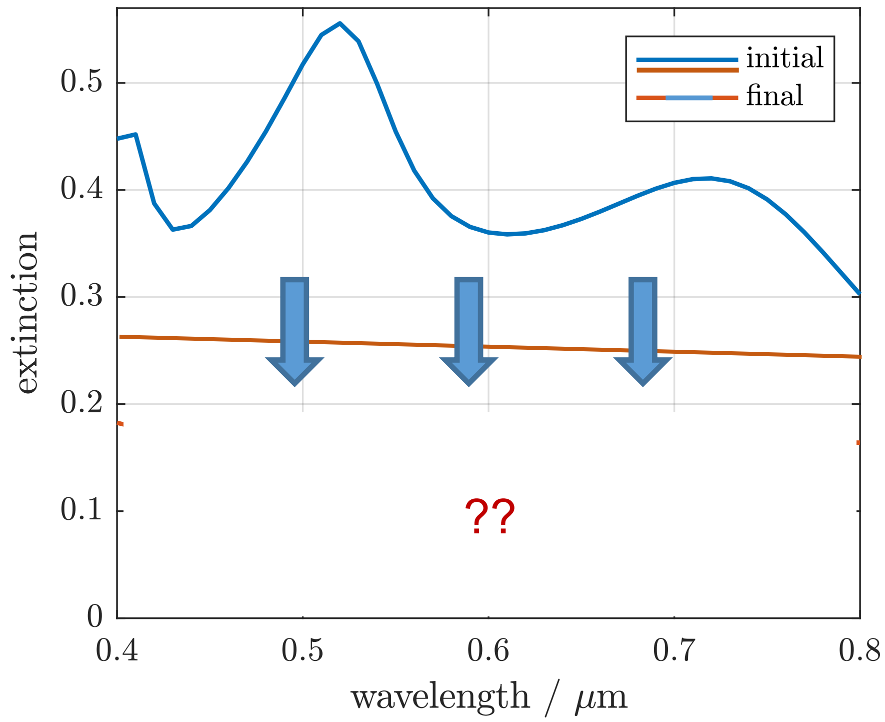
- similarities to “standard“ SG method used in machine learning, but more suited if integrand is expensive to evaluate (e.g. PDE ...)
- convergence of function value and design gradient ... see (*)
- overcome bad local minima ... no rigoros proof
- shares many properties with deterministic method ... w. i. p.

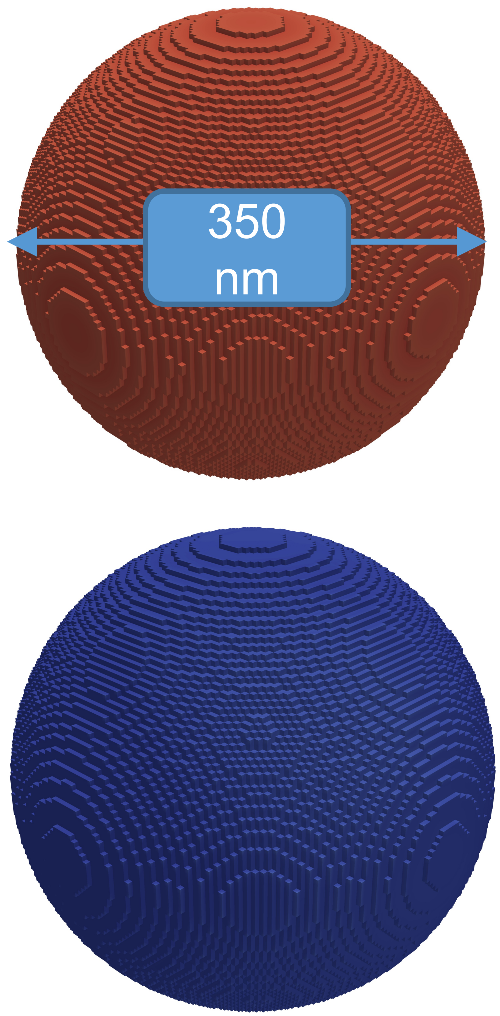
(*) L. Pflug, N. Bernhardt, M. Grieshammer, M. Stingl, *CSG: A new stochastic gradient method for the efficient solution of structural optimization problems with infinitely many states*, Struct. Multidiscip. Optim., **2020**

example: minimize visibility (= min extinction)

