The theoretical and mathematical description of nucleation in shear flow conditions

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Overview

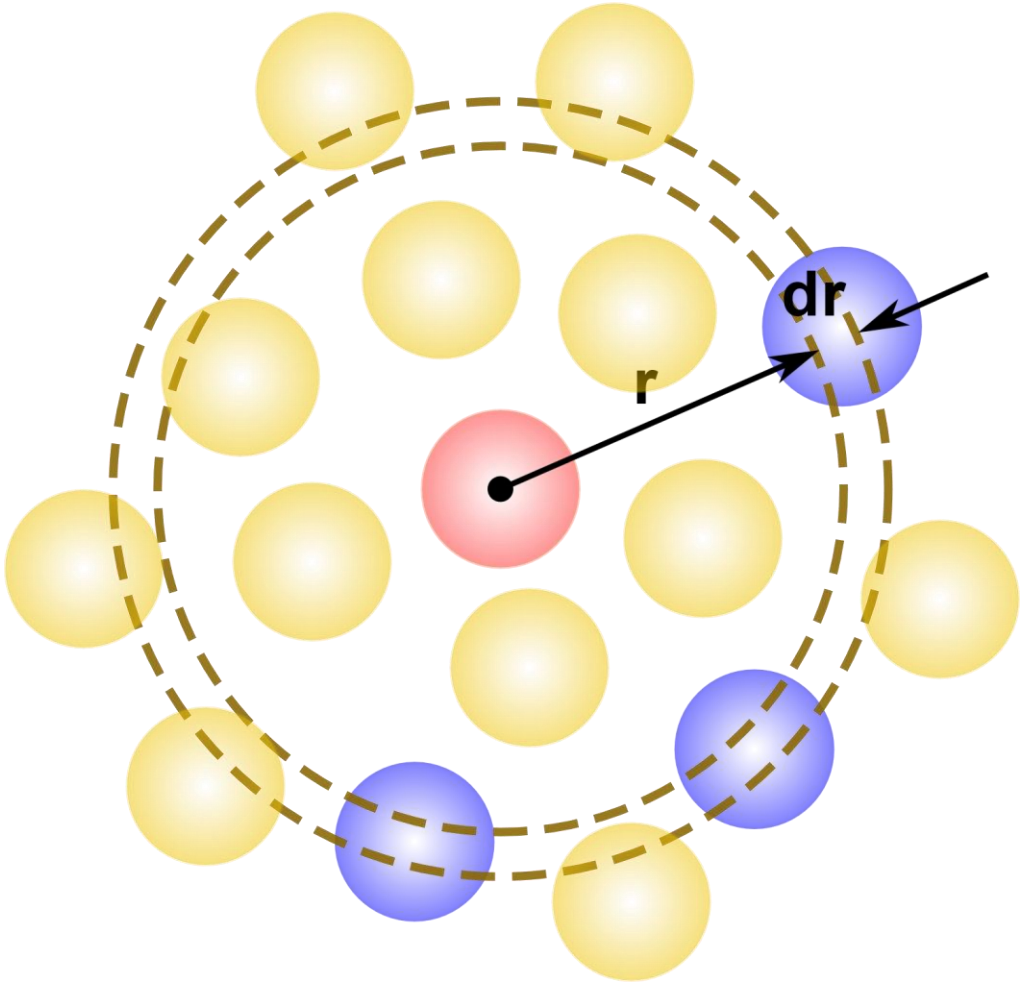
1. Microtructure of molecules in shear flows from the Smoluchowski diffusion-convection equation

2. Self-assembly of charge-stabilized molecules/colloids in shear flows

3. Crystal nucleation theory in shear flows

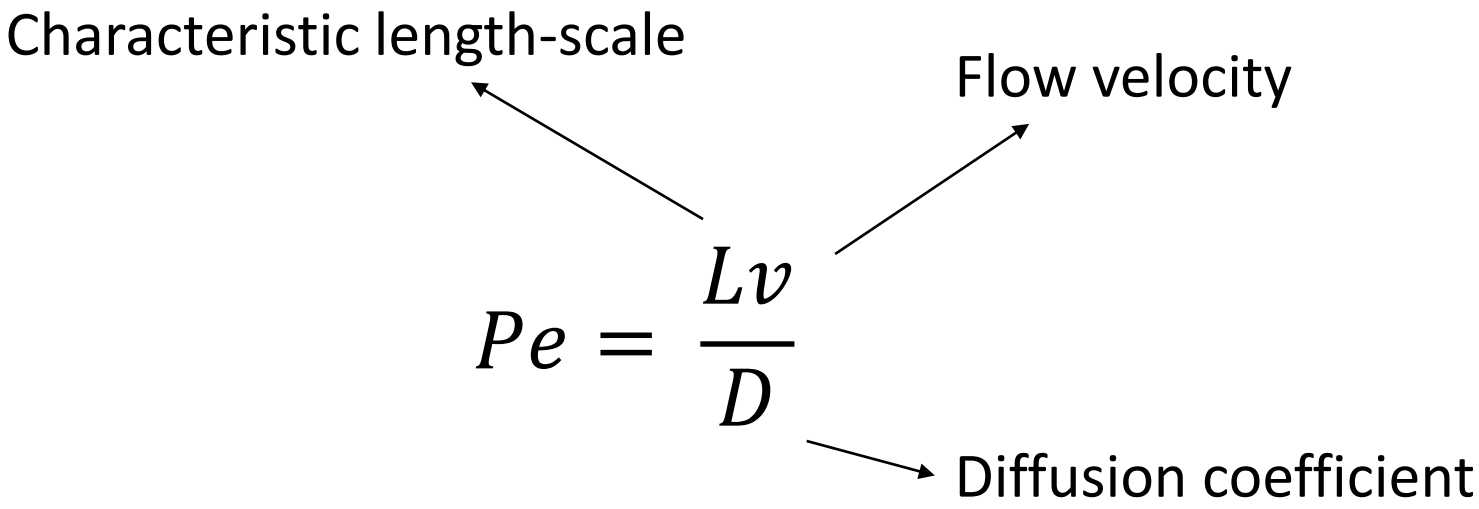
4. Comparison with experiments and new perspectives

Central tool: Pair-correlation function

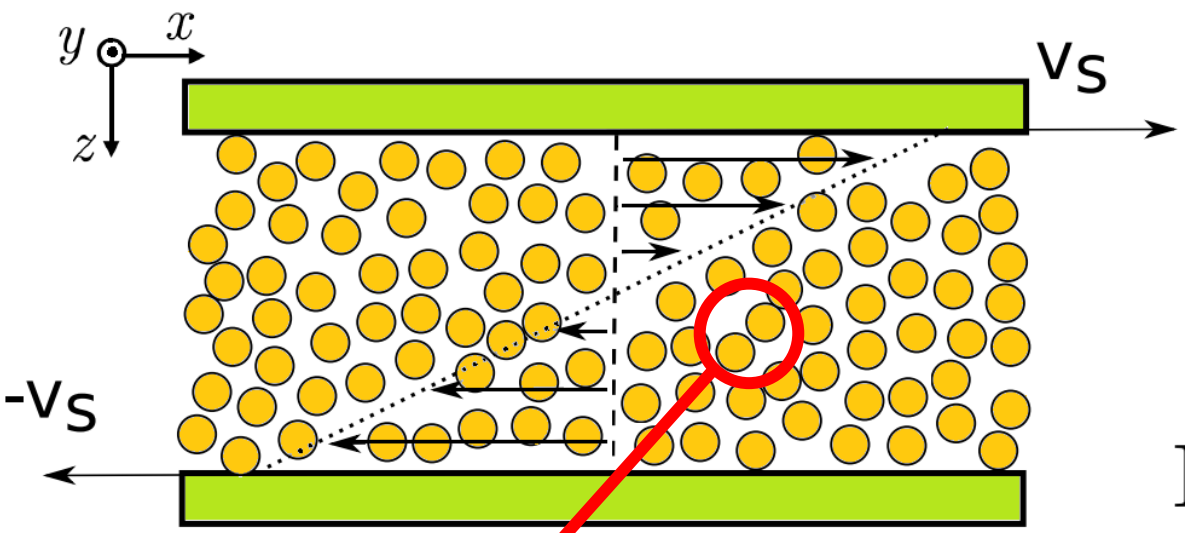


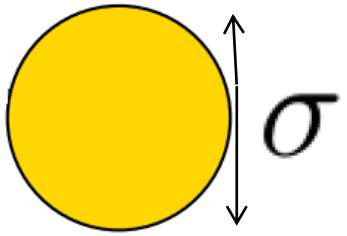
Probability of finding other molecules at distance *r* from a test molecule

Peclet number



Colloidal suspensions under shear flow





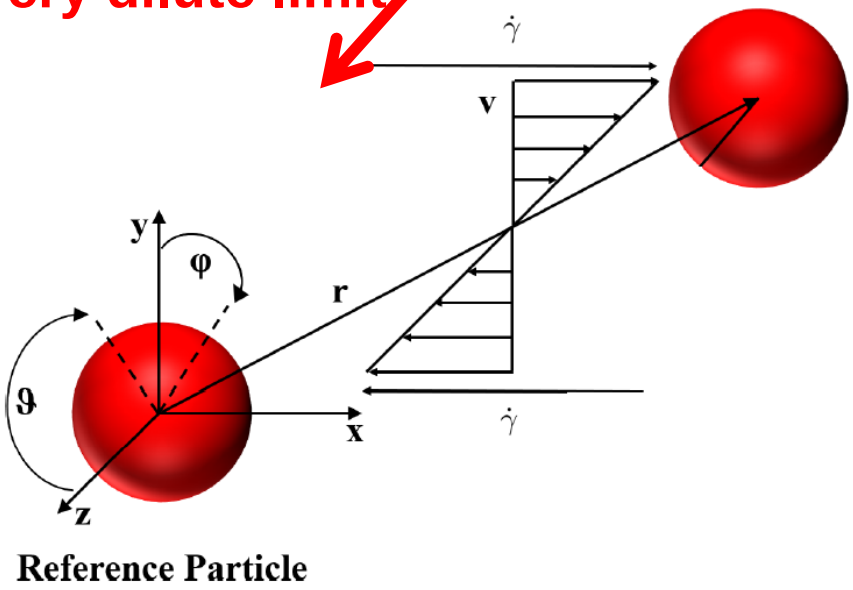
Peclet number

Shear rate

$$\mathrm{Pe} \equiv \frac{\dot{\gamma}}{D_0}\left(\frac{\sigma}{2}\right)^2$$

Stokes-Einsten diffusion coefficient

Very dilute limit



Reference Particle

How does *g(**r**)* varies in shear flow?

Pair correlation function of molecules in shear flow

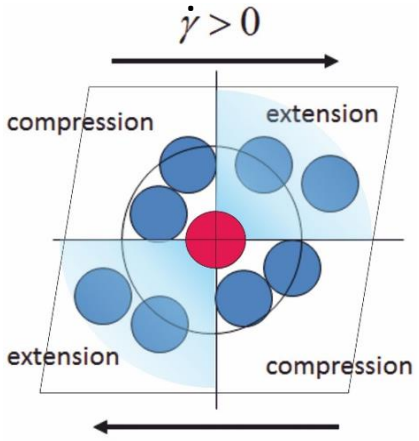
Pair-correlation function of dissolved molecules in shear flows (dilute)

Smoluchowski (Fokker-Planck) "convection-diffusion" equation:

$$D\nabla\cdot\left(G(r)\nabla g(\mathbf{r})-\frac{1}{k_BT}\mathbf{K}g(\mathbf{r})\right)=0$$

$$\mathbf{K}=-G(r)\nabla U(r)+\zeta\mathbf{v}(\mathbf{r}).$$

Dhont JFM 1989, Bławzdziewicz and Szamel, PRE 1993



After averaging over the angular section of interest, we can apply the **matched-asymptotics** (perturbative expansion)

Boundary layer: $\delta(\epsilon)$

small parameter $\epsilon = 1/\mathrm{Pe}$

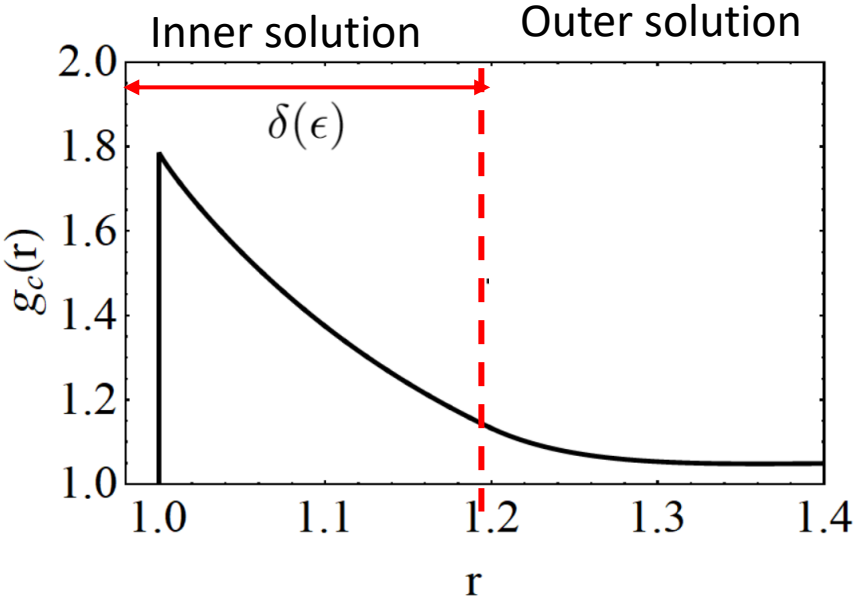
INNER SOLUTION: $\tilde{r}_c < \tilde{r} < \delta(\epsilon)$

$$g^{\mathrm{in}} = g_0^{\mathrm{in}} + \delta(\epsilon)g_1^{\mathrm{in}} + \delta(\epsilon)^2 g_2^{\mathrm{in}} + \dots$$

