Dynamics and phase behavior of quasi-2D dispersions

Gerhard Nägele

Institute of Biological Information Processing, IBI – 4

Forschungszentrum Jülich GmbH, Germany

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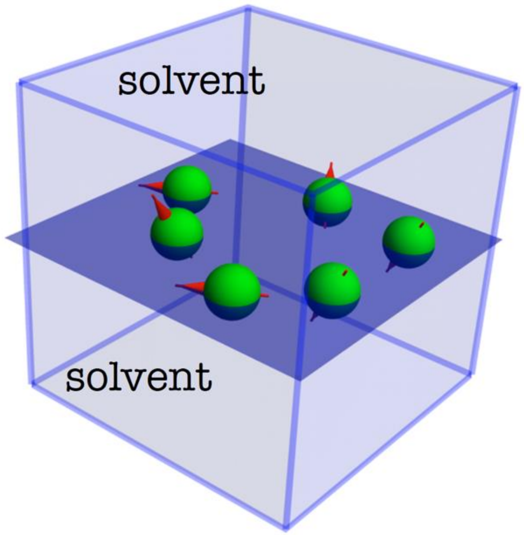
CONTENT

Quasi - 2D dispersions with competing SA – LR interactions

- Phase behavior, clustering and structure
- Dynamics without and with account of hydrodynamic interactions (HI)



Realization:

- Particles trapped in planar liquid interface
- Proteins attached to a membrane
- Q2D confinement using optical laser tweezers

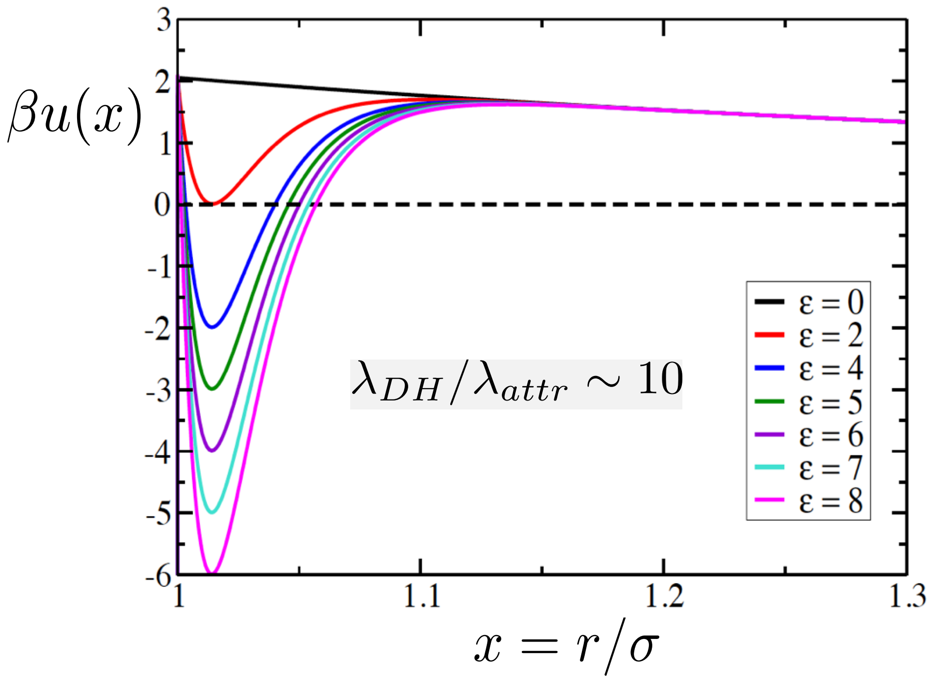
Applied methods:

- Langevin Dynamics simulations (LD without HI)
- Multi-particle collision dynamics (MPC with HI)

Tan, Calandrini, Dhont and **Nägele**, Soft Matter **20**, 9528 (2024)

Extended Lenard – Jones – Yukawa (LJY) model potential

represents short-range attractive plus long-range repulsive interactions (SA-LR)



$$\beta u(x) \;=\; 4\epsilon\left[\left(\frac{1}{x}\right)^{100} - \left(\frac{1}{x}\right)^{50}\right] + \frac{A\xi}{x}\exp\left(-x/\xi\right)$$

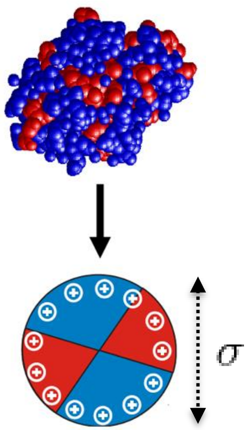
ε: strength of short - range attraction

$$A = 2 \quad (A \propto Z^2)$$

$$\xi = \lambda_{DH}/\sigma = 1.8$$

$$\beta u(x_{\min}) \approx 2 - \epsilon$$

$$T^* = \frac{1}{\epsilon} \sim \frac{k_B T}{|u(r_{\min})|}$$



hydrophobic patches

- LJY potential mimics low - salinity aqueous protein solutions (e.g., lysozyme in water)

Das, Riest, Winkler, Gompper, Dhont and **Nägele**, Soft Matter **14**, 92 (2018)