- material A 1+1i (red) ; material B 2+0i (blue)
- all particles oriented in same direction

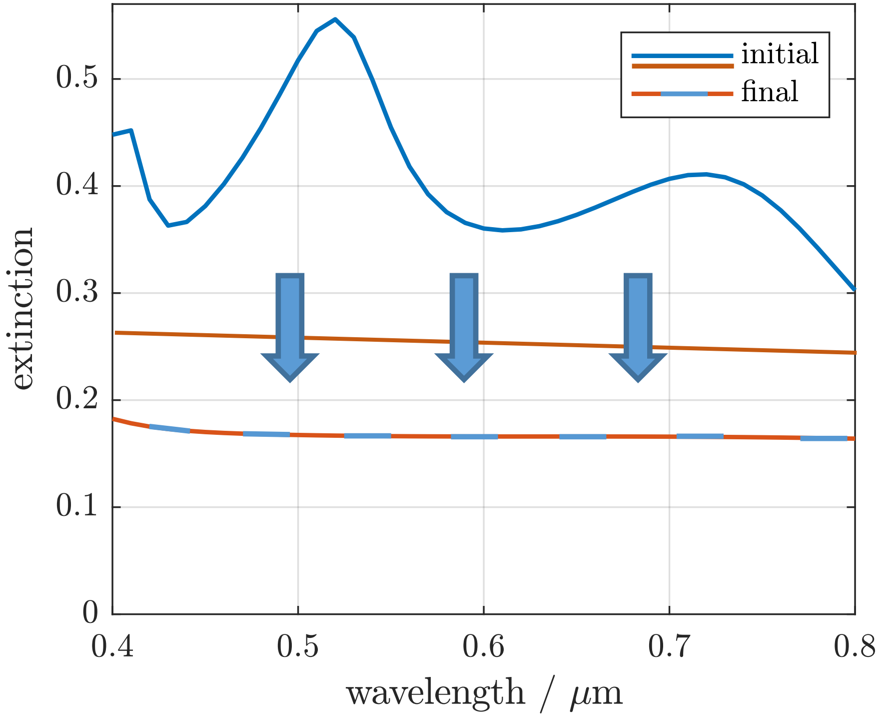
→ 2 state problems per wavelength