OUTER SOLUTION: $\delta(\epsilon) < \tilde{r} < \infty$

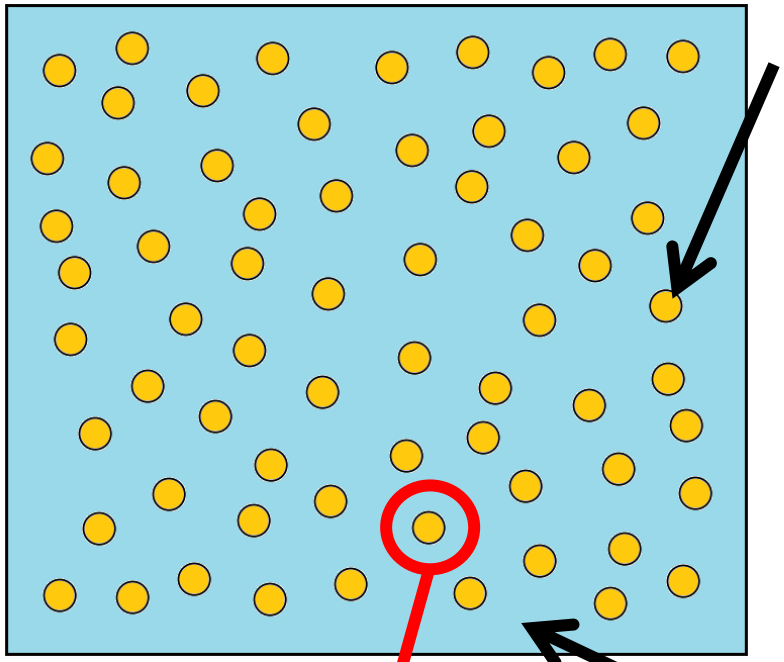
$$g^{\mathrm{out}} = g_0^{\mathrm{out}} + \epsilon g_1^{\mathrm{out}} + \epsilon^2 g_2^{\mathrm{out}} + \dots$$

and then match at the boundary later $\delta(\varepsilon)$

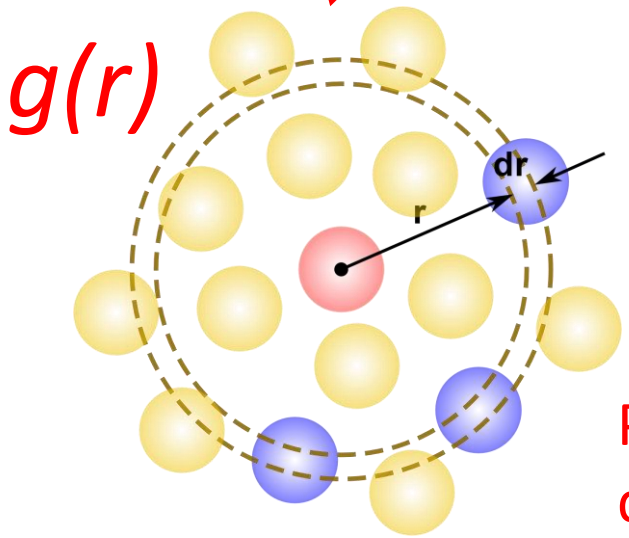


Banetta & Zaccone, PRE 2019

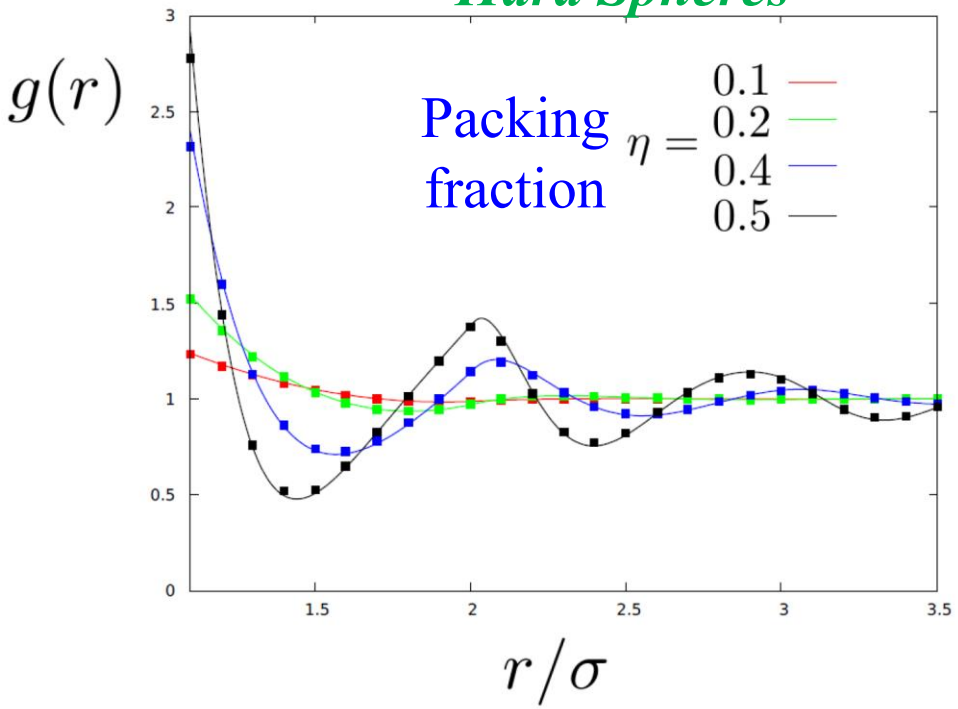
Molecules in solution and pair-correlation function



Molecules and/or nanoparticles, perform BROWNIAN MOTION



Hard Spheres

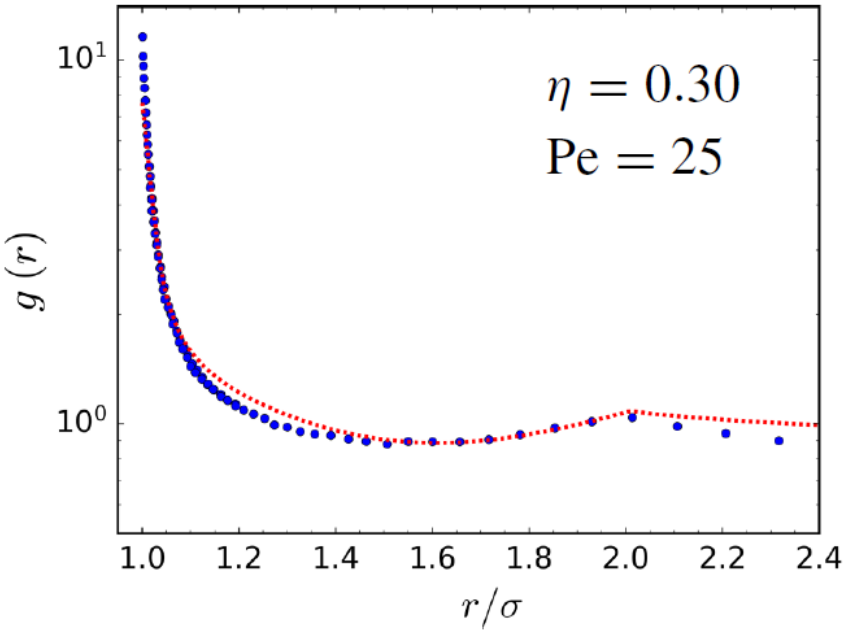


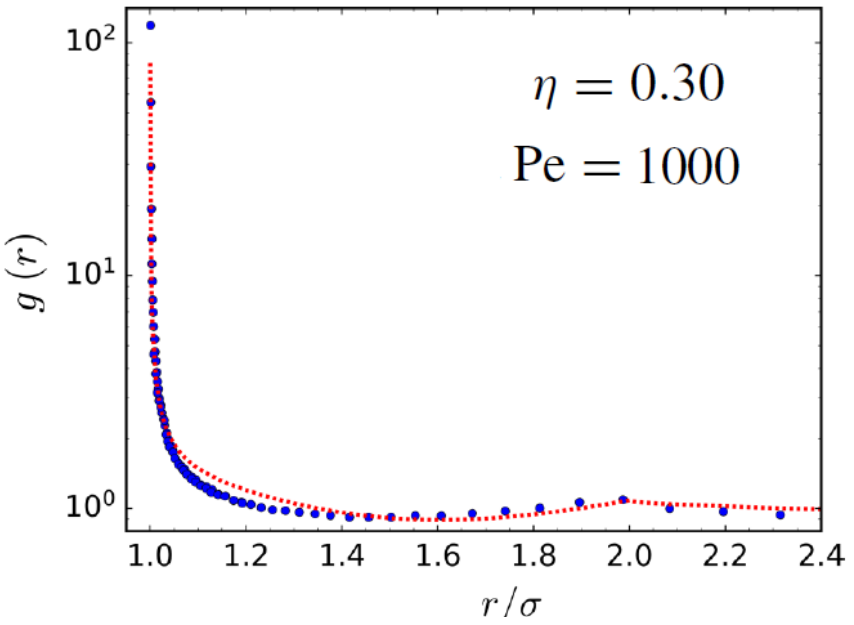
Probability of finding other particles at distance *r* from a test particle

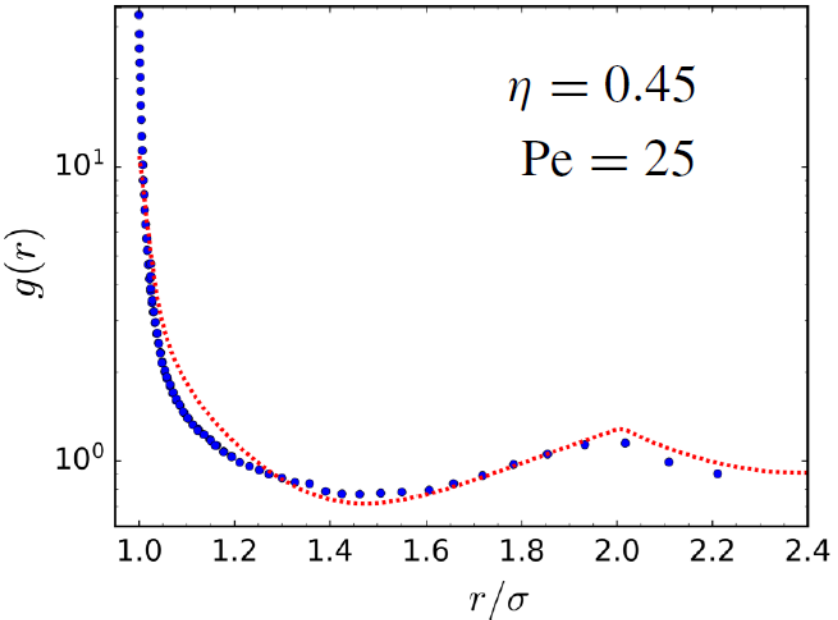
Validation

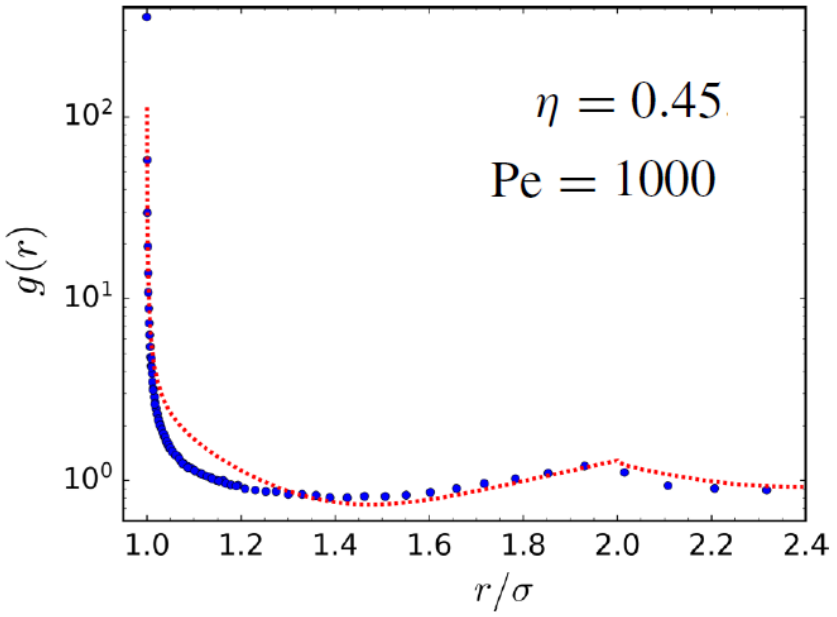
Our theory

Stokesian Dynamics Simulations (Morris and Katyal, Phys. Fluids 14, 1920 (2002))

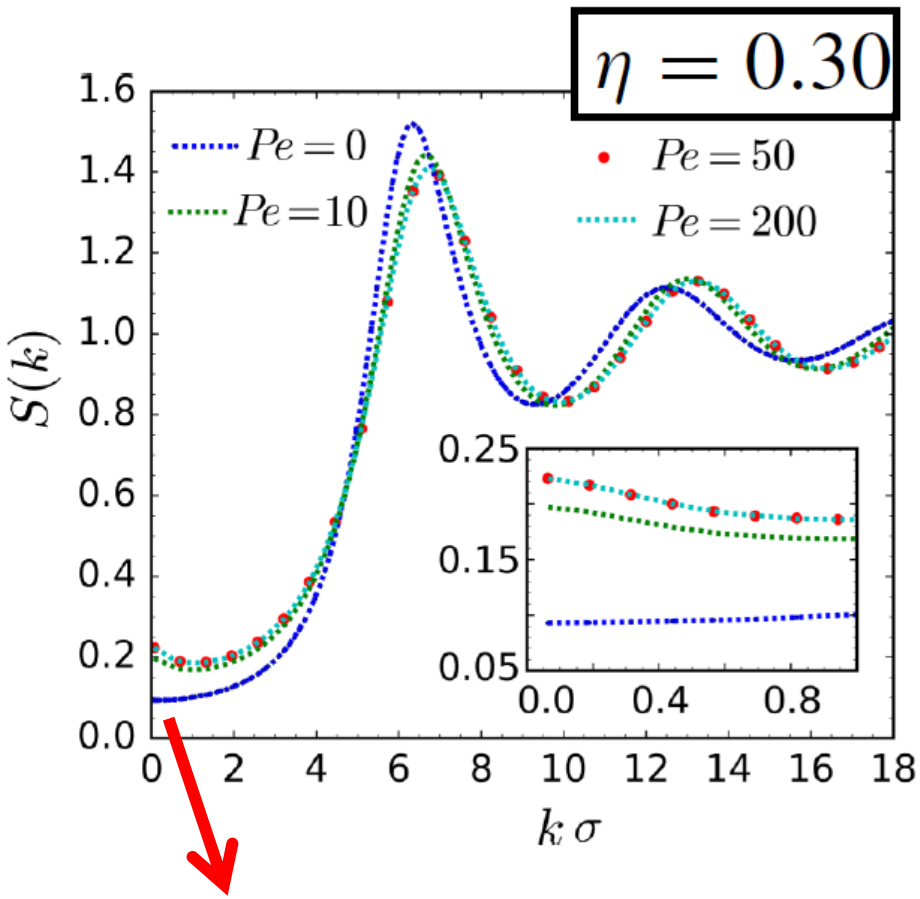


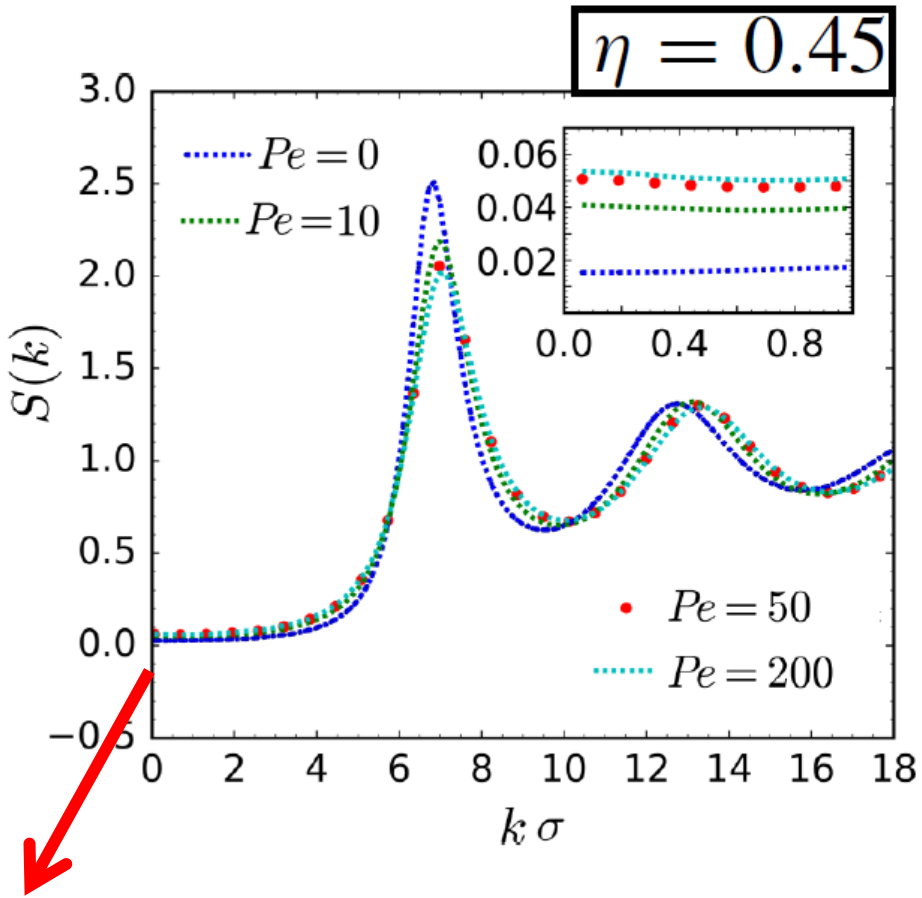






Divergence of the Structure Factor at k→0





Shear-induced uniform → non uniform transition (Brazovskii)?