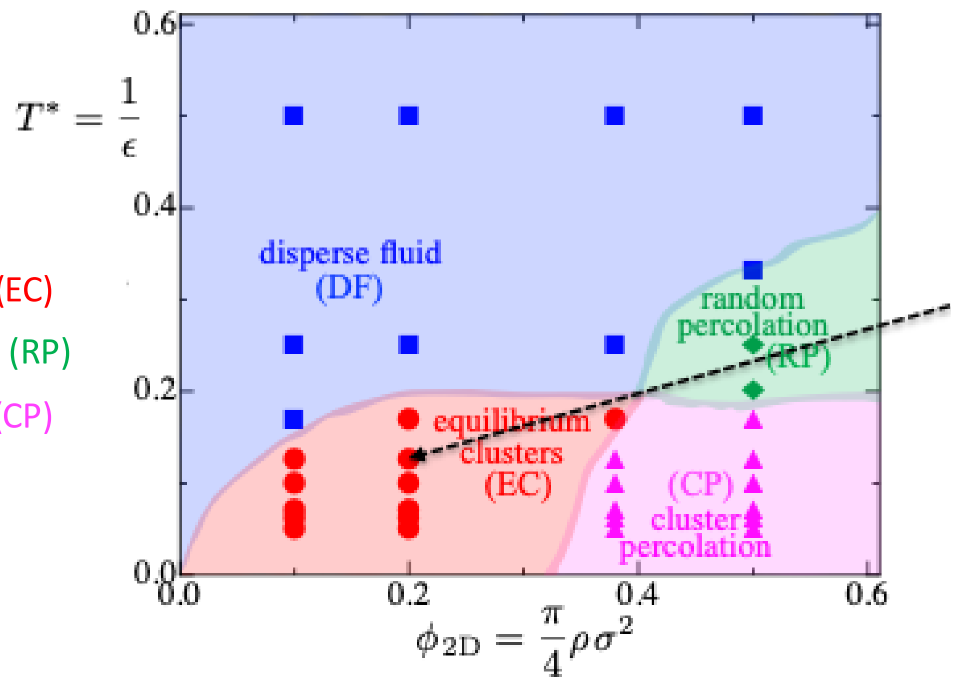
Q2D clustering and phase diagram (LD simulations)

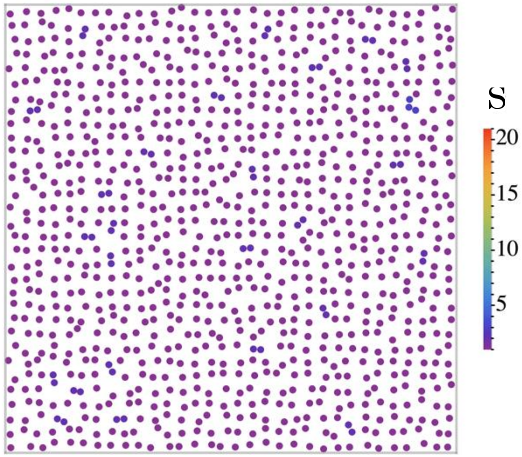
disperse fluid (DF)

equilibrium cluster (EC)

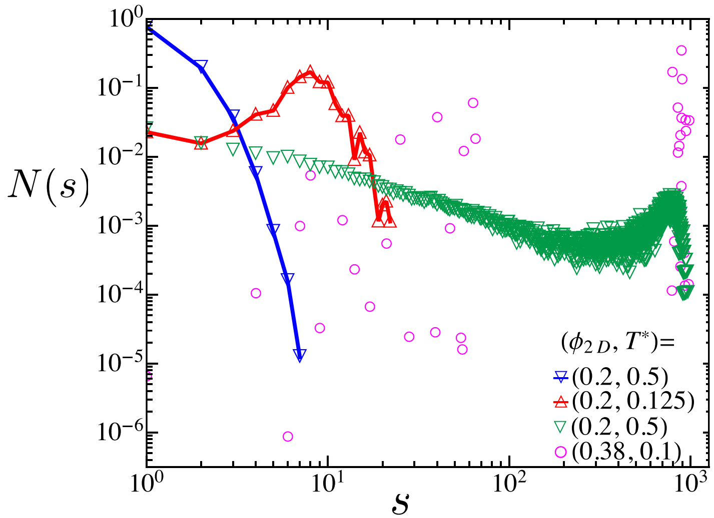
random percolation (RP)

cluster percolation (CP)





- (finite-sized) clusters formed: owing to **competitive interactions**
- Q2D state diagram similar to 3D state diagram in considered (ϕ_{2D}, T^*) range