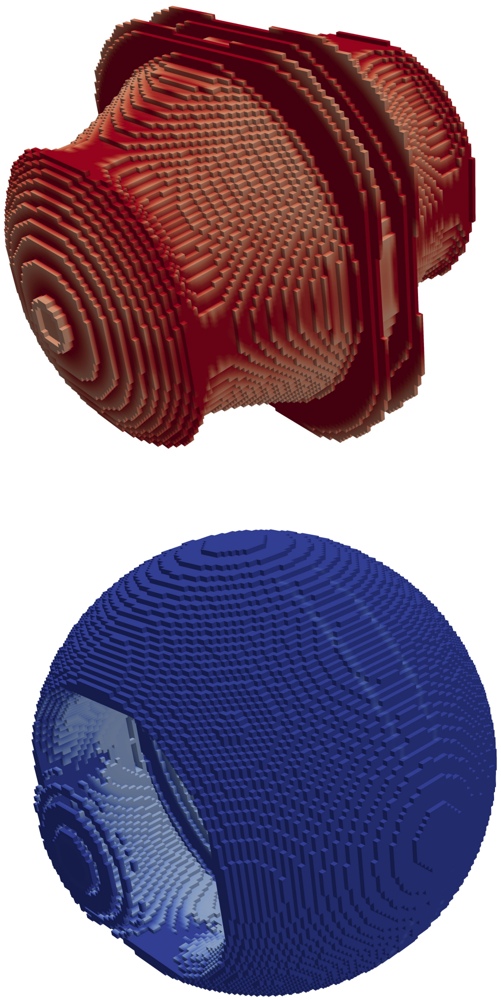




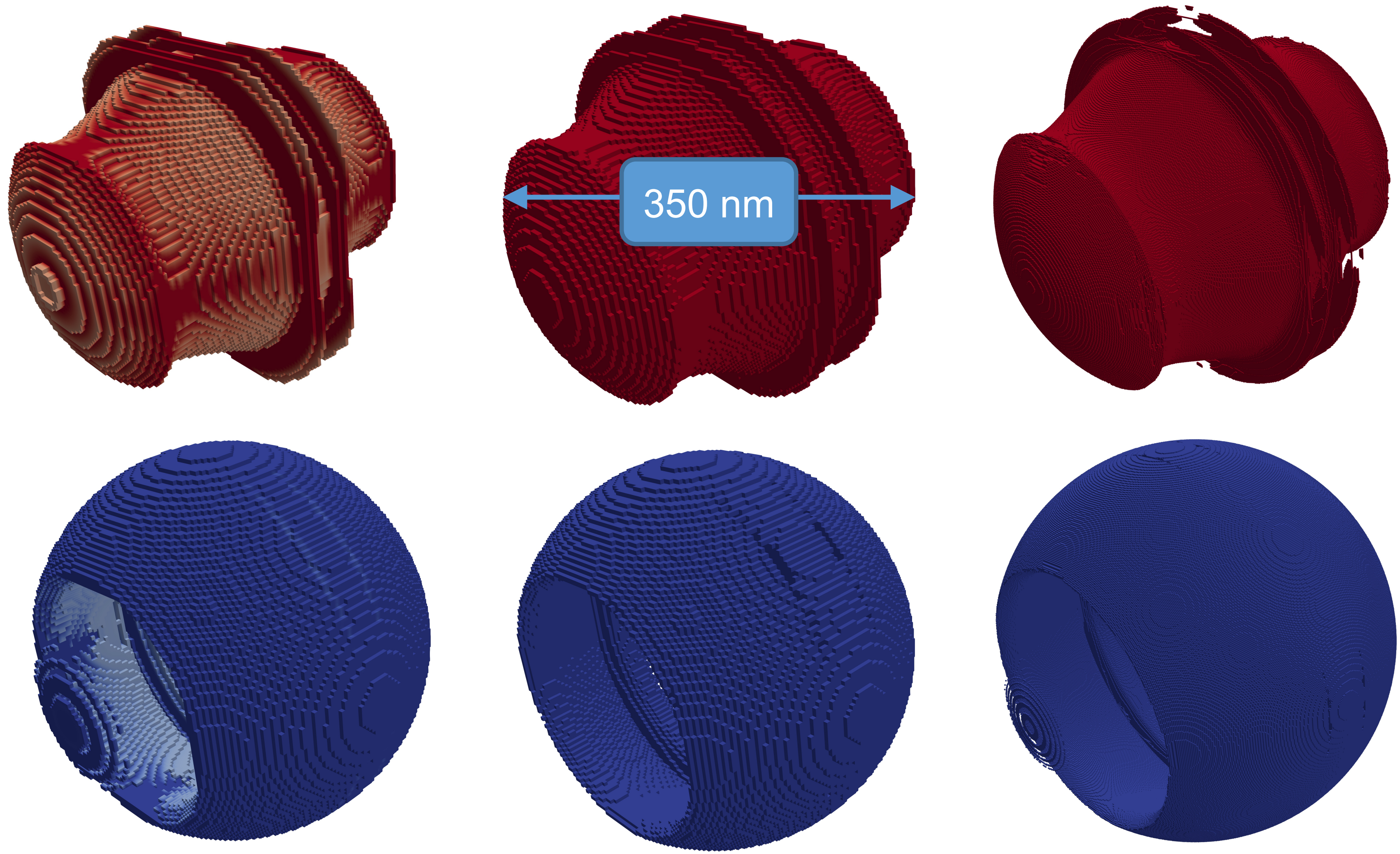
example: minimize visibility (= min extinction)