The structure factor S(k) can be measured experimentally!

Conclusions – pair correlation function in shear

Novel theoretical framework for the microscopic structure of molecules in liquids under shear flow, by **fully** taking into account the ***boundary layer-structure*** of convective diffusion and HIs.

Agreement with numerical results from literature ***with no fitting parameters***. Investigation of the value ***at contact*** of the pair correlation function

Possible divergence of the **structure factor** *S(k)* at *k -> 0* by increasing the Peclet number: Evidence of a shear-induced ***uniform->non uniform*** phase transition?

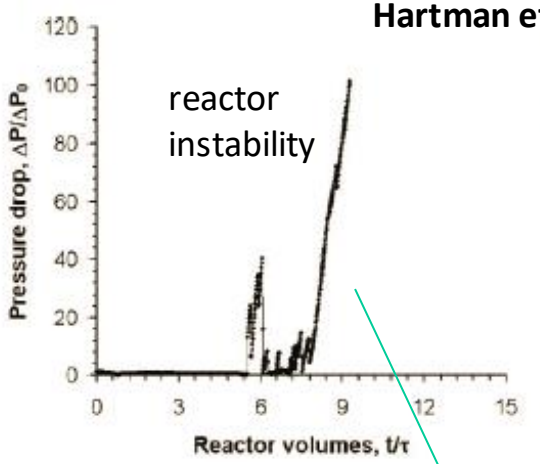
The theory can be extended to **any** pair potential!

Part 2 –
Self-assembly of charge-stabilized colloids in shear flows

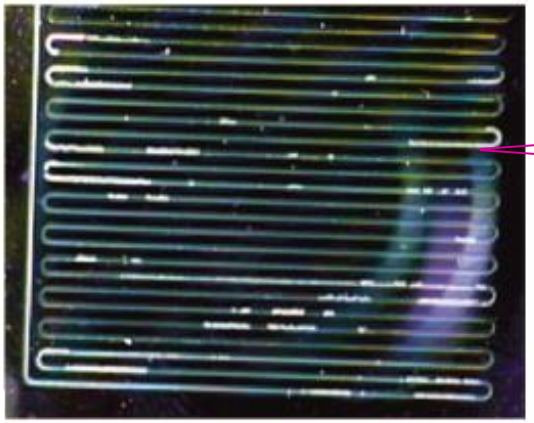
Uncontrolled self-assembly of nanoparticles in microfluidic reactors

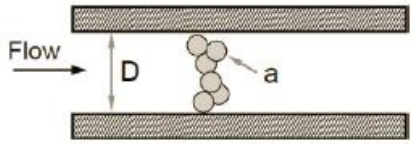
E.g., uncontrolled crystallization

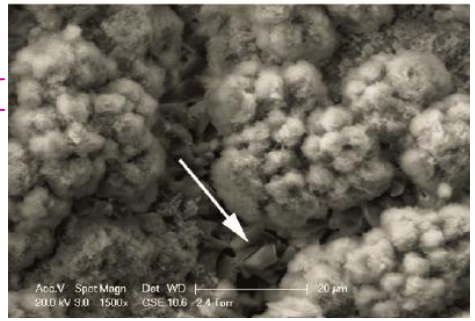
E.g., Pd-catalyzed C-N reactions in microreactors



Hartman et al, Org. Process Res. Dev. (2010)





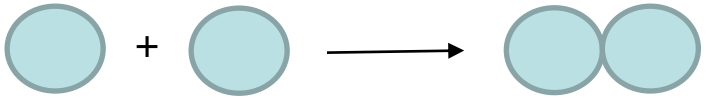


aggregation of by-product salt NPs

How can we understand
and control the “runaway”
of pressure drop/viscosity with time?

Brief reminder: Brownian aggregation (no flow)

Diffusion-limited **coagulation rate**



$$k_S = \frac{8}{3}\frac{kT}{\eta}$$

viscosity

Two Brownian particles stick upon contact
(due to mutual attraction):
independent of particles size because of mutual cancellation
of size-dependencies due to cross-section and diffusion

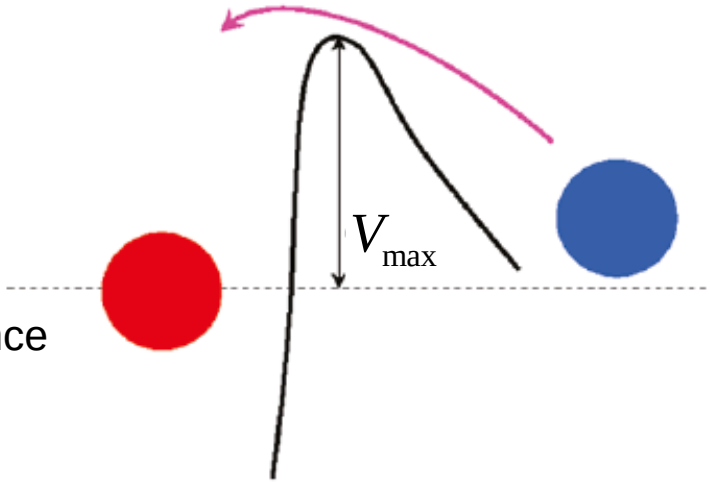
With charge-repulsion:

$$k_{agg} = \frac{k_S}{W} < k_S$$

aggregation rate is slower due to the repulsive barrier

$$W = \frac{k_S}{k_{agg}} = 2R\int_0^\infty \frac{\exp(\beta V_{\mathrm{tot}})}{(2a+h)^2 G(h)}\,\mathrm{d}h$$

colloidal (Fuchs) stability coefficient, W>1 in presence
of an energy barrier



Analytically solving the Smoluchowski eq. with shear flow

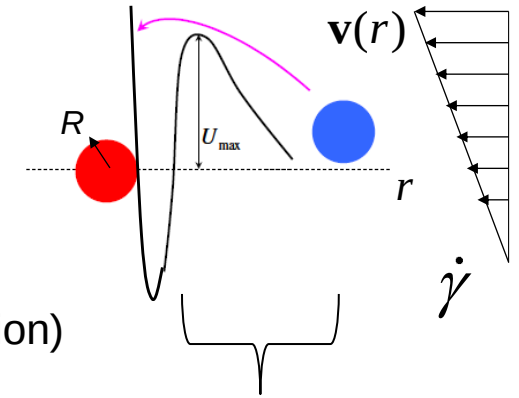
$$\frac{\partial g(\boldsymbol{r})}{\partial t} = \nabla \cdot (D\nabla g(\boldsymbol{r}) + b g(\boldsymbol{r})\nabla V - b\mathbf{v} g(\boldsymbol{r}))$$

(the left-hand side is set to 0)

diffusion

interaction potential e.g. **DLVO**

flow field (convection)



λ=interaction range

approximate analytical solution (singular perturbation):
Zaccone, Wu, Gentili, Morbidelli, PRE (2009)
From taking the flux of the concentration field, we get to the aggregation rate

$$k_{agg} = \frac{8\pi D_0 R \rho_0}{2\int_0^{\delta/R} \frac{dx}{G(x)(x+2)^2} \exp \int_{\delta/R}^{x} dx \left(\beta \frac{dV}{dx} + Pe \quad \tilde{\mathrm{v}}_r\right)}$$

$\delta = \sqrt{(\lambda/a)/Pe}$ **boundary-layer width**

Rate of thermally-activated barrier crossing in shear flow

$$\mathrm{div} \cdot [\beta D(-\nabla U + b\mathbf{v}) - D\nabla]g(\boldsymbol{r}) = 0$$

By taking the flux integral over the current ***J***, we obtain

The rate of particles that collide with the target particle by overcoming the potential barrier

$$k_{agg} = \frac{8\pi D_0 R \rho_0}{2\int_0^{\delta/R} \frac{dx}{G(x)(x+2)^2} \exp \int_{\delta/R}^{x} dx \left(\beta \frac{dV}{dx} + Pe \quad \tilde{\mathrm{v}}_r(x)\right)}$$

HIs

HIs

saddle-point approximation

$$\rho g(\boldsymbol{r}) =$$ concentration profile around the target particle

$$k_{agg} \approx 8\pi D_0 a c_0 \sqrt{\alpha Pe - \beta U_m''} e^{\beta U_m - 2\alpha Pe}$$

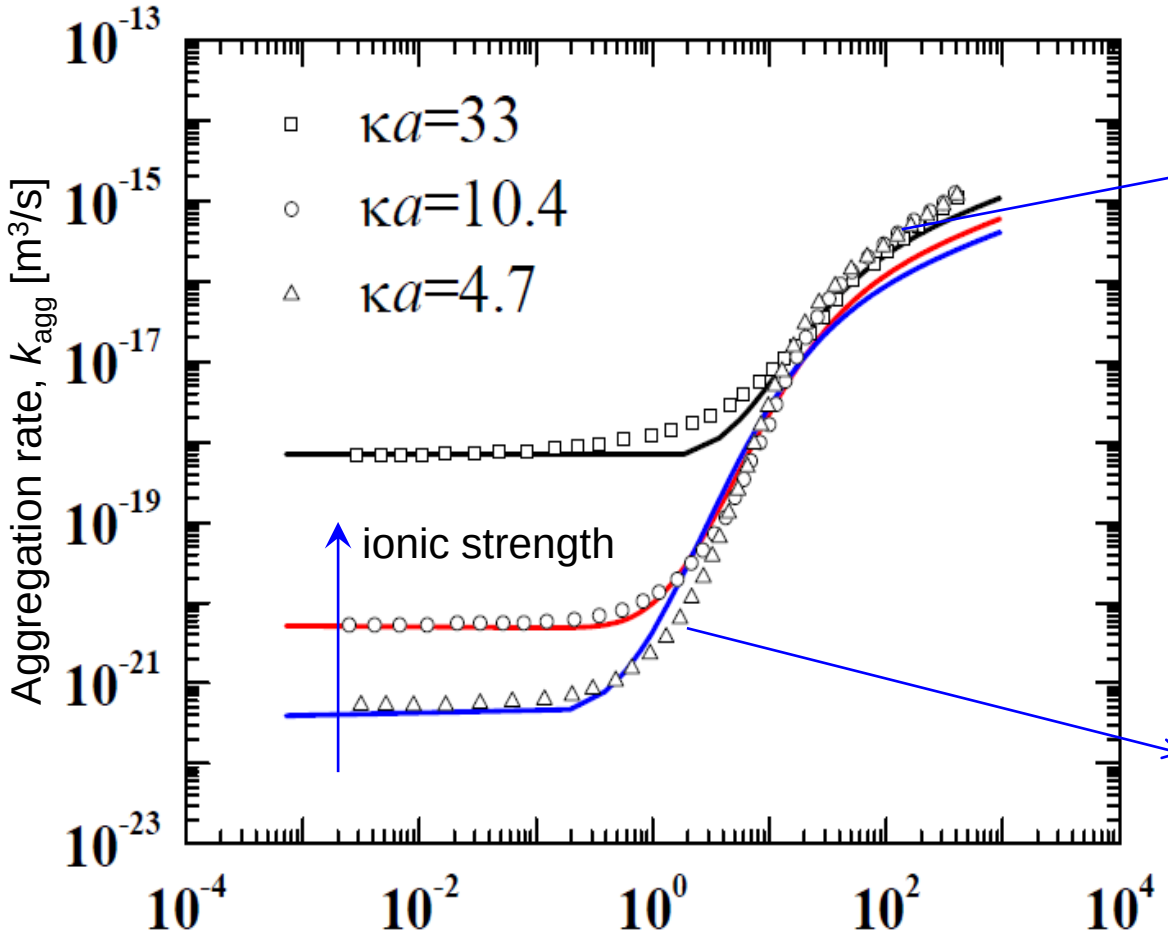
(***Kramers' rate with shear***)

Zaccone, Wu, Gentili, Morbidelli, PRE (2009)

Comparison with full numerical solutions

$$\frac{dC}{dt} = -k_{agg} C^2$$

C = number conc. of colloids



$$Pe = \frac{6\pi\mu\dot{\gamma}R^3}{kT}$$

old ballistic model by Smoluchowski (1917)

$$k_{agg} \propto \dot{\gamma}\,(2R)^3 \propto Pe$$

recovered at Pe=∞

$$k_{agg} \propto e^{-\beta U_{\max} + 2\alpha Pe}$$

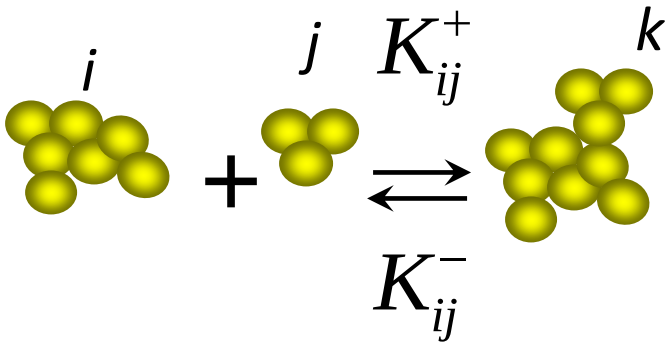
competition between shear and charge repulsion

From dimer formation kinetics to large-scale aggregation kinetics

SYSTEMATIC APPROACH: **population balance equation of colloidal clusters (PBE)**

C_k = conc. of clusters containing k particles

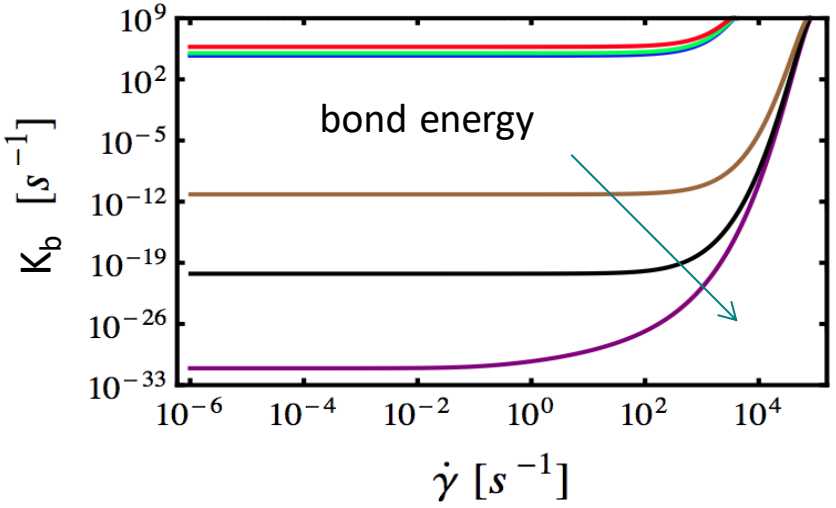
$$\frac{dC_k}{dt} = \frac{1}{2}\sum_{i,j=1}^{i+j=k} K_{ij}^{+} C_i C_j - C_k \sum_{i=1}^{\infty} K_{ik}^{+} C_i - K_k^{-} C_k + \sum_{i=k+1}^{\infty} K_{ik}^{-} C_i$$



K_{ij}^{+} **aggregation** rate → Analytical solution to Smoluchowski eq. with shear (**Zaccone et al. PRE 2009**), can be extended to clusters

K_{ij}^{-} **breakup** rate → Flow-induced stresses can tear the clusters apart!