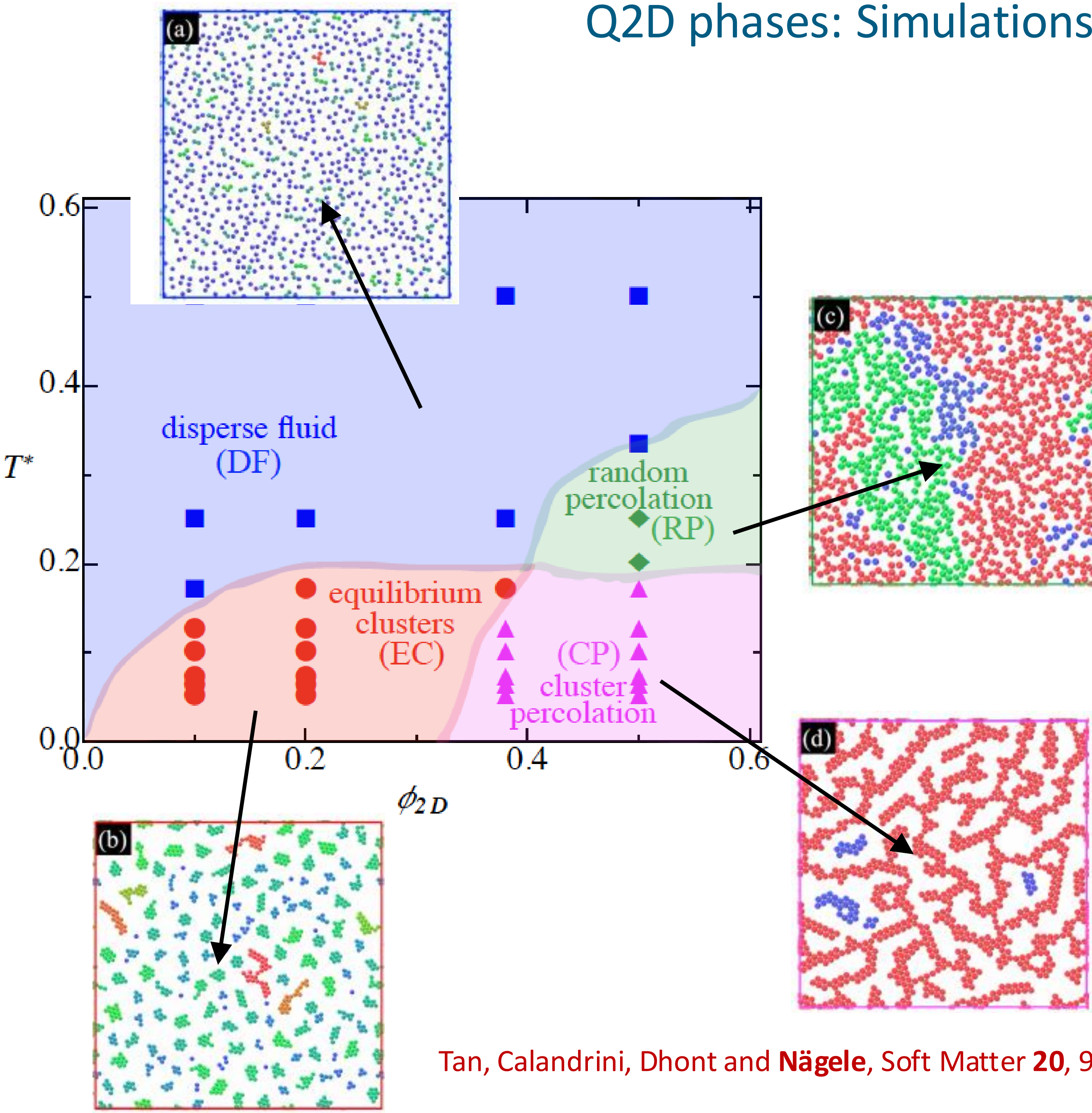
Cluster size distribution ***N(s)***:

fraction of proteins forming s-clusters

$$N(s) = \left\langle \frac{s}{N_p} n(s) \right\rangle$$

# of s - clusters

Q2D phases: Simulations snaphots

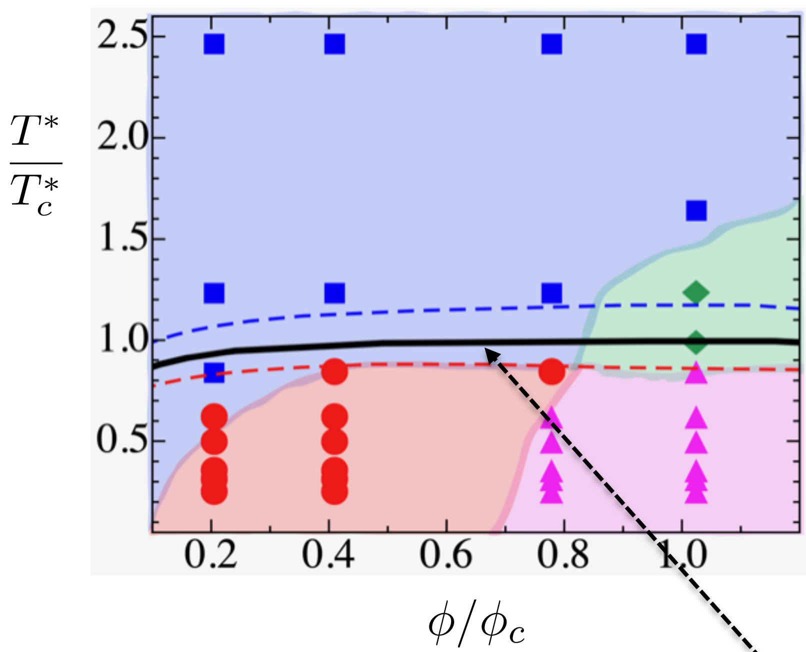


Tan, Calandrini, Dhont and **Nägele**, Soft Matter **20**, 9528 (2024)

