Aggregation kinetics of short-range attractive particles: Brownian Dynamics simulations vs. Smoluchowski equation

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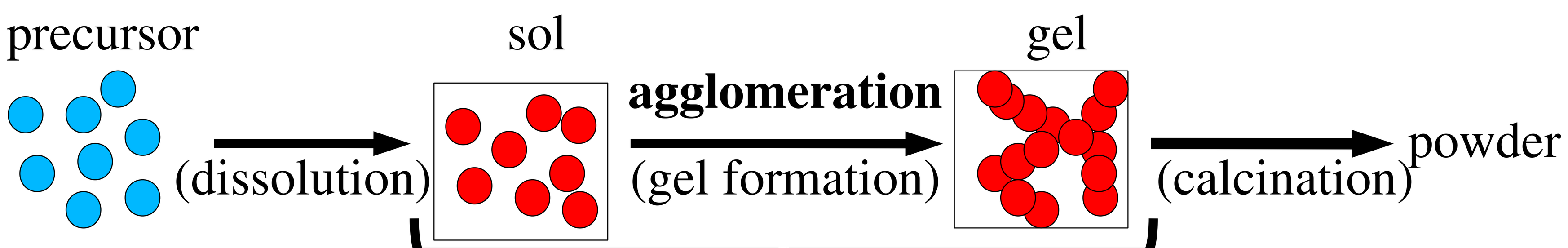
Introduction: We revisit the aggregation dynamics of particles interacting with short-range attractive interaction (SHRAT). Agglomeration of particles in suspensions is common in many technological and biological processes. Sol-gel synthesis of nanoporous structures is a prominent example [1,2]. However, the physical mechanism of process parameter influence on synthesis process is still unclear. Using Brownian Dynamics (BD) simulations we follow the relaxation of a homogeneous, thermodynamically unstable system towards equilibrium gel phase by agglomeration. The dynamics of the transition is characterized by the creation and growth of clusters with fractal dimension which exhibit an exponential size distribution. We model these systems by a Smoluchowski coagulation equation. A phenomenological time scaling law is introduced in order to collapse time evolution of the number of clusters and cluster size distribution onto a single universal curve.

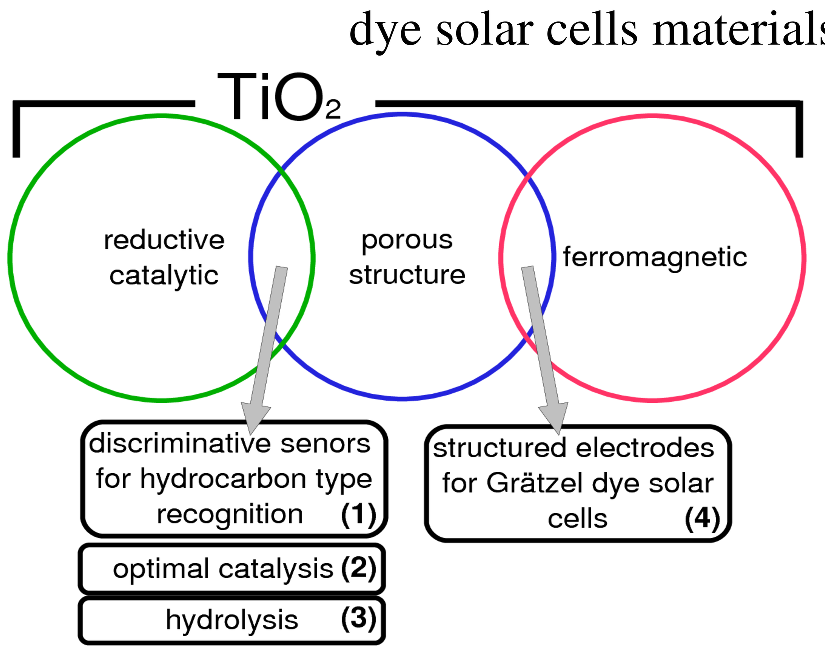
[1] A. Golubovic, M. Scepanovic, A. Kremenovic, S. Askrabic, V. Berec, Z. Dohcevic-Mitrovic, Z. V. Popovic, J. Sol-Gel Sci. Technol. 49, 311 (2009).
[2] A. Ponton, S. Barboux-Doeuff and C. Sanchez, Colloids Surf. A: Physicochem. Eng. Asp. 162, 177 (1999).