Nanoparticles aggregate breakup rate



Conchuir & Zaccone PRE 2013

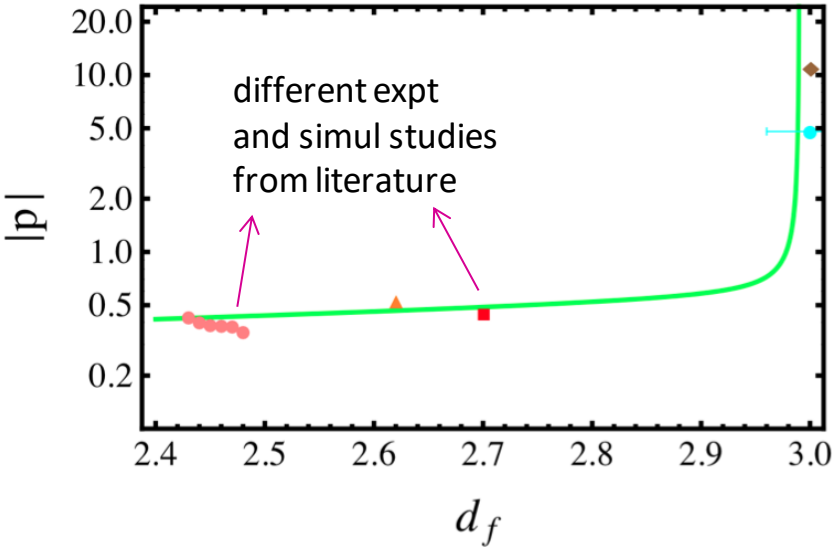
$$K_b = \frac{\sqrt{-\tilde{V}''_{\text{eff}}(r_{\max})\tilde{V}''_{\text{eff}}(r_{\min})}}{2\pi b \exp[\beta\tilde{V}_{\text{eff}}(r_{\max}) - \beta\tilde{V}_{\text{eff}}(r_{\min})]}$$

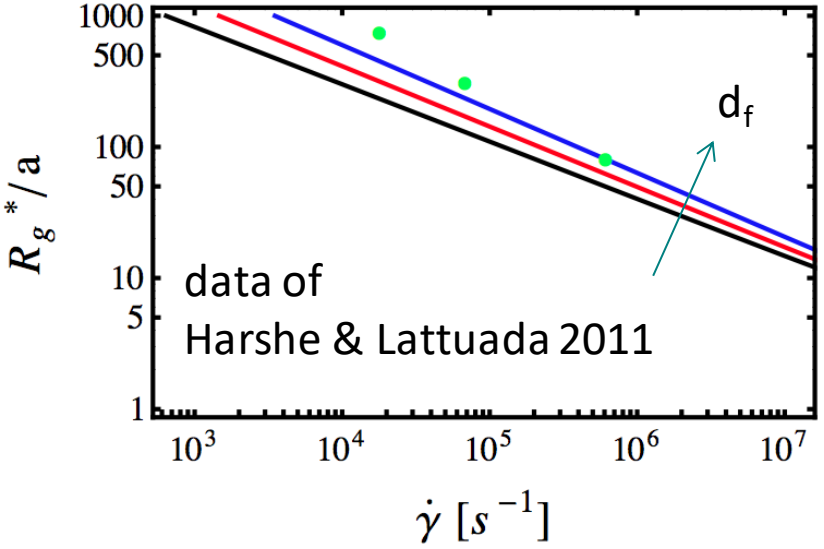
=0

instantaneous breakup
(no activation energy)

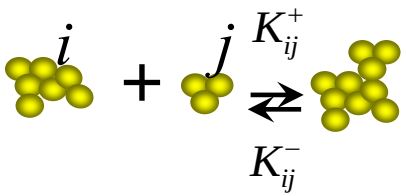
max cluster size surviving flow-stress $R_g^* \sim \dot{\gamma}^{-\frac{1}{d_f+\alpha(d_f)}} \sim \dot{\gamma}^p$

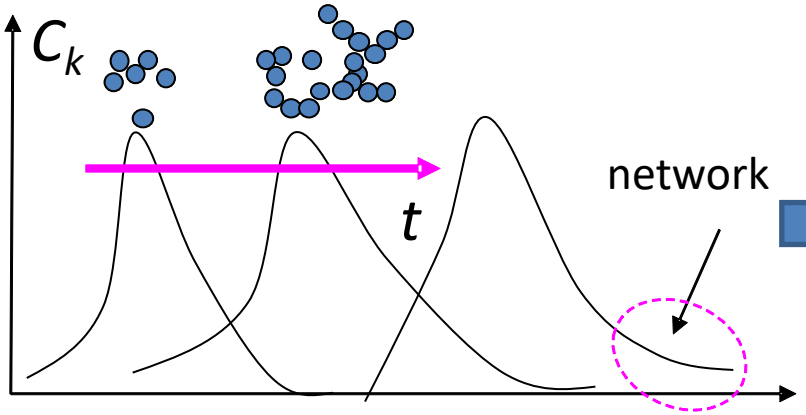
no fitting parameters!





Modelling of coagulation/clogging phenomena

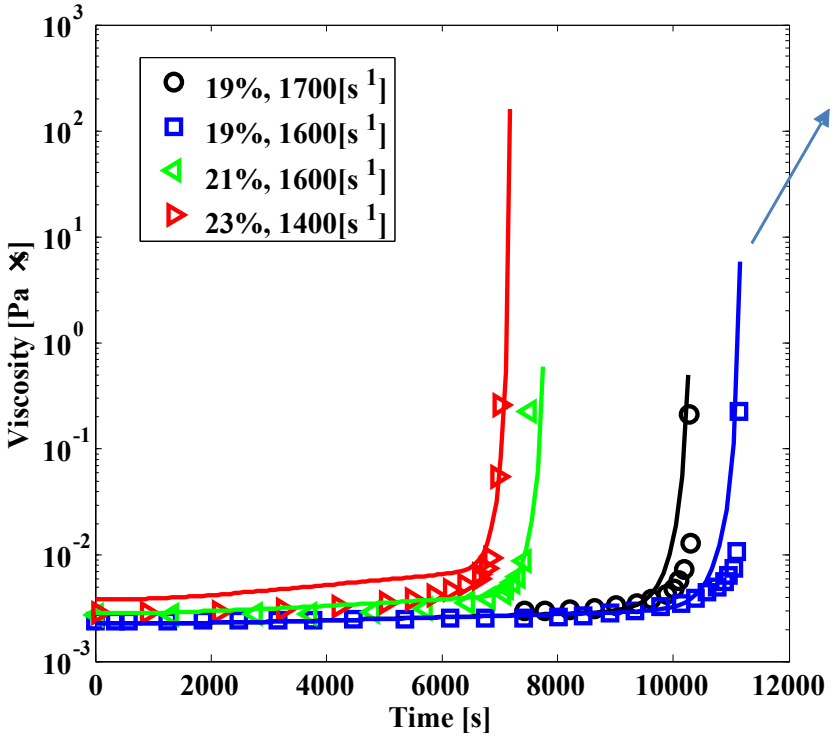




HYDRODYNAMIC MODELLING

VISCOSITY, ? P vs time

Quantitative description of the clogging instability:



quantitative prediction: flow-induced aggregation of NPs

- **AZ et al. PRL (2011), AZ et al. JCP (2010)**
- **Conchuir & AZ PRE (2013)**
- **Moussa, Lattuada, Conchuir, AZ, et al. Langmuir (2013)**

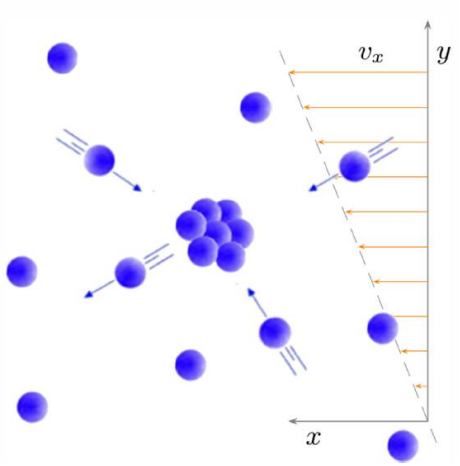
Overview – shear aggregation

● **Aggregation of NPs in shear flows**: there is a crucial interplay between colloidal interactions, Brownian motion and flow convection which can be disentangled using an approximate solution to the governing Smoluchowski eq. with shear (**Zaccone, Wu et al. PRE 2009**).
The resulting aggregation rate is the starting point to the numerical description of clustering phenomena and gelation, in agreement with experiments. The theory also provides an extension to Kramers' rate theory under shear flow and with HI at the two-body level.

● The Smoluchowski eq. with shear also governs shear-induced **aggregate breakup**, with an important role of hydrodynamic interactions mediated by the fractal structure. Analytical expressions for the fragmentation rate are possible also in this case leading to power-law dependencies (**Conchuir & Zaccone PRE 2009**).
The framework is directly applicable also to colloidal gels under shear.

Part 3 –
Theory of crystal nucleation in shear flows

Kinetic equations for nucleus growth



$$\frac{\partial Z(n,t)}{\partial t} = -Z(n,t)[q_+(n) + q_-(n)] + Z(n-1,t)q_+(n-1) + Z(n+1,t)q_-(n+1). \quad (1)$$

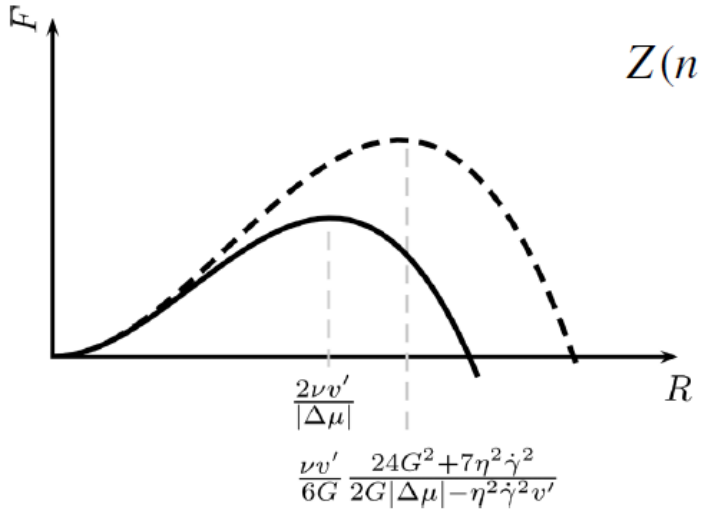
$$b(n)q_+(n) = b(n+1)q_-(n+1),$$
$$b(n-1)q_+(n-1) = b(n)q_-(n).$$

chemical equilibrium

Frenkel-Zeldovich

$$\frac{\partial Z}{\partial t} = \frac{\partial}{\partial R}\left[\lambda^2 q b \frac{\partial}{\partial R}\left(\frac{Z}{b}\right)\right] = \frac{\partial}{\partial R}\left[Db\frac{\partial}{\partial R}\left(\frac{Z}{b}\right)\right]$$

only 1-particle detach/attach events



$$Z(n) = \lambda Z(R),\ Z(n+1) = \lambda Z(R+\lambda)$$

$$b(R) \propto \exp[-F(R)/k_B T]$$

Boltzmann

Mura and Zaccone, PRE 2016

Nucleation rate in shear flow

$$J = -De^{-\frac{F(R)}{k_B T}} \frac{\partial}{\partial R}\left(Ze^{\frac{F(R)}{k_B T}}\right),$$

$K_N \equiv \frac{J}{N_{\text{tot}}}$ at steady-state, J = const

$$K_N = \frac{D(R^*)}{\pi k_B T}\sqrt{-F''(R^*)F''(R_0)}e^{-\frac{F(R^*)}{k_B T}}$$

$$= \frac{\left(8\nu + \frac{7\dot{\gamma}^2\eta^2\nu}{3G^2}\right)D(R^*)}{k_B T}e^{-\frac{F(R^*)}{k_B T}},$$

free energy barrier for nucleus growth under shear flow

$$K_N^0 = \frac{\left(8\nu + \frac{7\dot{\gamma}^2\eta^2\nu}{3G^2}\right)4a^2\pi(R^*+a)(D_a + D_{R^*})c_0}{k_B T \int_0^{\frac{\delta}{(R+a)}} \frac{dx}{(x+1)^2}\exp\left[\int_{\frac{\delta}{(R+a)}}^{x} dx\left(\frac{dU}{dx} - 4\text{Pe}\tilde{v}_{r,\text{eff}}\right)\right]}$$

rate of attachment of one particle to the nucleus

cfr. our previous solution to the Smoluchowski eq. (Zaccone et al. PRE 2009)