Reduced state diagram and SA binodal

SA reference system mapped on 2D square – well potential system

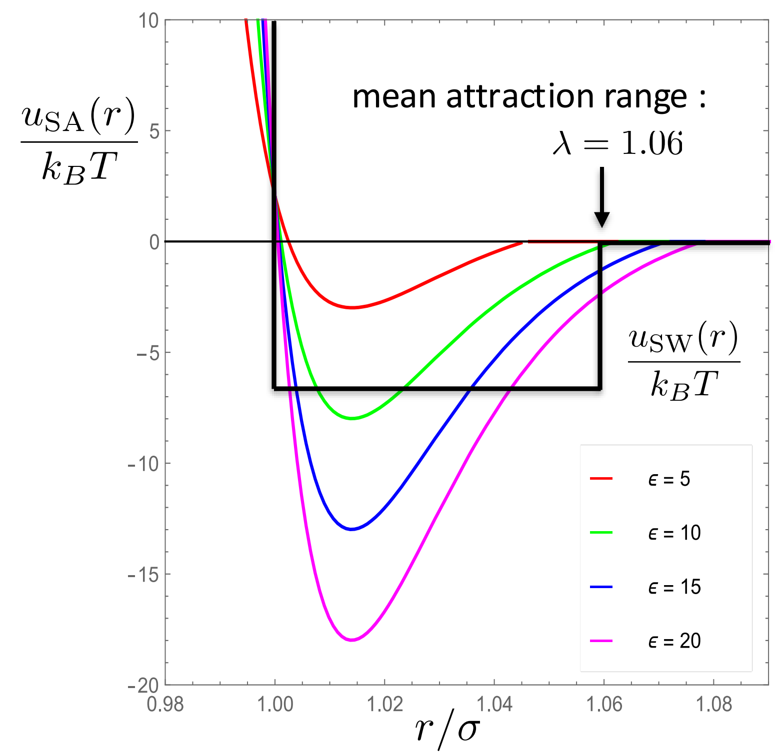
Metastable binodals of square – well system calculated using 2nd – order perturbation theory



$\lambda = 1.06$

$T_c^*(1.06) = 0.203$

$\phi_c(1.06) = 0.488$



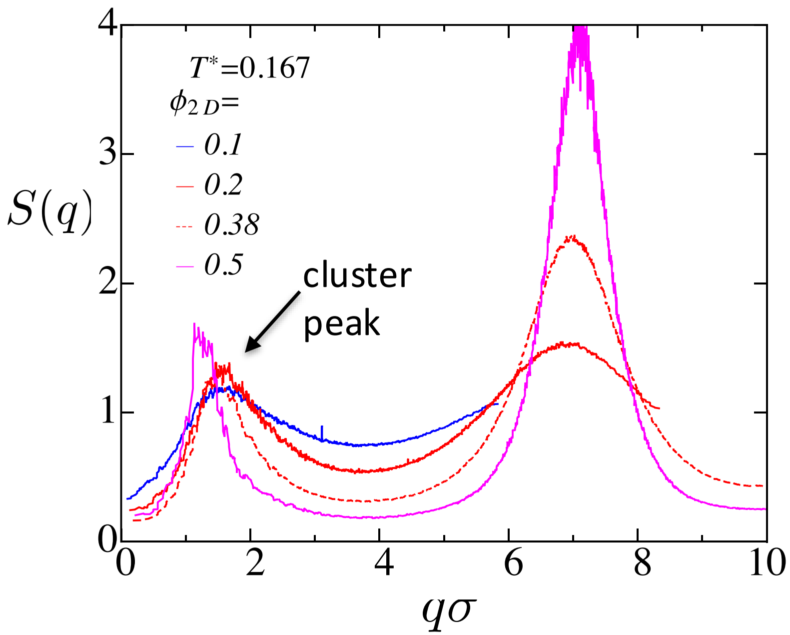
LR frustrates

SA gas – liquid transition by inducing cluster formation

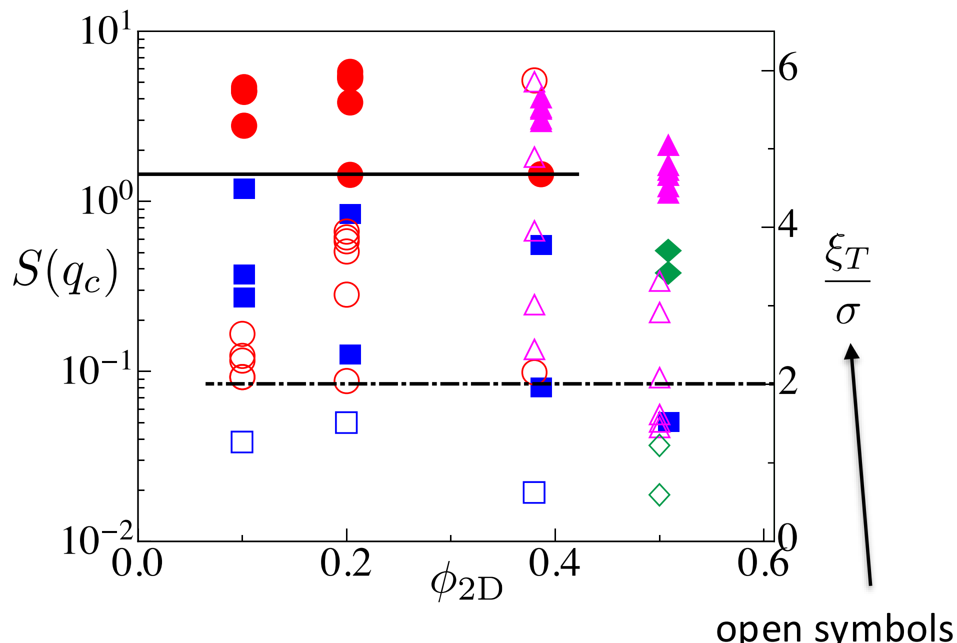
- Perturbation theory prediction: SA gas – liquid binodal sensitive to attraction range λ (in 2D)