- material A 1+1i (red) ; material B 2+0i (blue)
- all particles oriented in same direction
  → 2 state problems per wavelength
- 200 optimization iterations
- ~ 400 state problems per wave length





convergence of design & regularization

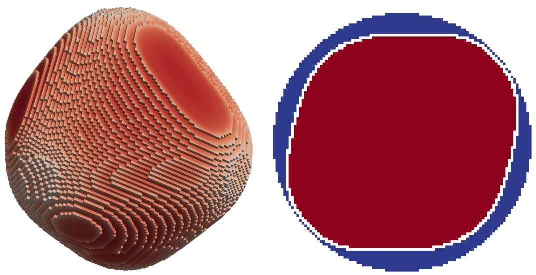


~.5*100^3 dipoles | + regularization | ~.5*400^3 dipoles (HPC)

dipole distance a few atoms!

(relative) expected extinction ...

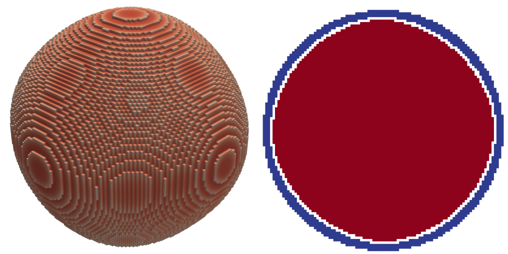
3 orientations



J = 0.45

~800 state problems

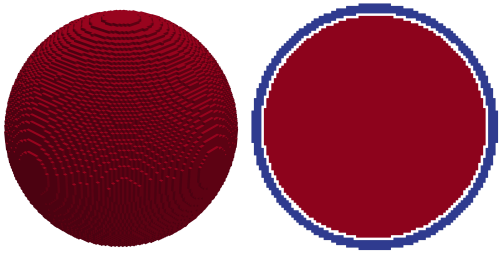
9 orientations