Free energy of nucleus growth in shear

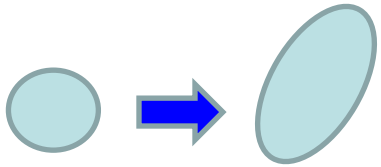
$$F(R) = -\frac{4}{3}\pi R^3 \frac{|\Delta\mu|}{v'} + 4\pi R^2 \nu$$

free energy
of classical nucleation

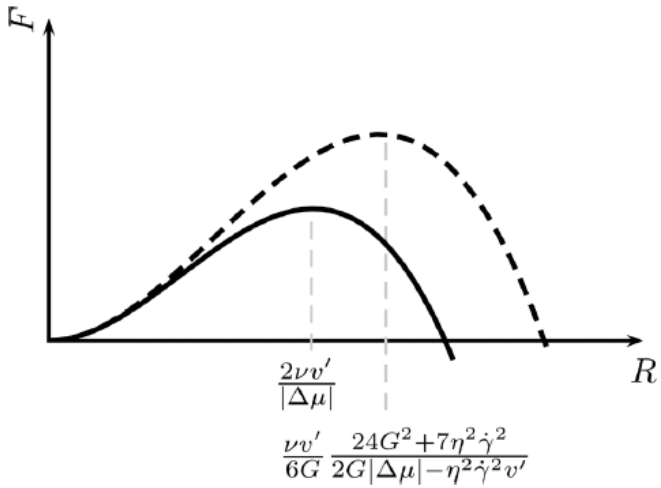
volume term

surface tension term

Under shear flow it gets modified to:



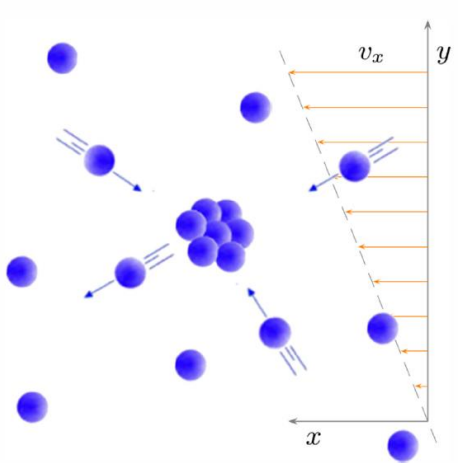
$$F = -\frac{4}{3}\pi R^3 \frac{|\Delta\mu|}{v'} + 4\pi R^2 \nu \left(1 + \frac{7}{24}\frac{\eta^2\dot{\gamma}^2}{G^2}\right) + \frac{1}{2}\frac{\eta^2\dot{\gamma}^2}{G}\frac{4}{3}\pi R^3,$$



elastic nucleus deformation under
shear flow stress $\frac{F_s}{V} = \frac{1}{2}\sigma_{ik}u_{ik}$

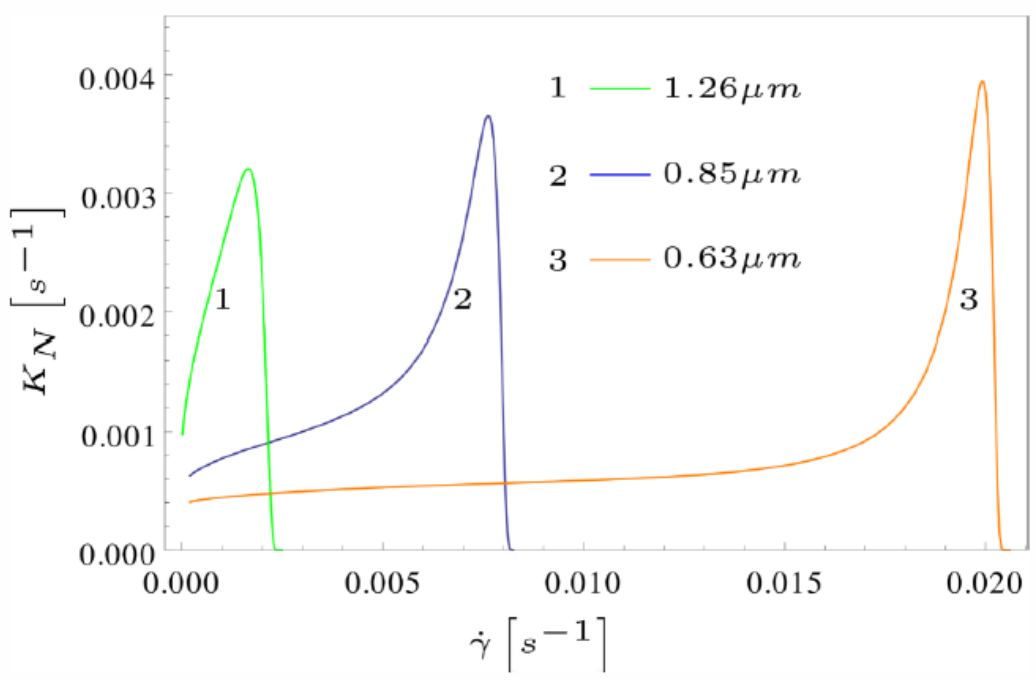
Mura & Zaccone, PRE 2016

Crystal nucleation in shear flows



We have extended the Frenkel-Zeldovich formulation of classical nucleation theory to include the effect of shear flow

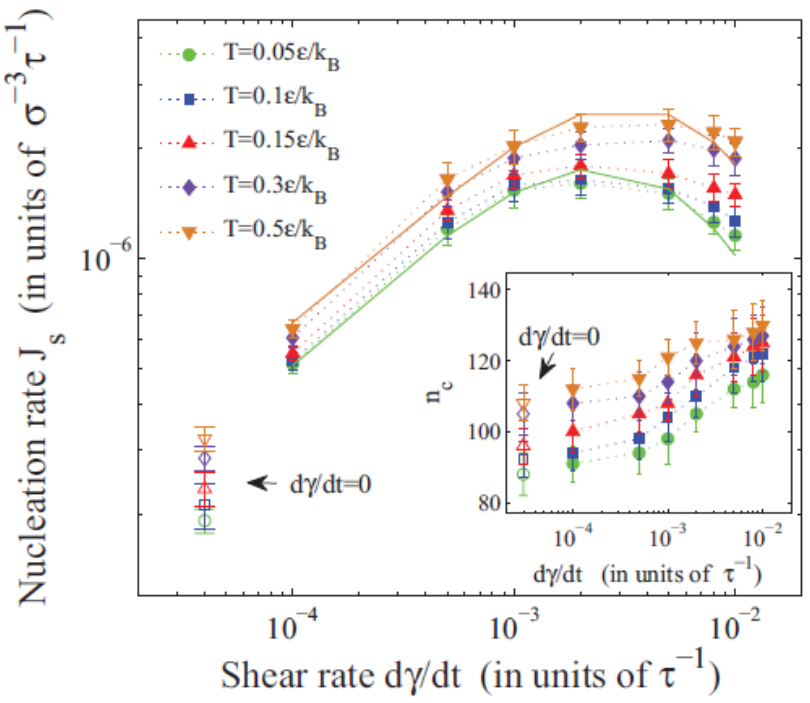
The prefactor is calculated from an analytical solution to the Smoluchowski convective-diffusion eq. while the energy barrier is calculated accounting for the strain energy



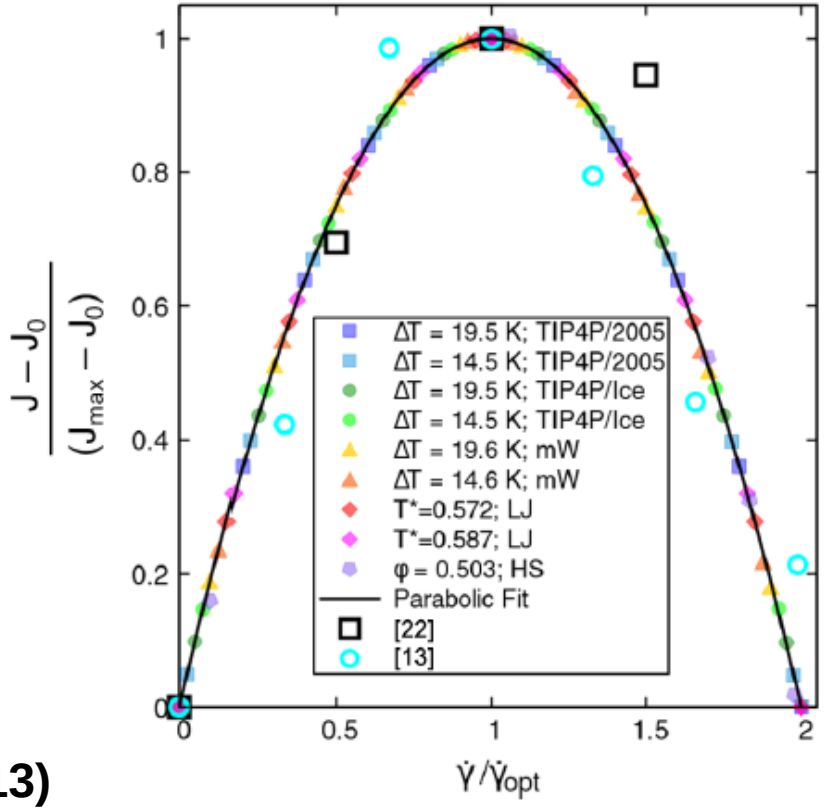
Theory predicts that nucleation rate has a strong maximum as a function of shear rate due to competition between transport and strain energy

Mura and Zaccone, PRE 2016

Confirmation of the “peak” prediction - simulations data



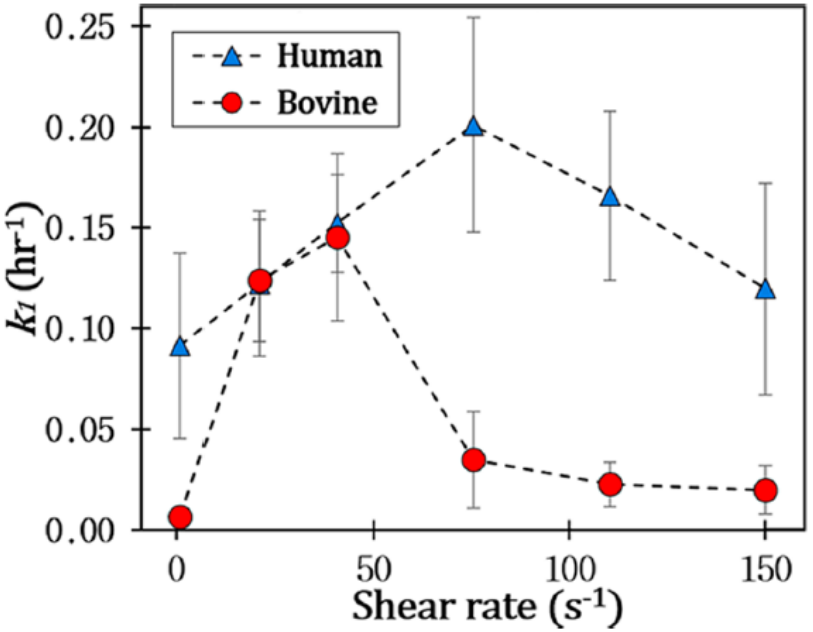
Mokshin, Galimzyanov, Barrat, PRE (2013)

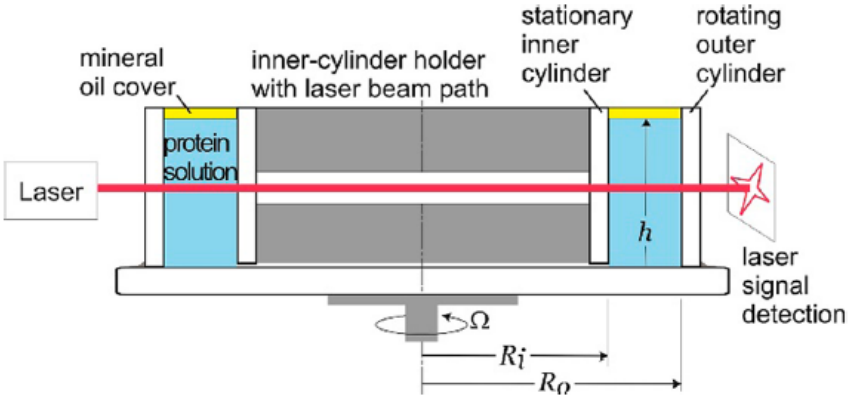


Goswami, Dalal, Singh, PRL (2021)

Confirmation of the universal “peak” prediction - experimental data (1)

Nucleation rate of **insulin** in water solution in rotating Couette device





McBride, Tilger, et al. JPhysChemB (2015)

Confirmation of the universal “peak” prediction - experimental data (2)

CRYSTAL GROWTH & DESIGN

pubs.acs.org/crystal

Article

Coll. with the Scheid Group at ULB, Belgium

Experimental and Theoretical Investigation of Nonclassical Shear-Induced Nucleation Mechanism for Small Molecule

Robin Debuysschère, Bart Rimez, Alessio Zaccone, and Benoit Scheid*

Cite This: *Cryst. Growth Des.* 2023, 23, 4979–4989

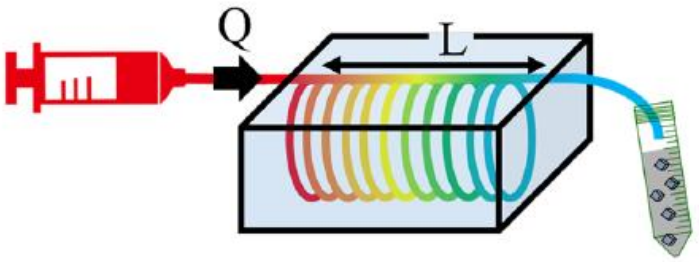
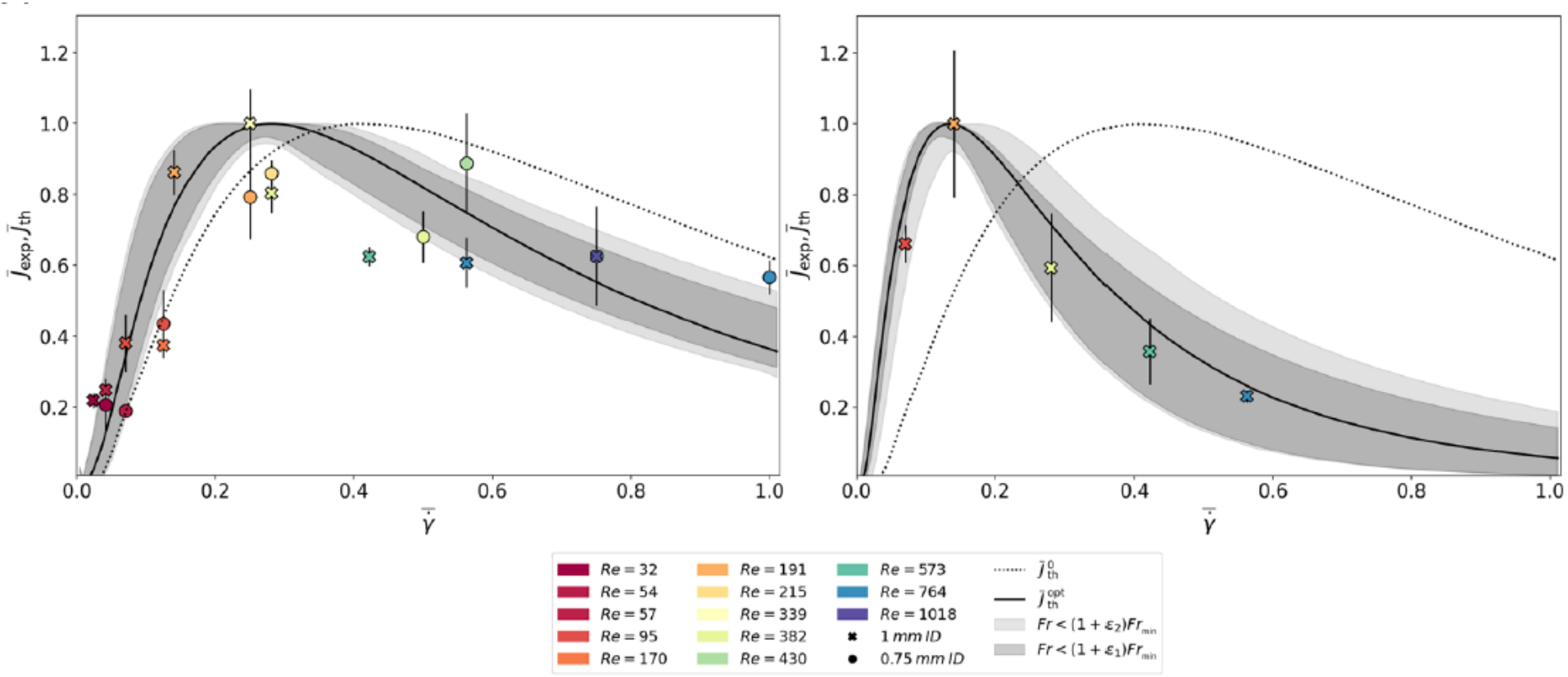