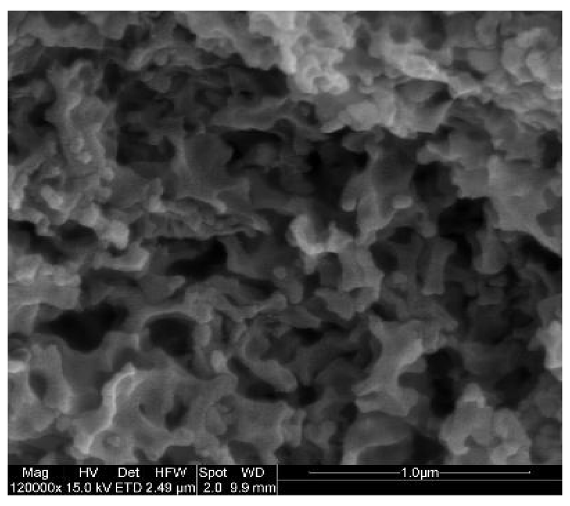
1. Agglomeration dynamics in sol-gel process



- controllable in room conditions
- takes place on the scale of hours

applications: synthesis of nanoporous TiO2 materials for sensor, catalyic, dye solar cells materials



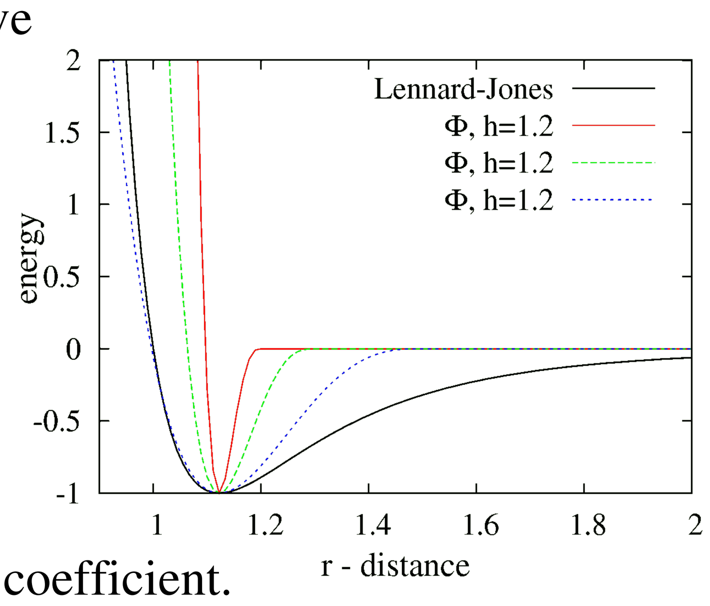


SEM image of nanoporous TiO_2.

2. Model: SHRAT potential and Smoluchowski equation

(a) For particle interaction a short-range attractive (SHRAT) potential with smooth cut-off is used:

$$\Phi(r)=\phi_0 r_0^{-4}[3(h-r)^4-4(h-r_{min})(h-r)^3],\ r\leqslant h$$



Influence of suspension is introduced through delta correlated with zero-mean random force. R(t) in Brownian dynamics:

$$\dot{X}=-\nabla\Phi/\zeta+\sqrt{2D/\zeta}R(t)$$

where ζ is friction coefficient, and D - diffusion coefficient.