Clustering indicators: DF (blue) to EC (red) transition

2D static structure factor



height and width of cluster peak of *S(q)*



cluster peak height:	$S(q_c) \approx 1.4 \quad (\approx 2.7 \text{ in 3D})$
cluster peak thermal width:	$\zeta_T/\sigma \approx 2 \sim \xi \approx 1.8$
Coordination number:	$\langle z_b \rangle \approx 1.6 \quad (\approx 2.4 \text{ in 3D})$

3D – Indicators:

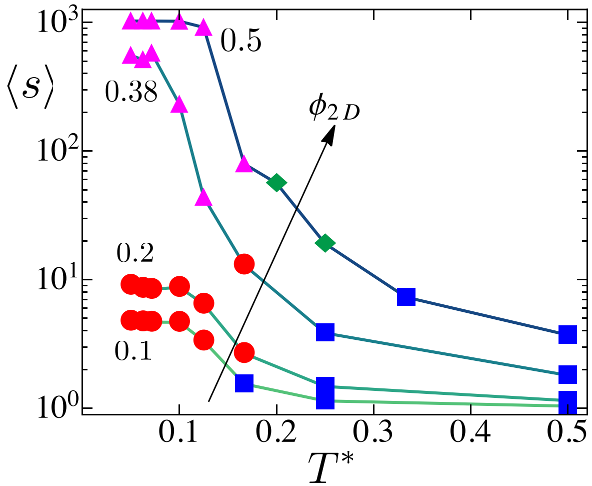
Godfrin, Castaneda - Priego et al., Soft Matter **10** (2014)

Bollinger & Truskett, JCP **145** (2016)

- Values of cluster peak indicators for DF to EC transition in Q2D are different from those in 3D

Global statistics of clusters

mean cluster size (N = 1000)



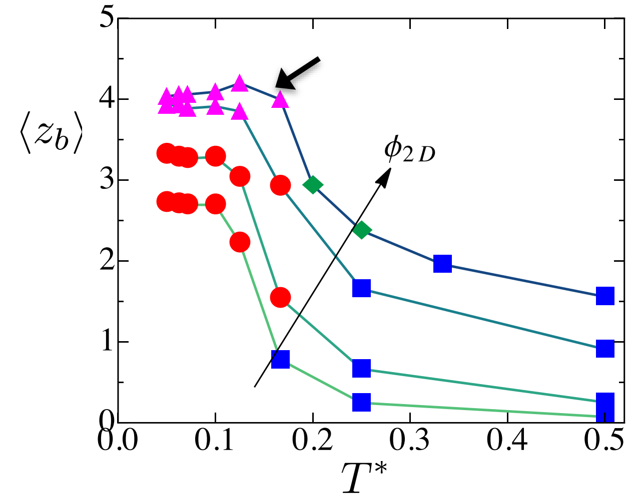
disperse fluid (DF)

equilibrium cluster (EC)

random percolation (RP)

cluster percolation (CP)

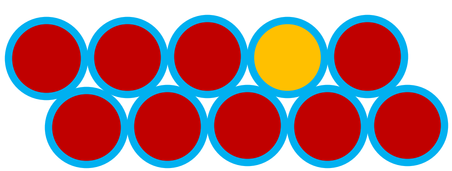
coordination number

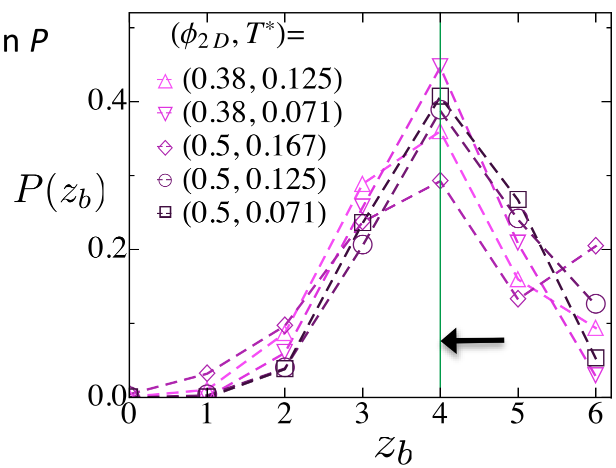


Discrete probability distribution function *P* of bond number z_b per particle

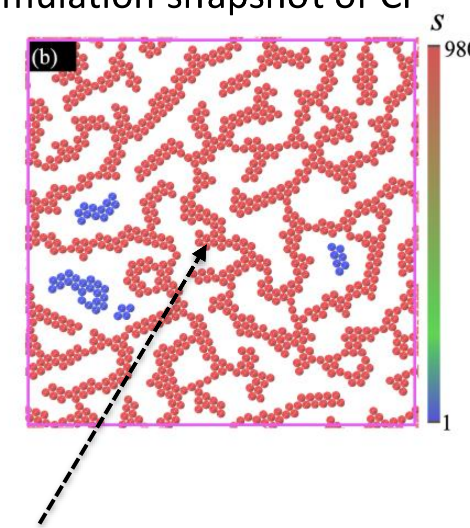
Example:

cluster percolated systems (CP)