Table 1. Experimental Parameters: Flow Rate (Q), and Internal Diameter (ID) and Associated Reynolds Number (Re) and Length (L) of the Microfluidic Tube to Evaluate the Effect of Shear Rate ($\dot{\gamma}$) on the Nucleation Rate

Test	Q [ml/min]	ID [mm]	Re	$\dot{\gamma}$ [s^{-1}]	L [m]
1	1.67	1.0	32.0	284	0.42
2	1.25	0.75	32.0	503	0.56
3	2.96	1.0	57.0	503	0.74
4	5.0	1.0	95.0	849	1.25
5	2.11	0.75	54.0	849	0.94
6	3.75	0.75	95.0	1509	1.67
7	8.89	1.0	170.0	1509	2.22
8	10.0	1.0	191.0	1698	2.5
9	7.5	0.75	191.0	3018	3.33
10	17.78	1.0	339.0	3018	4.44
11	20.0	1.0	382.0	3395	5.0
12	8.44	0.75	215.0	3395	3.75
13	30.0	1.0	573.0	5093	7.5
14	15.0	0.75	382.0	6036	6.67
15	40.0	1.0	764.0	6791	10.0
16	16.88	0.75	430.0	6791	7.5
17	22.5	0.75	573.0	9054	10.0
18	53.33	1.0	1018.0	9054	13.33
19	30.0	0.75	764.0	12072	13.33

Confirmation of the universal “peak” prediction - experimental data (2)



- Non-classical mechanism: intermediary amorphous structures are formed first, which are sensitive to the shear flow as described by the theory
- Sensitivity analysis was performed on the physical quantities that could not be measured ⇨ interval of confidence in the comparison with theory

Conclusions – nucleation in shear

TAKE-HOME MESSAGE: CRYSTAL NUCLEATION THEORY HAS BEEN EXTENDED TO SYSTEMS UNDER SHEAR FLOW

THERE IS A COMPETITION BETWEEN SHEAR-ENHANCEMENT OF THE ATTACHMENT RATE OF A MOLECULE TO THE NUCLEUS AND THE MECHANICAL EFFECT OF SHEAR RISING THE ENERGY BARRIER FOR NUCLEATION

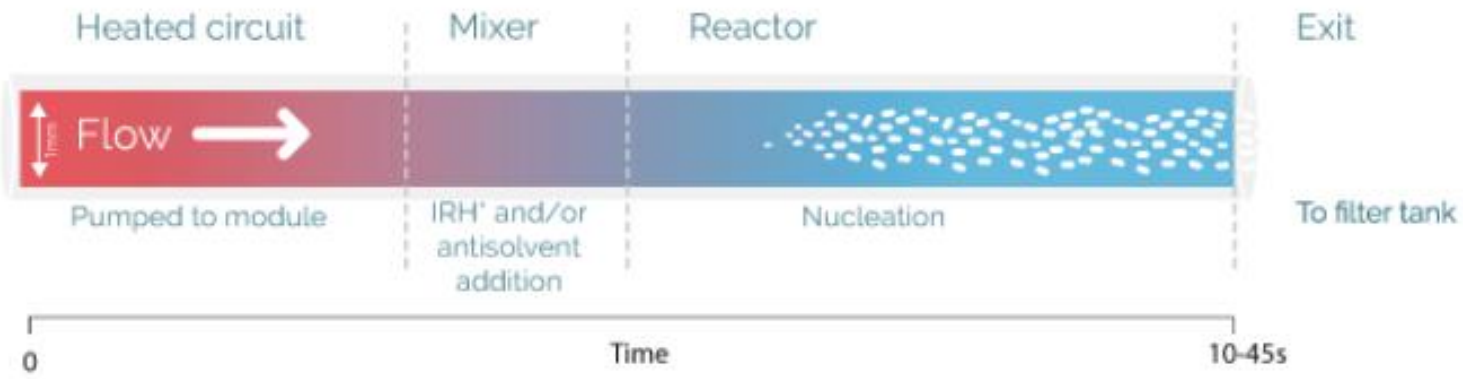
THIS LEADS TO A MAXIMUM IN THE NUCLEATION RATE VS THE FLOW RATE

FUTURE WORK: STUDY THE MODEL MORE SYSTEMATICALLY FOR DIFFERENT MOLECULAR SYSTEMS AND FLOW CONDITIONS

More details in Mura & Zaccone PRE (2016) – theory and Debruysschere et al. Cryst. Growth Design (2023) – expt validation

NB: for polymers situation slightly different, theories by Graham & Olmsted

From theoretical physics to real-world technological impact: flow-reactors (1)



*Internal Resistive Hydrodynamics

Secoya
FLUIDIFY PHARMA

Industrial customers:
Bayer, Pzitzer, among others

Industrial crystallization equipment: the SCT-ICE

From theoretical physics to technological impact: nuclear reactor waste (2)

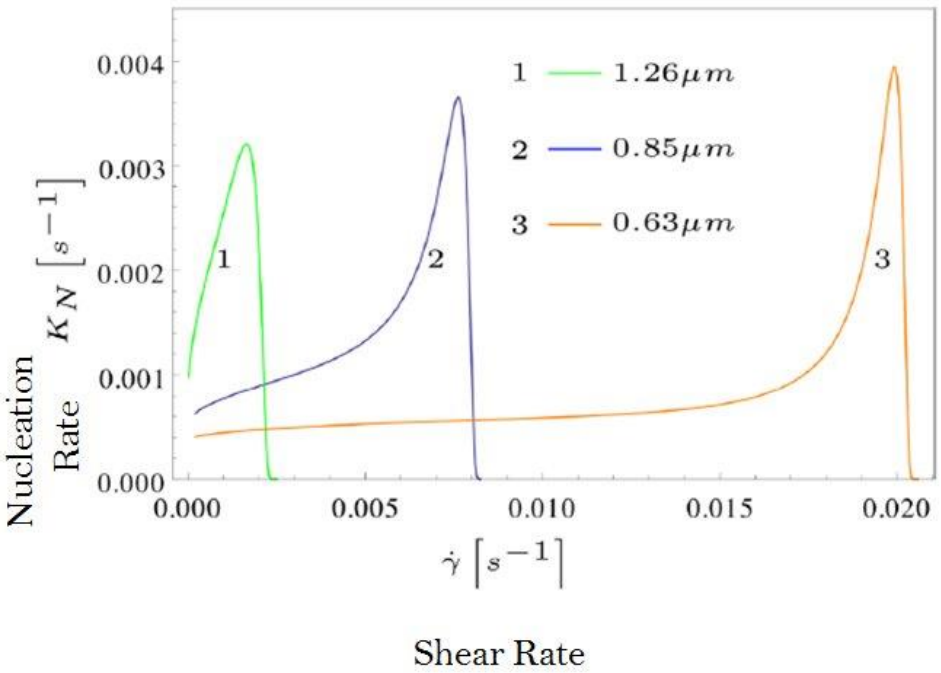
INTERNATIONAL JOURNAL OF Applied Glass SCIENCE

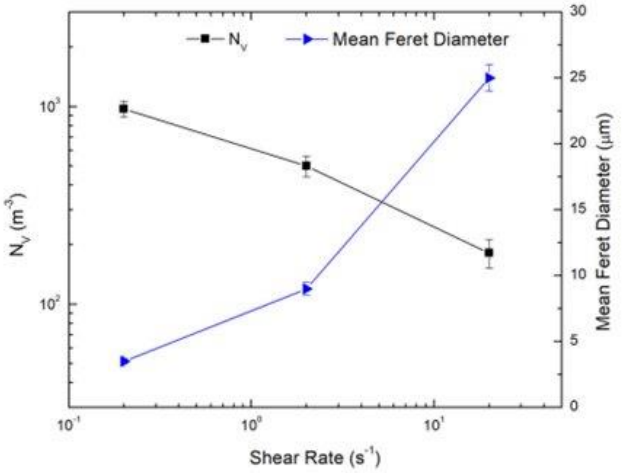
Precipitation of cerianite crystals and its effect on the rheology of a simplified nuclear glass melt

Jeanini Jiusti, Elise Regnier, Norma Maria Machado, Mohamed Leith Ghazzai, Vincent Malivert, Muriel Neyret, François Faure

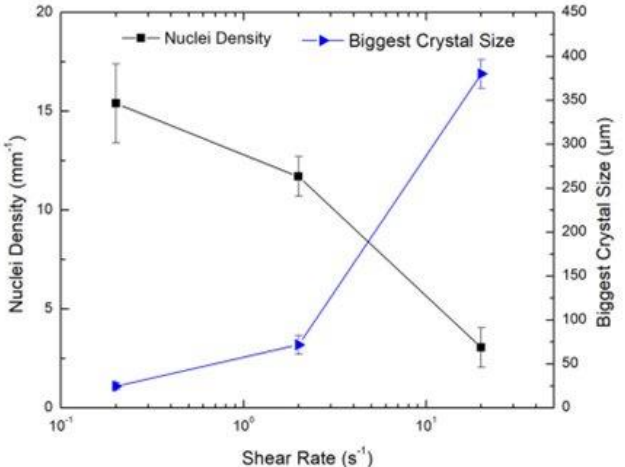
nuclear waste melt crystallization enhanced by shear flow:
since the atomic packing density is larger in the crystal than in the glass, this allows for a higher nuclear waste storage density

FEDERICA MURA AND ALESSIO ZACCONE **Phys. Rev. E 2016**





Jiusti et al. **Applied Glass Science 2023**



Future developments: chemically reactive systems

A can convert to B that forms drops (which nucleate),
and viceversa,
droplet material B turns into precursor A inside droplets,
while B is replenished outside (irreversible reactions)

PHYSICAL REVIEW LETTERS **130,** 248201 (2023)

Nucleation of Chemically Active Droplets

Noah Ziethen, Jan Kirschbaum, and David Zwicker*
Max Planck Institute for Dynamics and Self-Organization, Am Faßberg 17 37077, Göttingen, Germany

$$\tilde{F}(R) \approx -gV + \gamma A + F_{\text{react}}(R)$$

conc. inside drop

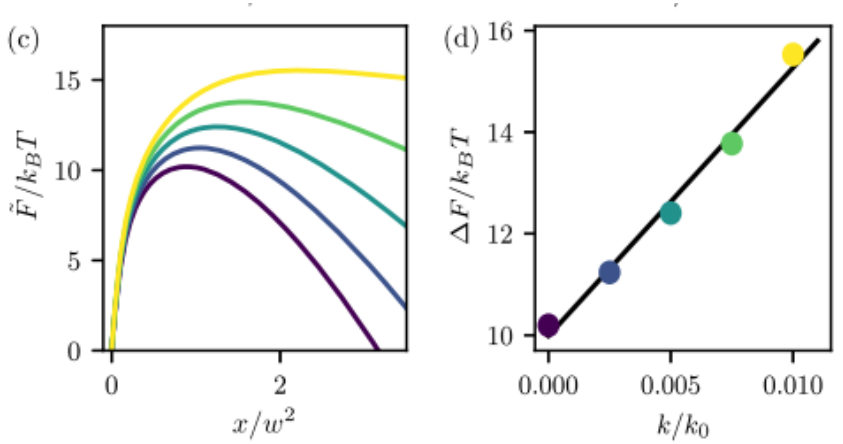
$$F_{\text{react}}(R) \approx \frac{\pi(c_{\text{in}} - c_0)^2}{16\Lambda_{\text{d}}} kR^4$$

diffusive mobility

reaction rate

$$\Delta F \approx \frac{\pi\gamma^2}{g}\left[1 + k\frac{\gamma^2(c_{\text{in}} - c_0)^2}{16g^3\Lambda_{\text{d}}}\right]$$

reaction rate increases
the nucleation barrier



Potential ideas & challenges for future work

1. Investigate shear-induced breakup rate of nuclei
2. Improve determination of surface energy (e.g. atomistic simulations)
3. Exploit chemical reactions to increase the nucleation rate
4. Turbulent conditions?
5. ….