(b) Smoluchowski equation :

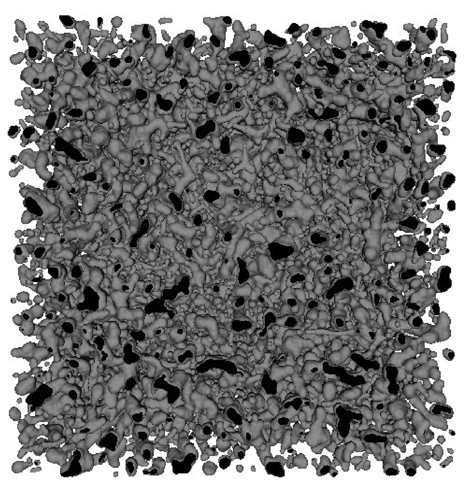
$$\frac{dN_k}{dt}=\frac{1}{2}\sum_{i+j=k}K_{ij}N_iN_j-N_k\sum_{j=1}^{\infty}K_{kj}N_j$$

agglomeration to create particles of size k — particles lost in process of agglomeration

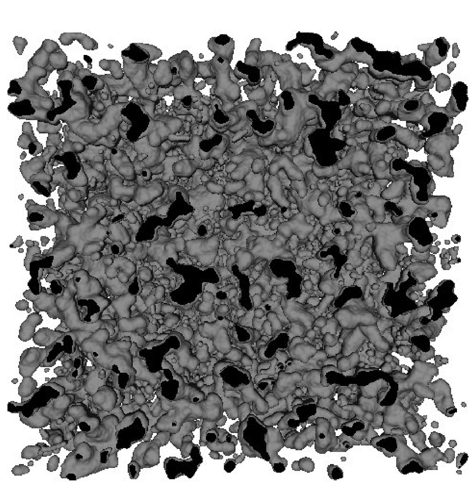
Challenges:

(1) time consuming to calculate ~(largest cluster)^2
(2) with time size of the larger cluster increases
(3) K_{ij} not known

(c) Evolution of structure:

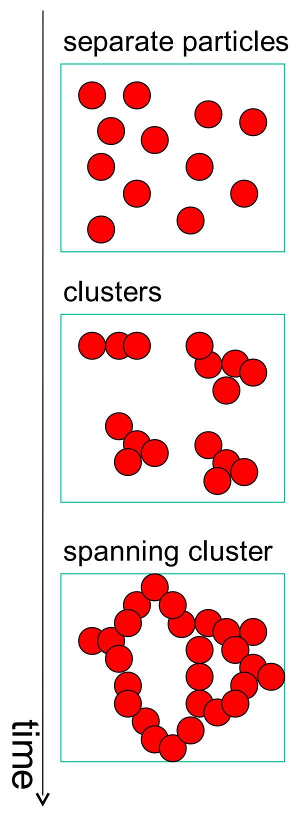


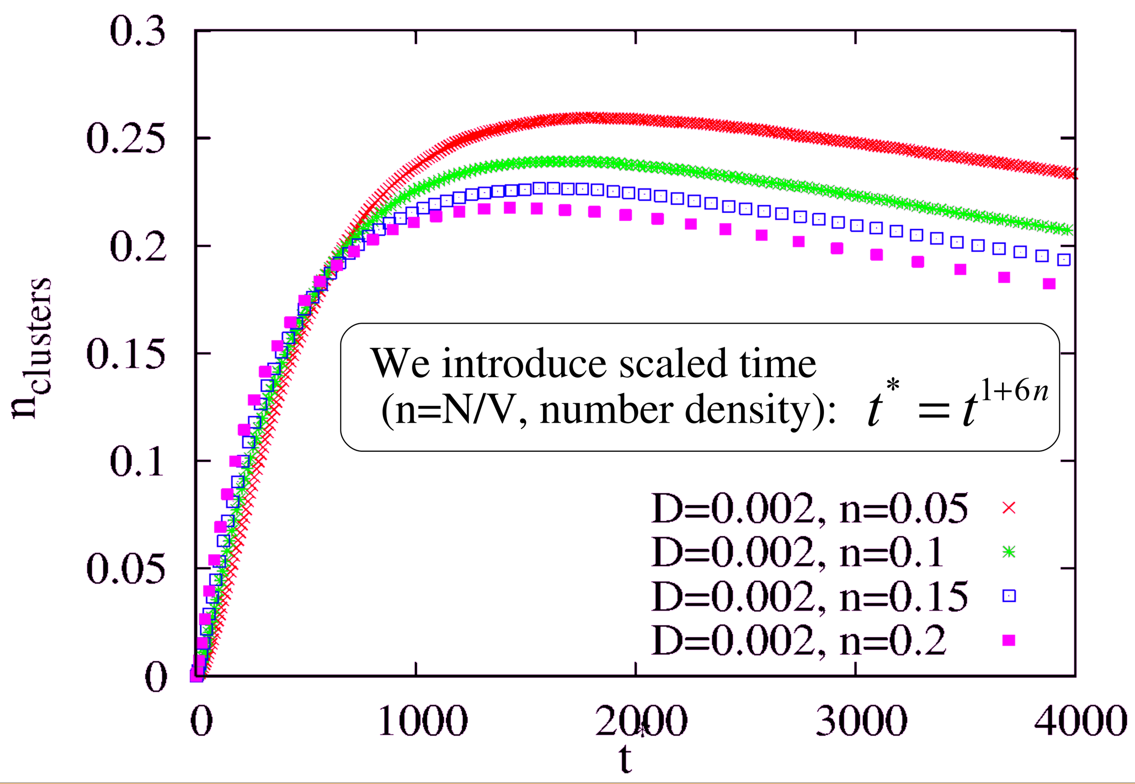
$t/t_{ref}=100$



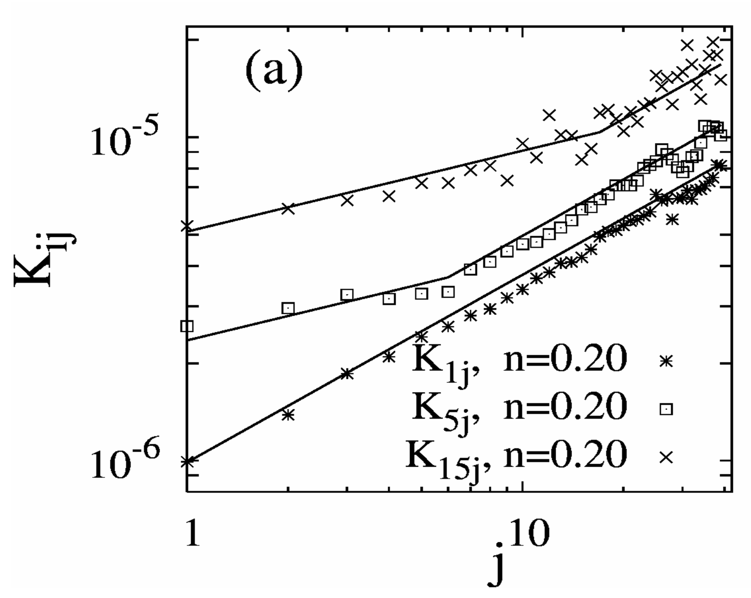
$t/t_{ref}=300$

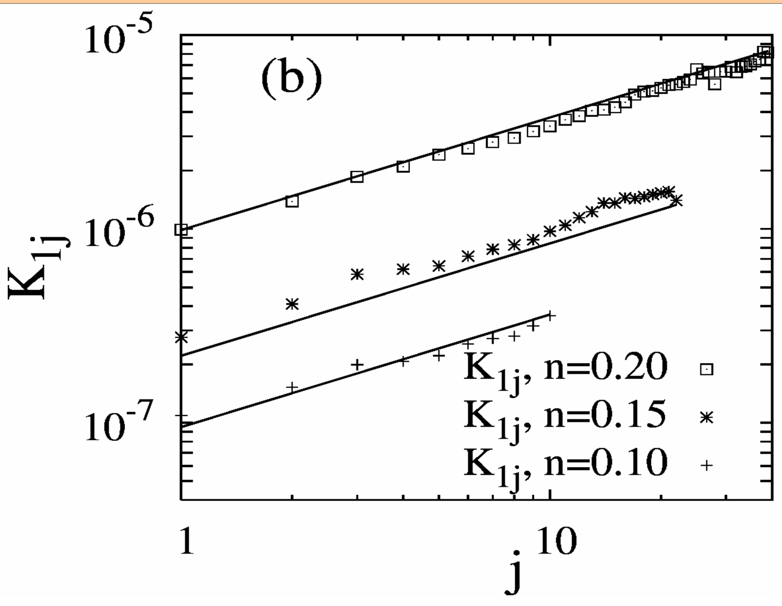
3. Total number of clusters





4. Smoluchowski equation kernel