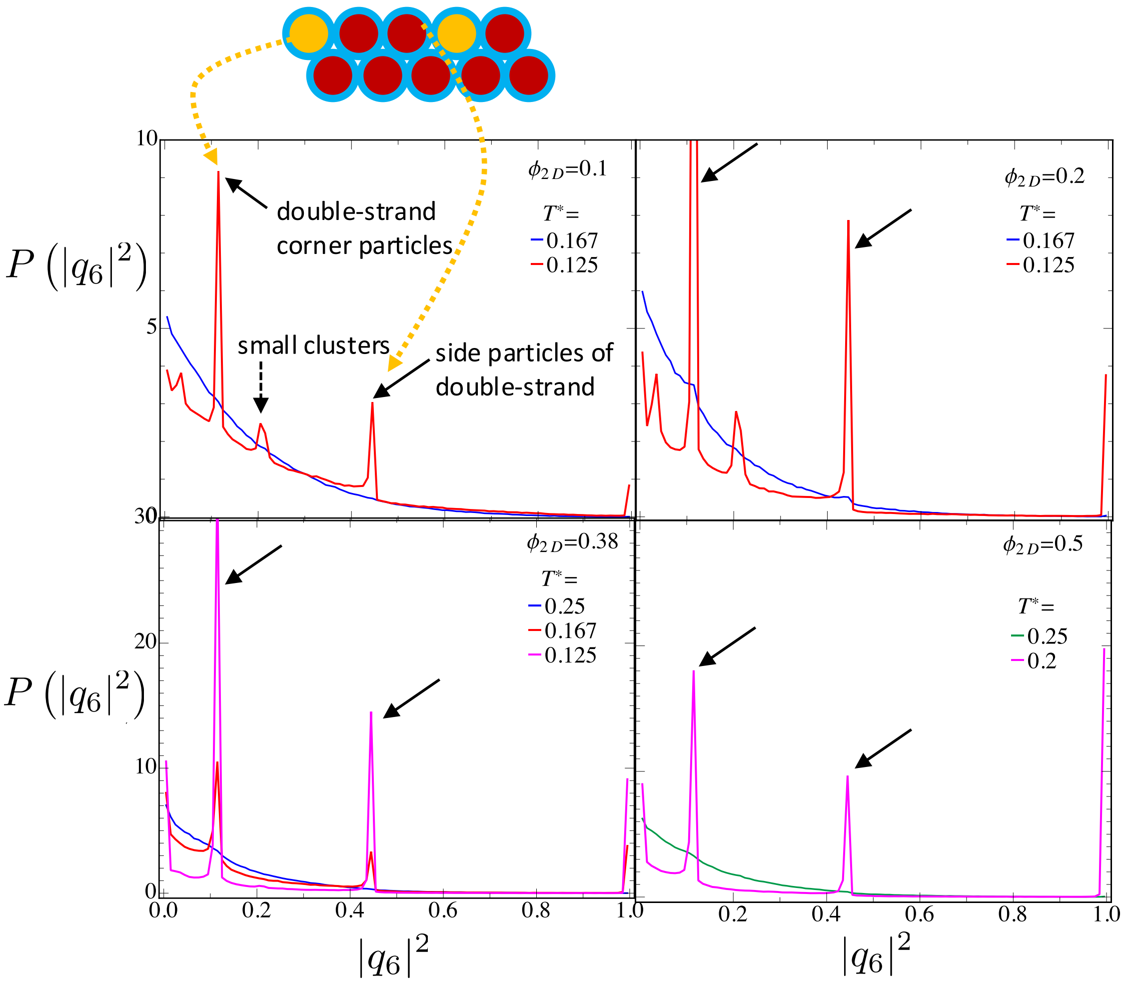


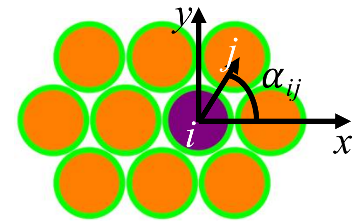
simulation snapshot of CP



Tan, Calandrini, Dhont and **Nägele**, Soft Matter **20**, 9528 (2024)

Probability distribution P of hexagonal bond orientation order parameter $|q_6|^2$