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Students & post-docs on these projects

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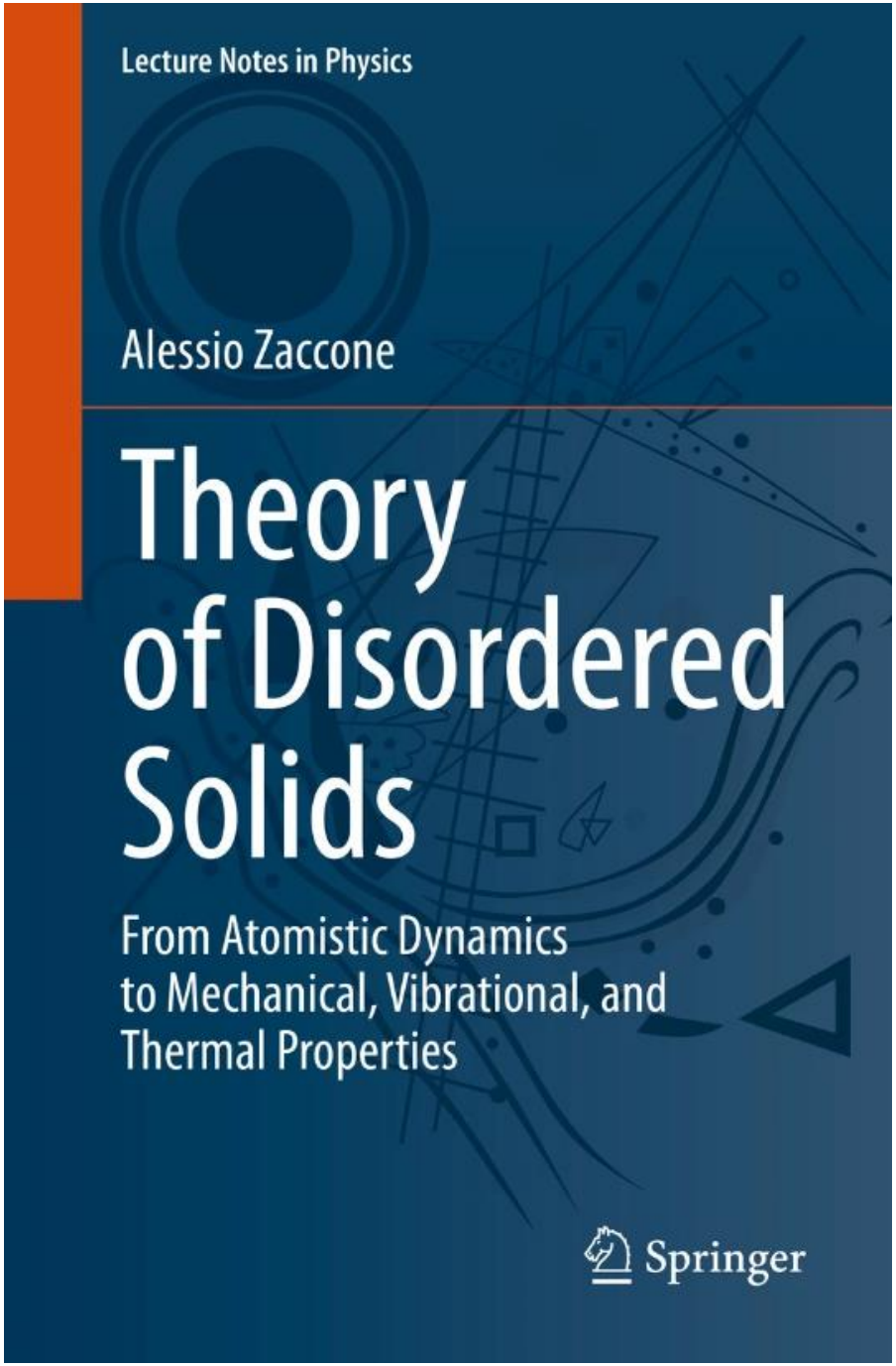
U.S. Army Research Office Grant under Cooperative Agreement No. W911NF-19-2-0055

European Research Council
ERC Consolidator Grant "Multimech"
(officially started 2023)

Now out and available!



Percus-Yevick theory (1)

$$g(\mathbf{r}_1, \mathbf{r}_2) = g(\mathbf{r}_1 - \mathbf{r}_2) \equiv g(\mathbf{r}_{12}) = g(|\mathbf{r}_{12}|) \equiv g(r_{12}) \equiv g(12)$$

$$h(12) \equiv g(12) - 1$$

$$h(12) = c(12) + \rho \int \mathrm{d}^3\mathbf{r}_3 \, c(13)\, h(32) \qquad \text{or:}$$

$$h(r) = c(r) + \rho \int \mathrm{d}\mathbf{r}' c(r') h(|\mathbf{r} - \mathbf{r}'|)$$ **Ornstein-Zernike** eq.

which comes from a formal perturbative expansion:

$$h = c + \rho c * c + \rho^2 c * c * c + \ldots$$

$$c(r) = -\beta v(r) \qquad r \gg \sigma$$

Under extremely dilute conditions $h(r) \simeq c(r)$

Percus-Yevick theory (2)

$$h(r) = -1 \qquad r < \sigma$$

hard-core impenetrability

$h(r) = g(r) - 1$

$$c(r) = 0 \qquad r > \sigma$$

for HS there are no direct interactions outside the hard-core contact diameter

Percus-Yevick closure

together with the Ornstein-Zernike equation they form a closed set of relations for the unknown functions $h(r)$ and $g(r)$

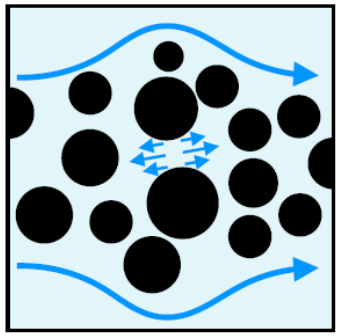
Analytically solved by **Wertheim, Phys. Rev. Lett. (1963)** with more details in **Wertheim, J. Math. Phys. (1964)**

$$g(\sigma) = \frac{1 + \frac{\phi}{2}}{(1 - \phi)^2} \qquad \text{in } d{=}3$$

Leutheusser, Physica (1984)

$$g(\sigma^+) = \frac{(1 + 18\eta + 6\eta^2)^{3/2} - 1 + 33\eta + 87\eta^2 + 6\eta^3}{60\eta(1 - \eta)^3} \qquad \text{in } d{=}5$$

Hydrodynamic interactions at the two-particle level (1)



● Lubrication forces (resistance of incompressible solvent being squeezed as two particles approach)

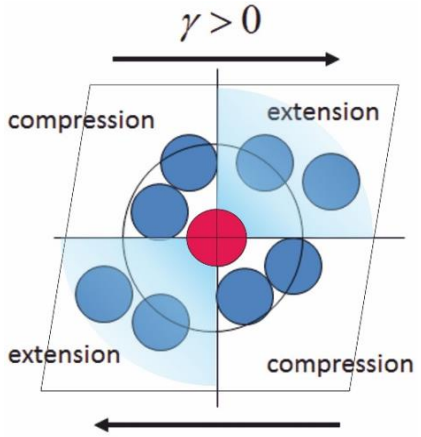
$$G(h) = \frac{6h^2 + 4h}{6h^2 + 13h + 2}$$

interpolation form
of Stimson & Jeffery's 1926
solution to Stokes equation for two spheres

$$D(r) = G(r)D_0$$

● Hydrodynamic interaction due to the mutual relative motion of the two particles

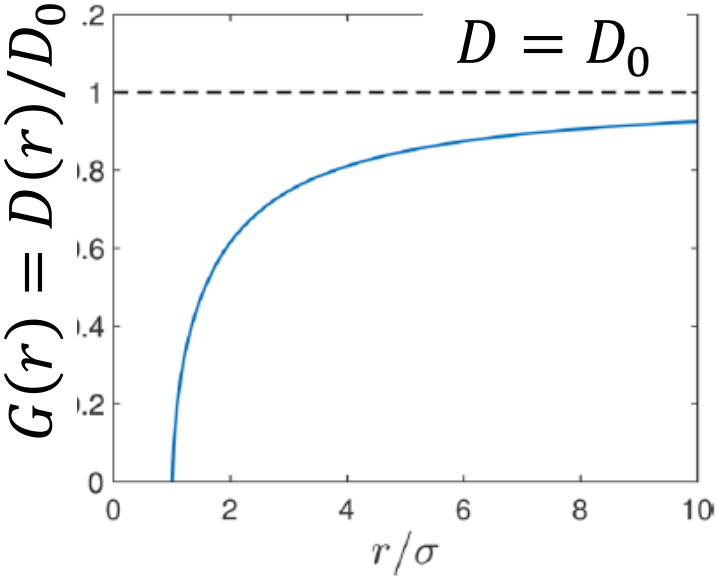
$$\tilde{v}_{r,\mathrm{eff}}(x) \equiv \langle \tilde{v}_r^+(\mathbf{r}) \rangle = -(1/3\pi)(x+2)[1 - A_S(x)]$$



hydrodynamic function
from Batchelor & Green's solution
for HI of two particles in a linear flow field

Hydrodynamic interactions at the two-particle level (2)

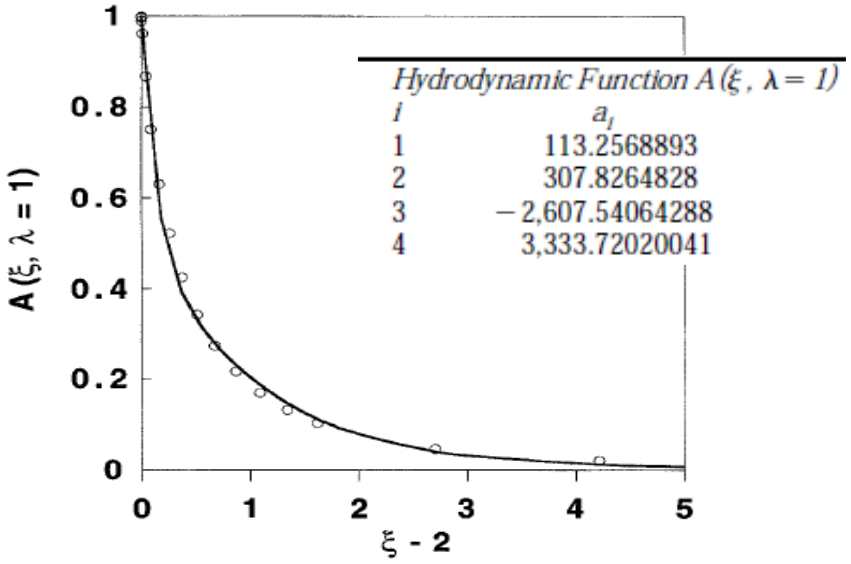
- Lubrication forces



$$G(h) = \frac{6h^2 + 4h}{6h^2 + 13h + 2}$$

$$h = (r - 2a)/2a$$

- Hydrodynamic function



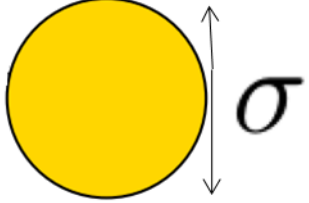
$$A(\xi, \lambda = 1) = \sum_{i=1}^{4} \frac{a_i}{\xi^{i+4}};$$

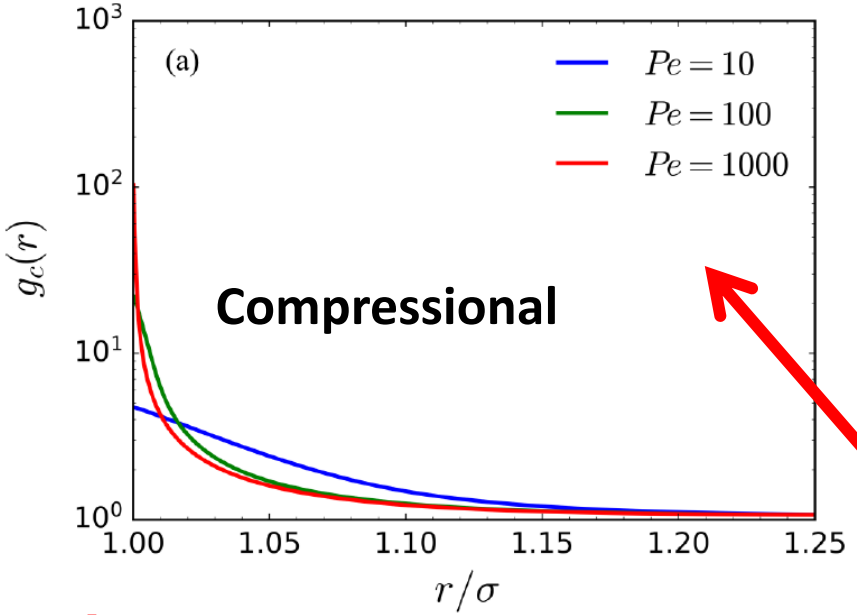
$$\xi = (r - 2a)/2a$$

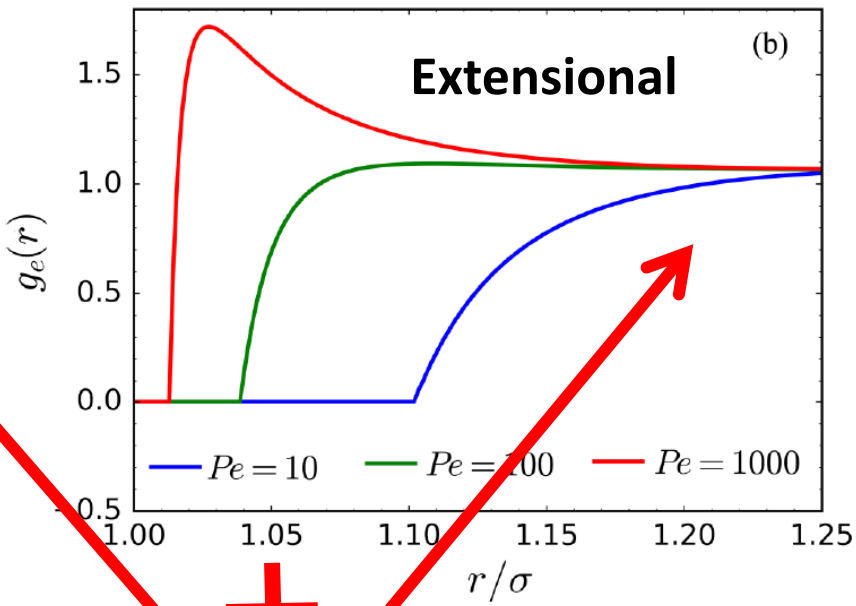
→ both hydrodynamic effects act as to slow-down the relative particle motion → effective “repulsion”

Hard-spheres

$$\beta u_{\mathrm{HS}}(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geqslant \sigma \end{cases}$$