J = 0.44

~1200 state problems

all orientations



J = 0.44

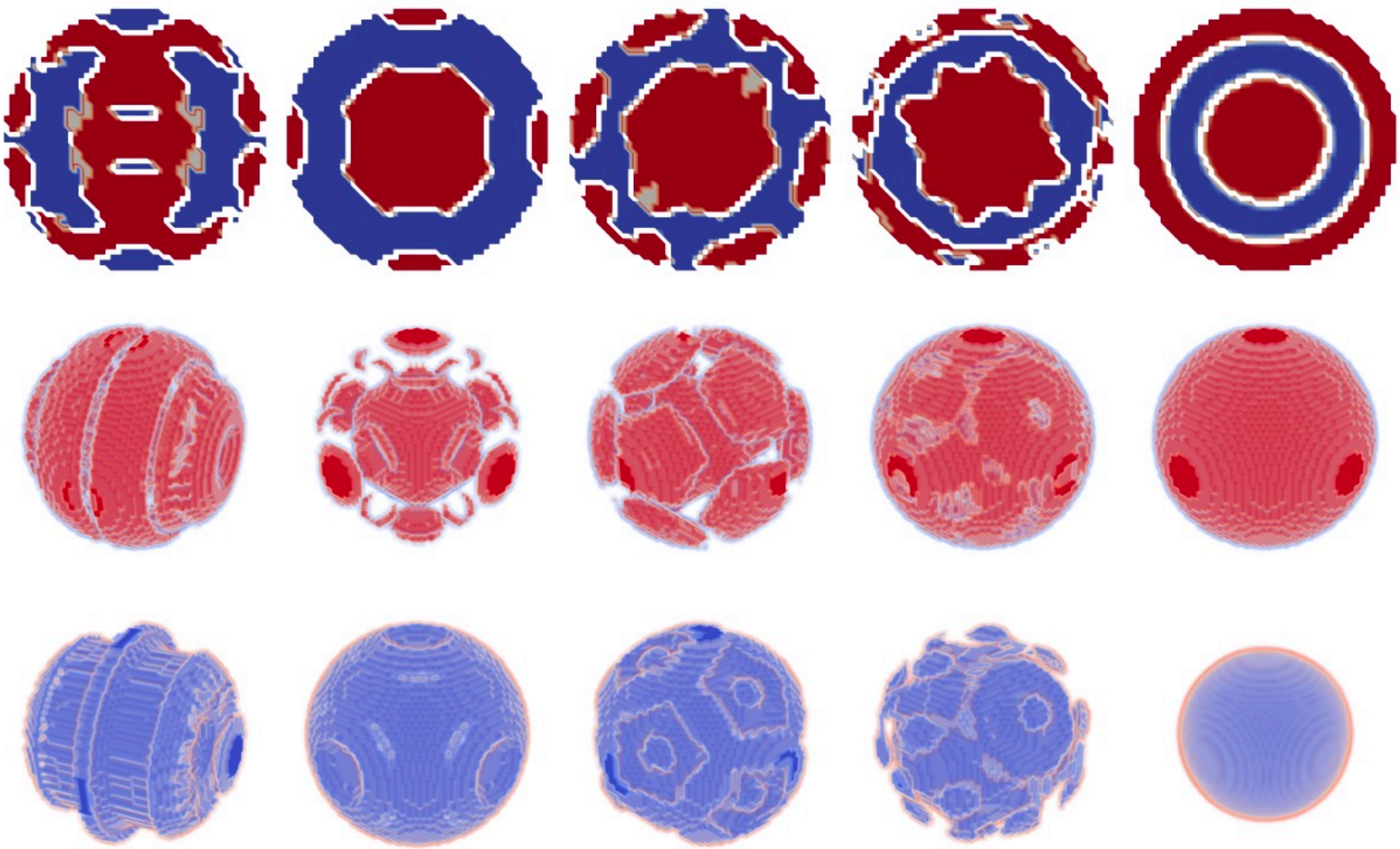
~1000 state problems

- J: expected extinction by evaluation of optimal design with 64 directions
- scenario “all orientations” computed by new stochastic gradient method (*)
- 9 orientations good enough here (note size of particle = 350 nm)

(*) L. Pflug, N. Bernhardt, M. Grieshammer, M. Stingl, *CSG: A new stochastic gradient method for the efficient solution of structural optimization problems with infinitely many states*, Struct. Multidiscip. Optim., **2020**