local hexagonal orientational order parameter amplitude around protein *i*

$$q_6^i = \frac{1}{6} \sum_{j \in N_i^{(6)}} \exp\{i6\alpha_{ij}\}$$

perfect hexagonal crystal: $\left\langle |q_6|^2 \right\rangle = 1$

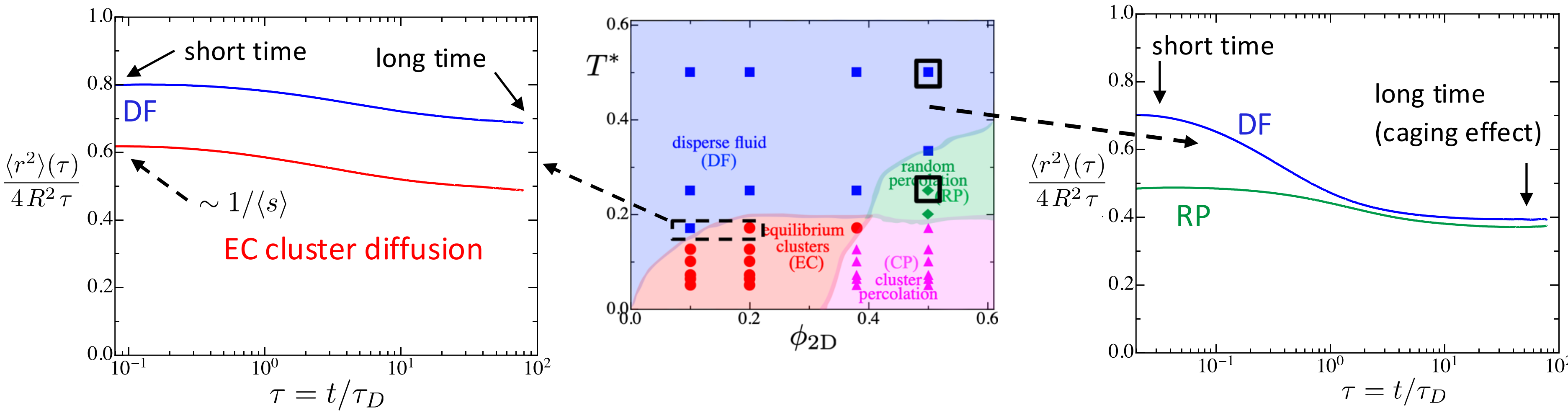
disordered: $\left\langle |q_6|^2 \right\rangle = 0$

disperse fluid (DF)
equilibrium cluster (EC)
random percolation (RP)
cluster percolation (CP)

- Random percolation phase (RP) has weak orientational order akin to DF phase: monotonic decay of bond orientational probability distribution
- Small cluster peaks, observed in EC, vanish in CP characterized by percolated clusters

Short- and long-time self-diffusion of Q2D - SALR proteins

Langevin dynamics evaluated in overdamped regime (w/o HI)



$\tau_D = R^2/d_0$: characteristic diffusion time across particle radius $R = \sigma/2$

d_0 : single – protein diffusion coefficient

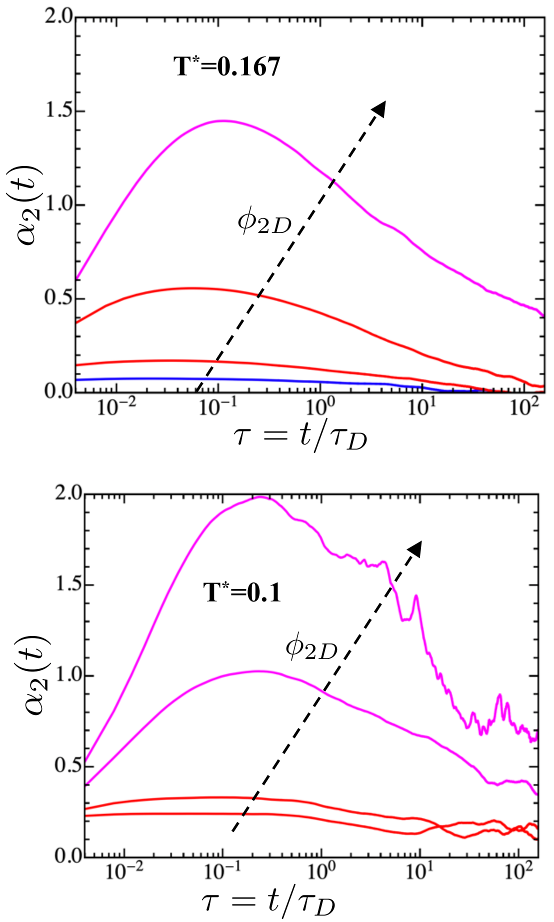
- Similar long-time behaviour of non-clustured DF and RP systems (at same ϕ_{2D}): cluster lifetimes similarly small
  Similarity between two phases also mirrored in static structure factors
- Cluster particles in EC phase diffuse slower than corresponding DF particles since former are part of clusters

Tan, Calandrini, Dhont and **Nägele**, to be submitted (2025)