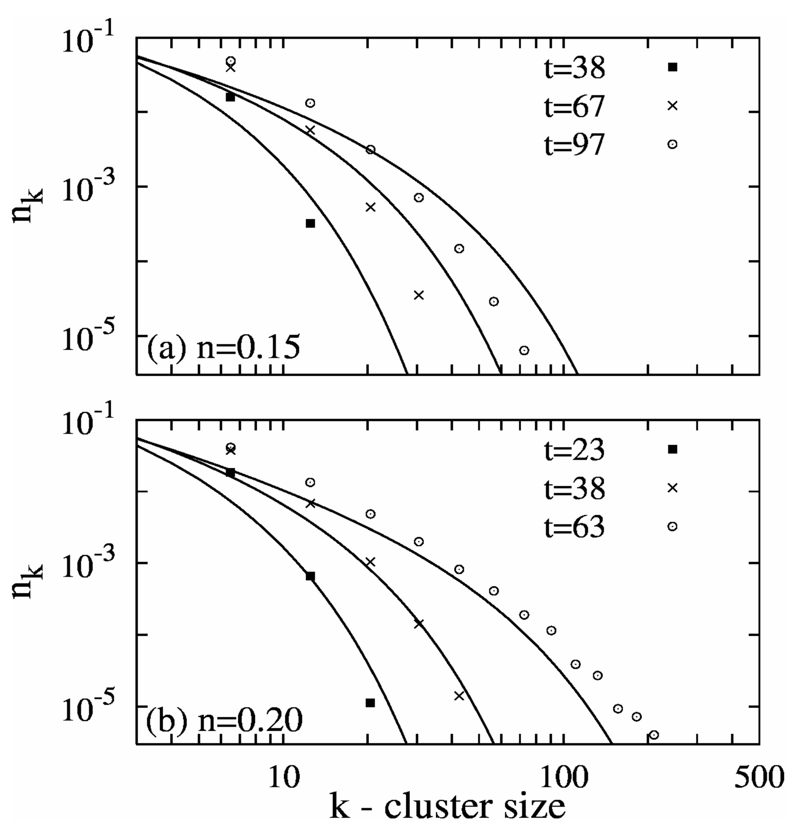




$$K_{ij}=\begin{cases}C(n,D)\ i^{0.6}j^{0.25}, & i>j\\ C(n,D)\ i^{0.25}j^{0.6}, & i\leq j\end{cases}$$

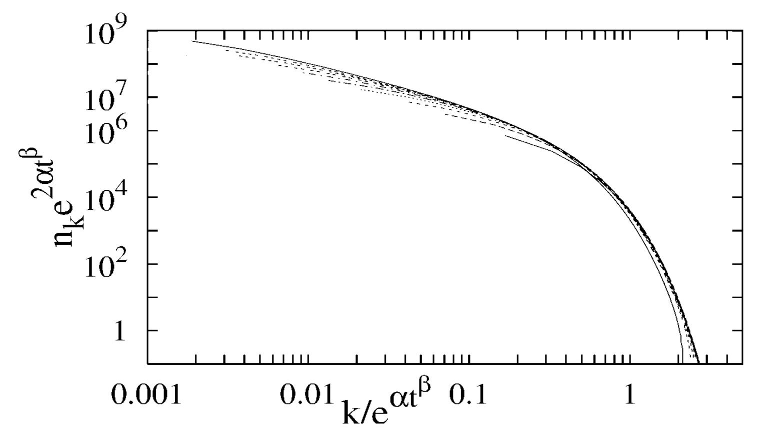
where C(n,D) is function of number density and diffusion rate.