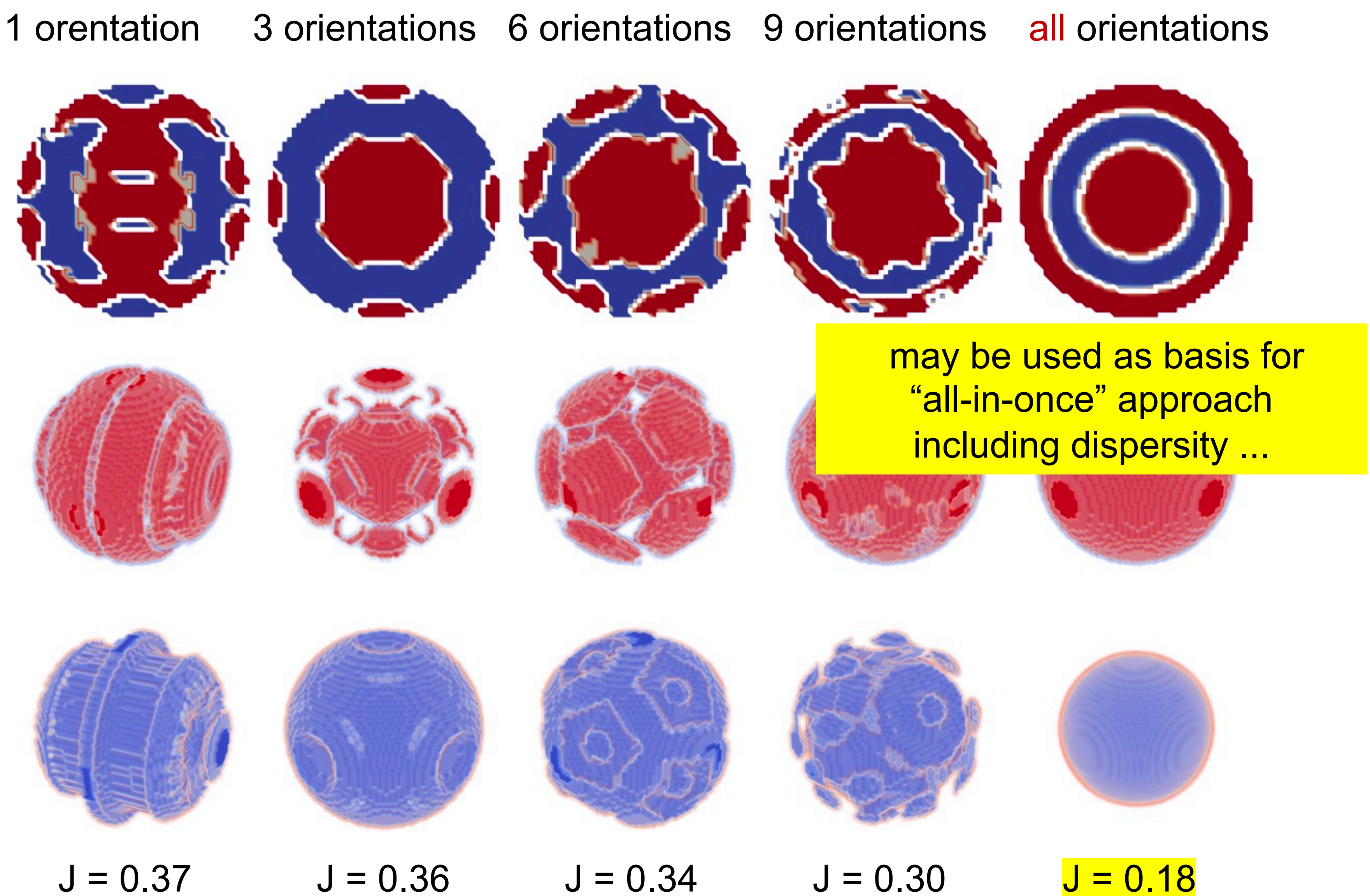
example: min extinction, large particle (1000 nm)

1 orentation | 3 orientations | 6 orientations | 9 orientations | all orientations