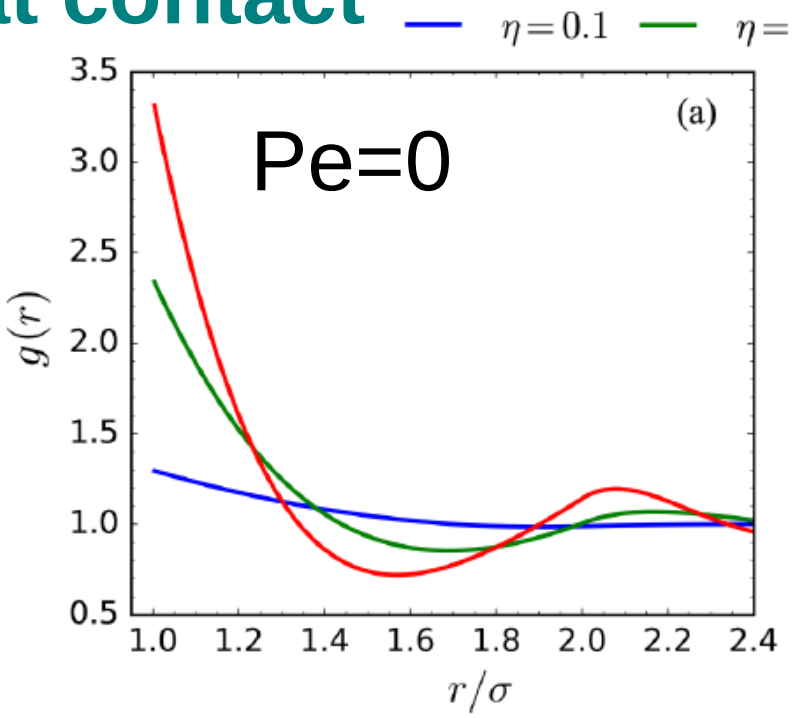
At larger concentrations…

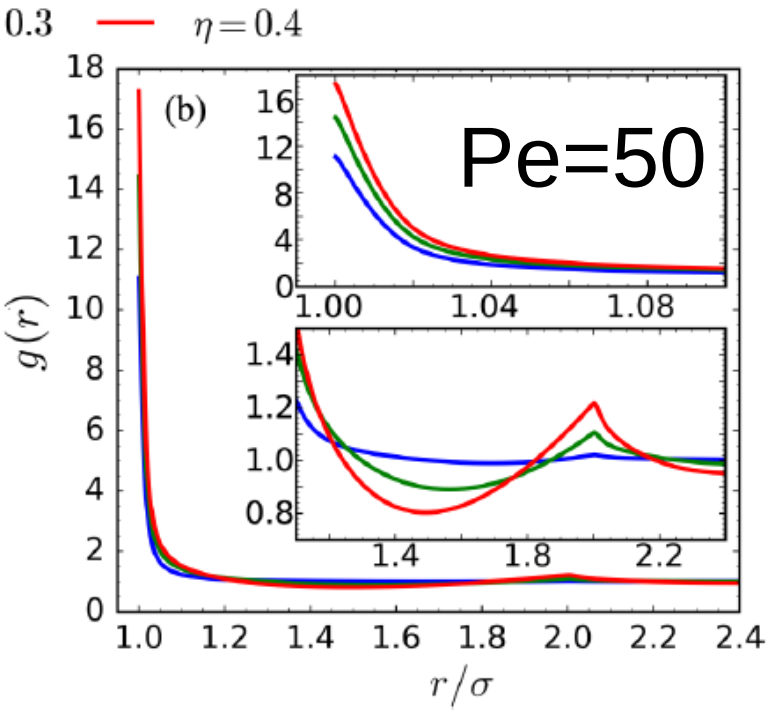
$$\beta u_{\mathrm{eff}}(r, \mathrm{Pe}) \equiv \begin{cases} \infty & r < \sigma \\ -\log[g_0(r)] & r \geqslant \sigma \end{cases}$$

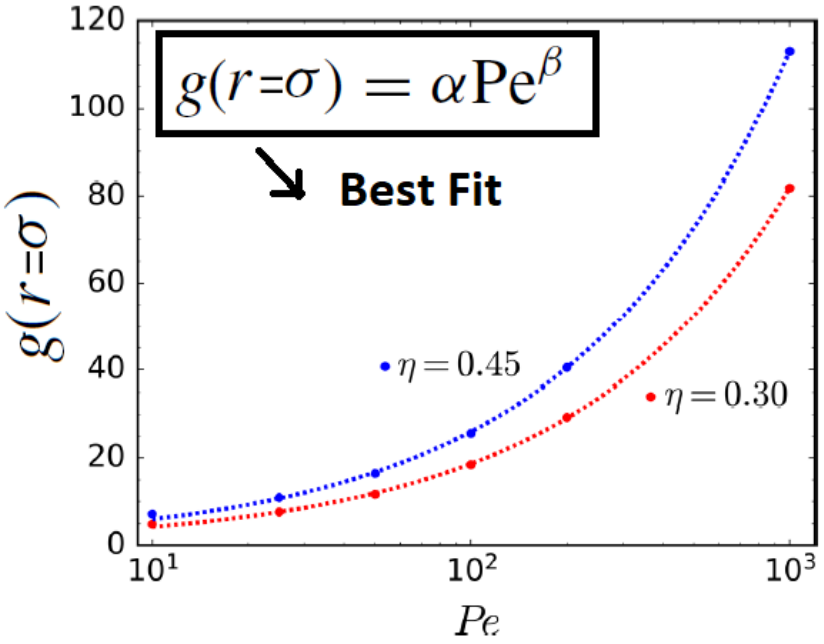
$$\begin{cases} h(r) = c(r) + \rho \int_V d\mathbf{r}_3 \, c(|\mathbf{r}_1 - \mathbf{r}_3|) h(|\mathbf{r}_3 - \mathbf{r}_2|) & \textbf{ORNSTEIN-ZERNIKE} \\ c(r) = g(r) - g(r) e^{\beta u(r)} & \textbf{PERCUS-YEVICK} \end{cases}$$

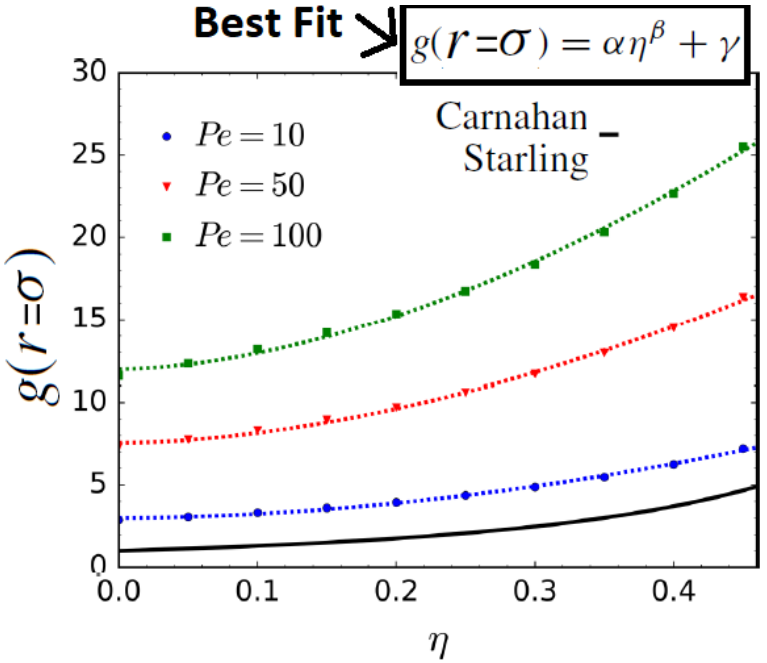
Banetta *et al.*, PRE 2022

g(r) at contact

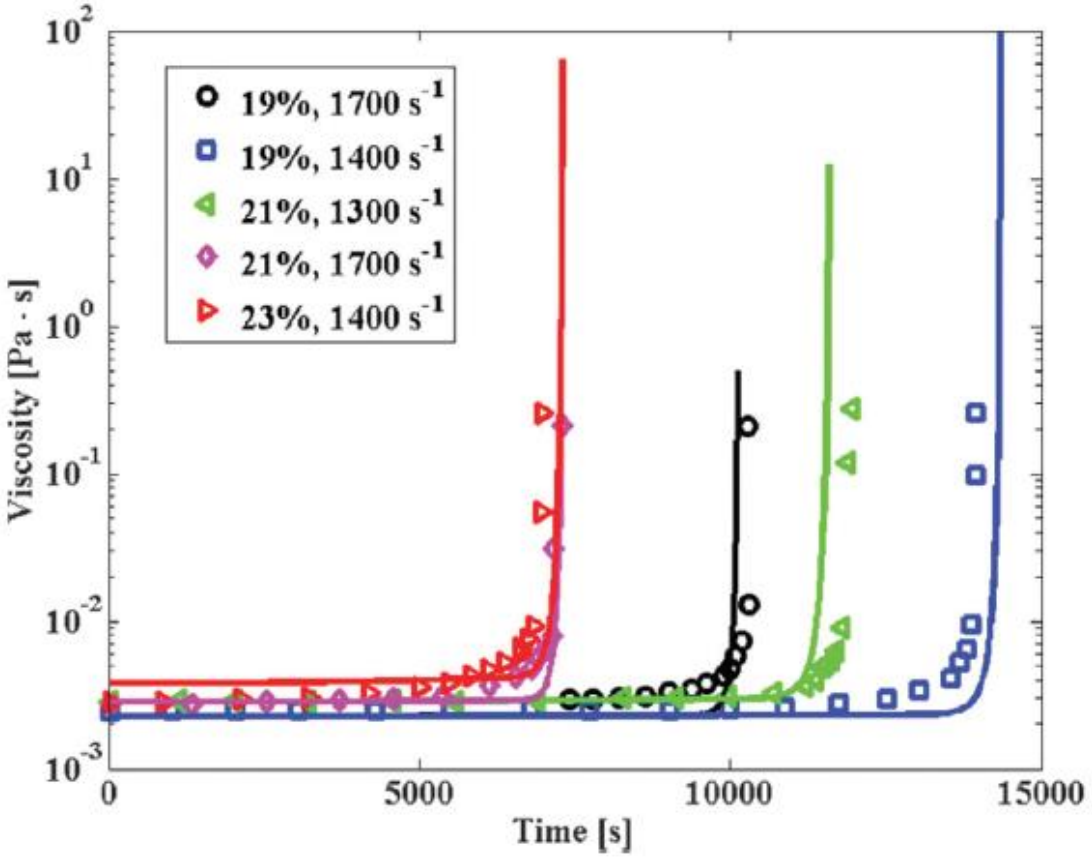








Comparison with experimental data (1)



Initial conditions:
Polystyrene colloids (monodisperse)
R=60 nm
φ = 0.21
charge-stabilized, V_{max} ~ 60kT
Ionic strength: 17mM of NaCl
Device: Couette-geometry rheometer,

$$\dot{\gamma} = 1700 \ \ s^{-1}$$

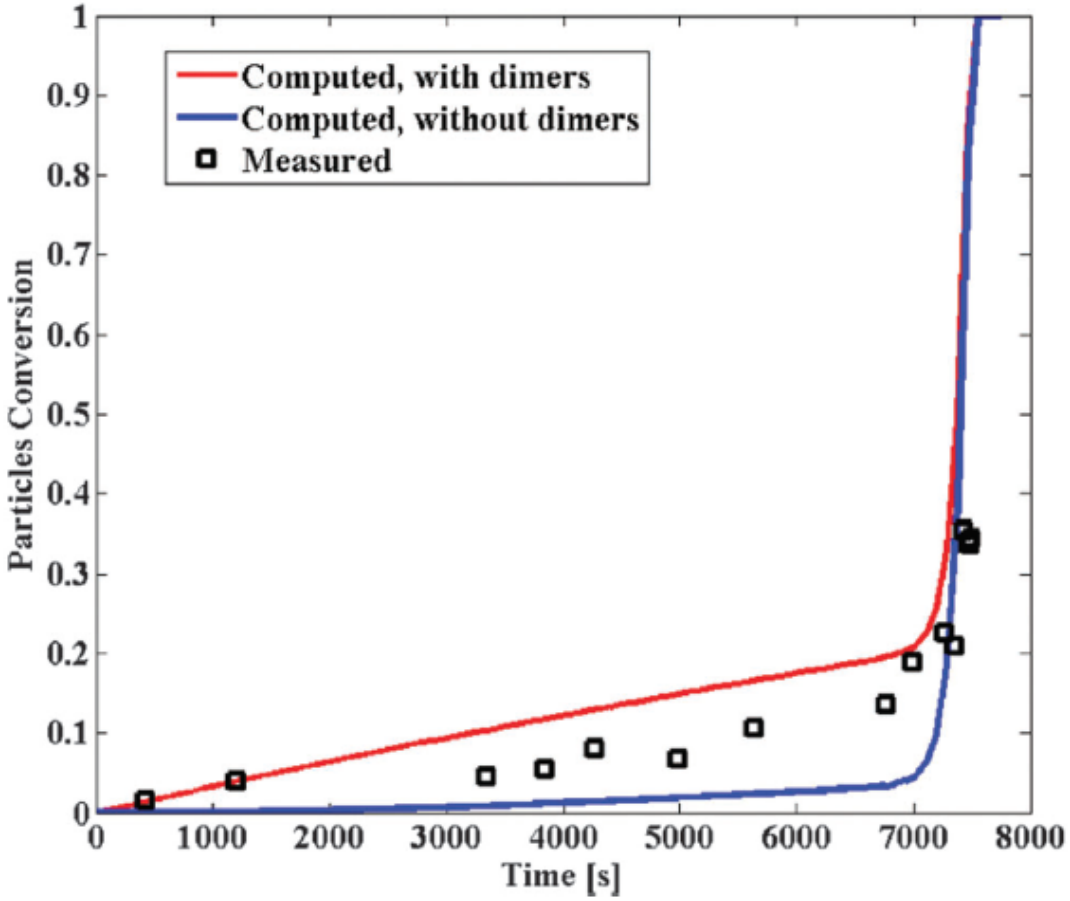
Expt. data from
Zaccone et al. PRL 2011

W ~ 10^8 (static Fuchs coefficient) is the only adjustable parameter (within the error bar on the electrostatics characterization)
Viscosity model: extension of Einstein for clusters with vol. frac. given by R_H

Lattuada, Zaccone, Wu, Morbidelli, Soft Matter (2016)

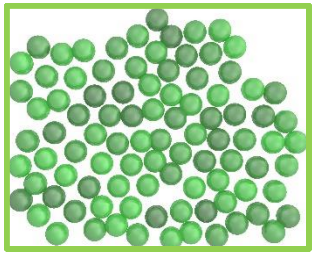
Comparison with experimental data (2)

Conversion of primary particles to (large) clusters measured by **filtration**, expt. data from **Zaccone, Gentili, et al. PRL 2011**



Predicting the evolution of viscosity

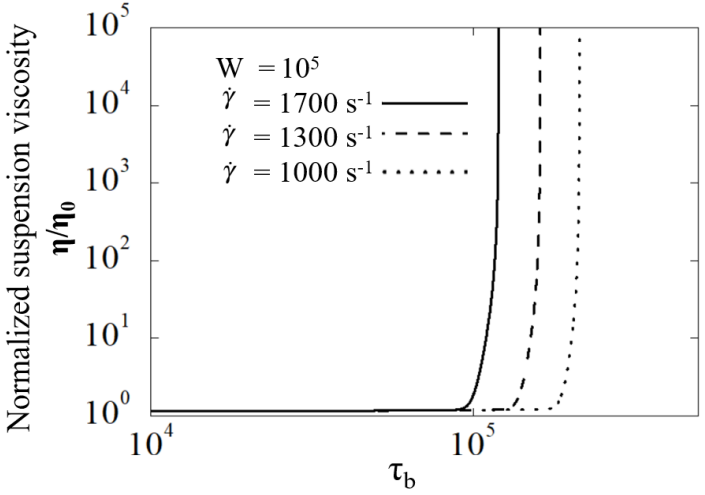
Effective packed



$$\phi = \frac{4}{3}\pi \int_0^{\infty} n(\xi,t) R_g^3 d\xi = \frac{4}{3}\pi \sum_{i=0}^{M} N_i R_{g,i}^3$$

$$\frac{\eta}{\eta_0} = \left(\frac{1-\phi/\phi_{cr}}{1-(k_0\phi_{cr}-1)\phi/\phi_{cr}} \right)^{-\phi_{cr}[\eta]/(2-k_0\phi_{cr})}$$

Shear rate



Colloidal stability