5. Smoluchowski equation vs. BD results

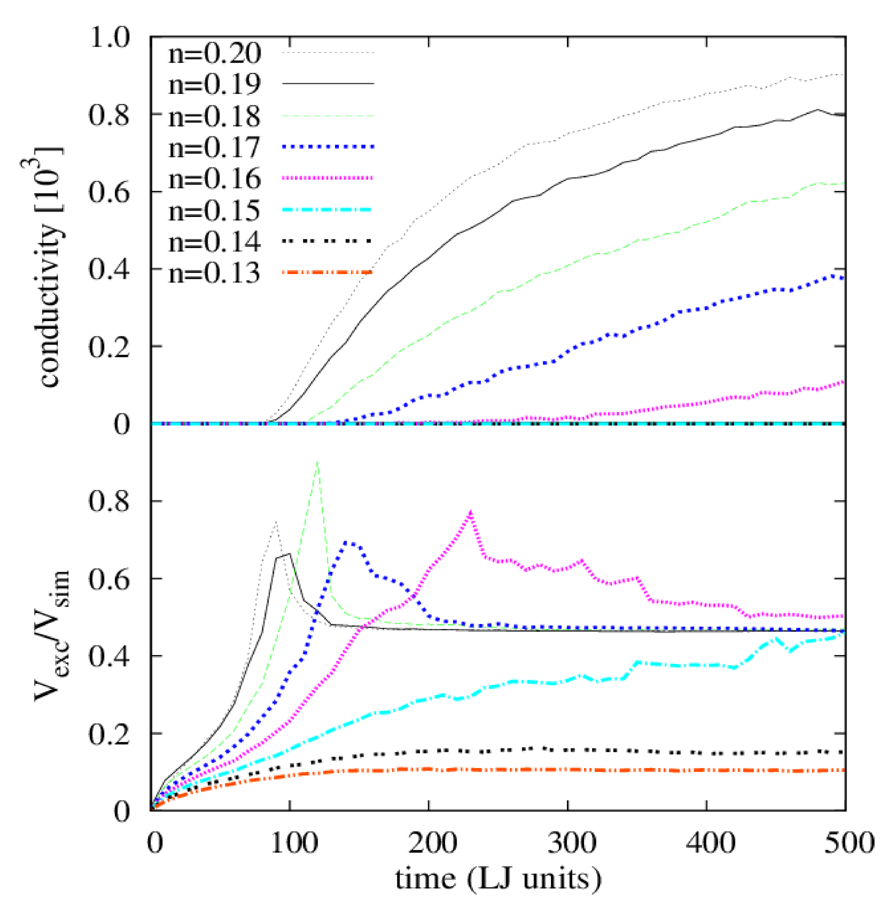


Using obtained Smoluchowski kernel we can calculate time evolution of cluster size distribution (n_k).

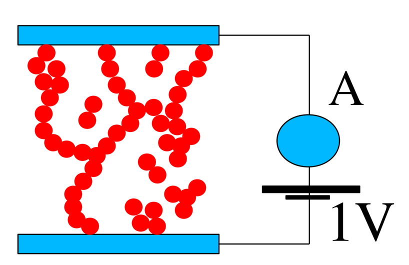
We can also find scaling law which colapses all curves onto a single master curve.



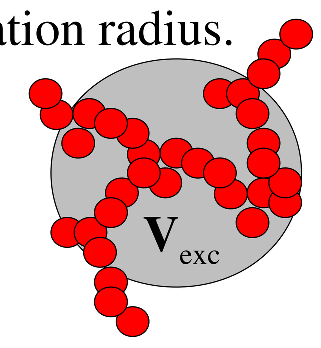
6. Formation of percolating cluster



Conductivity of the system.



Excluded volume calculated from giration radius.



$$r_k^2=\langle(\Sigma_{i=1}^k(\mathbf{r}_i-\mathbf{r}_{cm})^2)/k$$

Support: Serbian Ministry of Science (III45018, ON171017), Swiss National Science Foundation (SCOPES), and European Commission (EGI-InSPIRE, PRACE-1IP, HP-SEE)