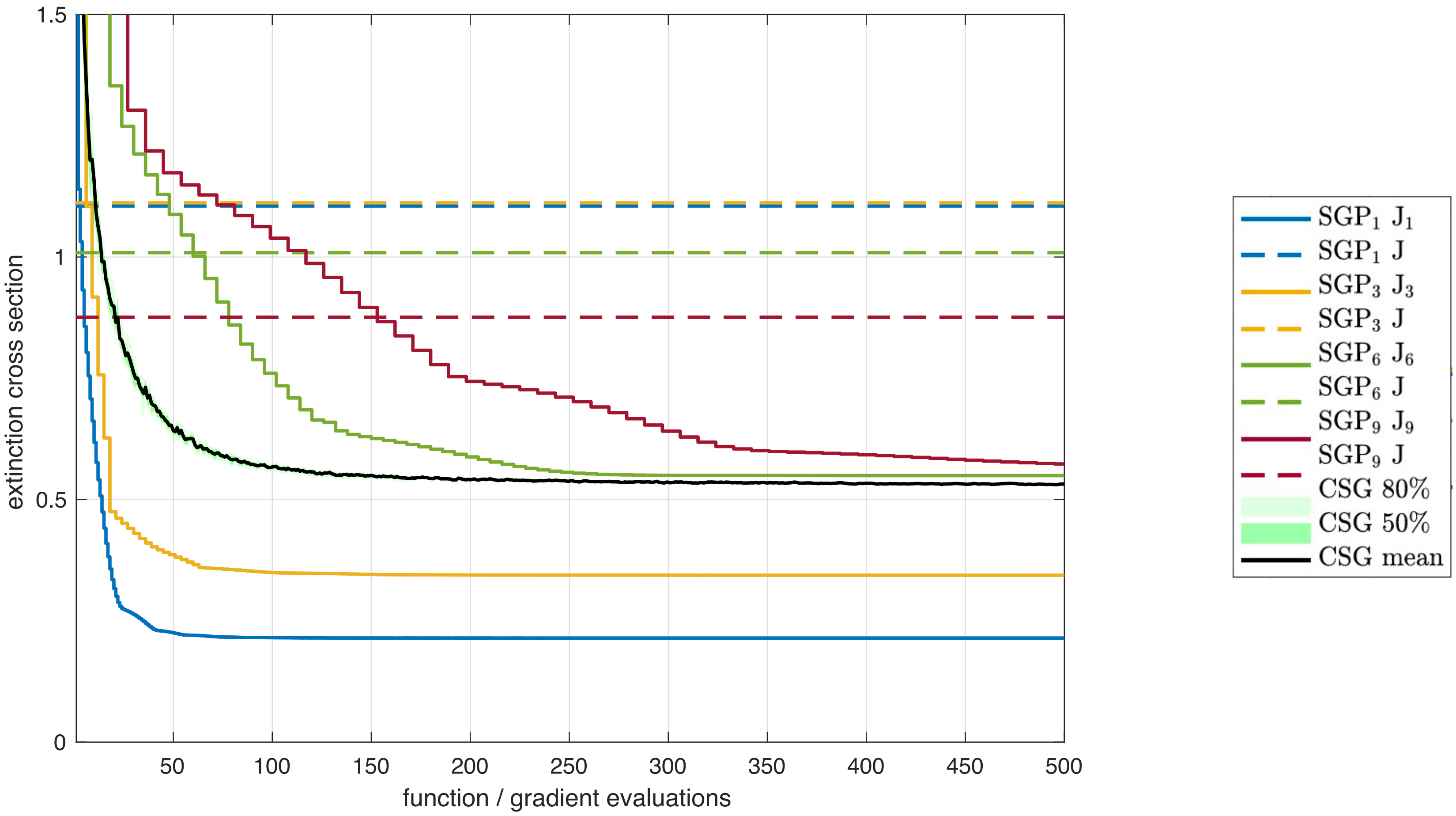


J = 0.37 | J = 0.36 | J = 0.34 | J = 0.30 | J = 0.18

example: min extention, large particle (1000 nm)



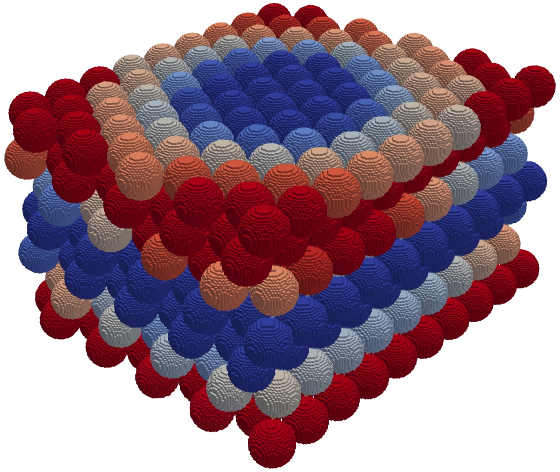
example: min extinction, large particle (1000 nm)



- CSG quantiles pretty tight in this example
- CSG not only better but also faster than SGP with 6, 9, ... orientations

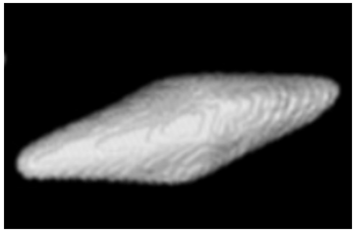
two stage:

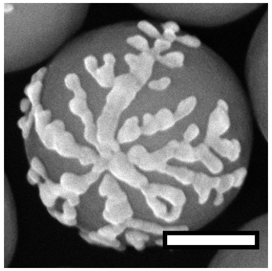
- include dispersity (e. g. 1d size distribution; particle size easily scaled by dipole distance ... change only one input paramter in DDA solver!)
- optimize more realistic systems (gold, silver, ...)
- optimization of supra particles



all at once:

- fully coupled process-structure-optimization
- higher dimensional parametrizations
- tighten gap between both approaches





THANK YOU VERY MUCH!