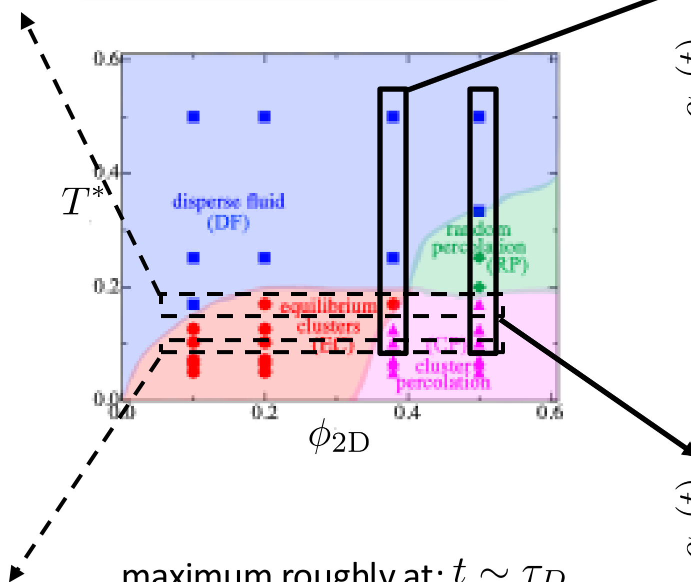
Q2D non - Gaussian parameter

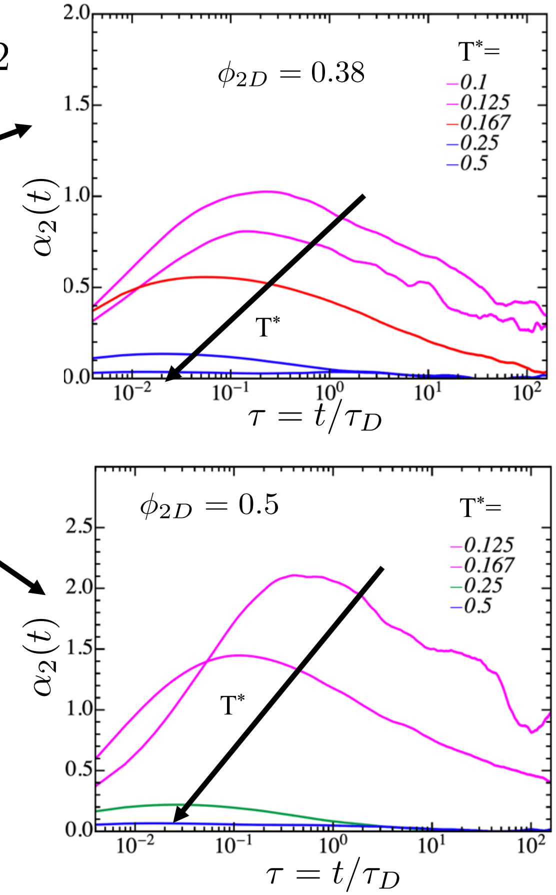
Measure of bonding / caging effects in overdamped regime (here Langevin dynamics w/o HI)

Deviation from Gaussian displacement statistics:



$$\alpha_2(t) = \frac{\langle r^4 \rangle (t)}{2\,\langle r^2 \rangle^2 (t)} - 1 \quad > -1/2$$

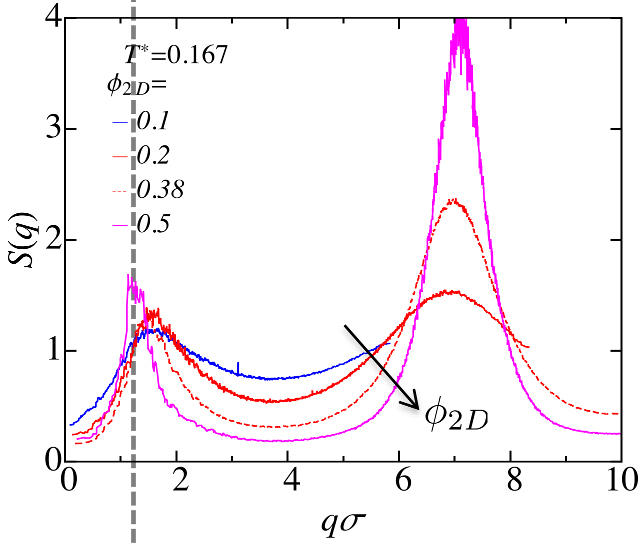




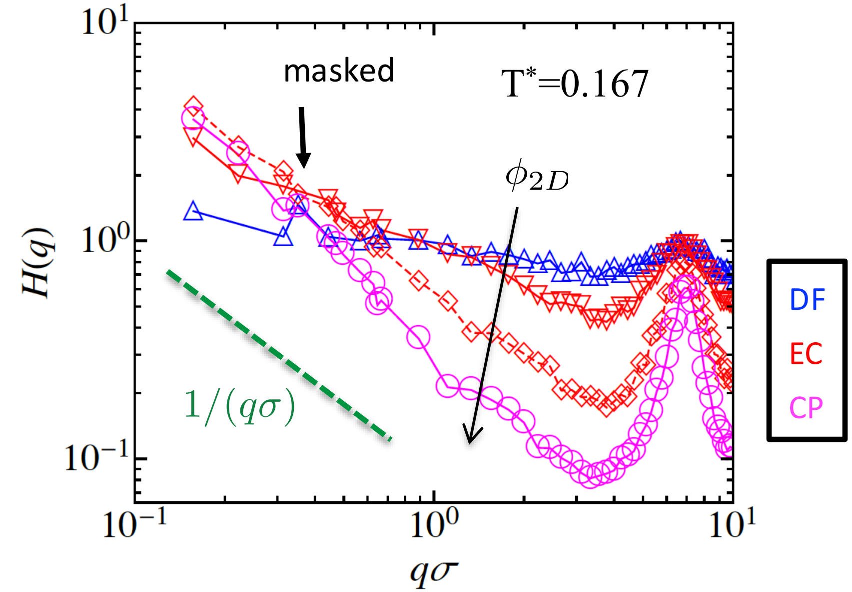
maximum roughly at: $t \sim \tau_D$

- Cluster percolation phase (CP) is dynamically and structurally most heterogeneous: hallmarked by order of magnitude increase of $\alpha_2(t)$ relative to non-clustered phases
- Non – clustured DF and RP states are the least **dynamically heterogeneous**

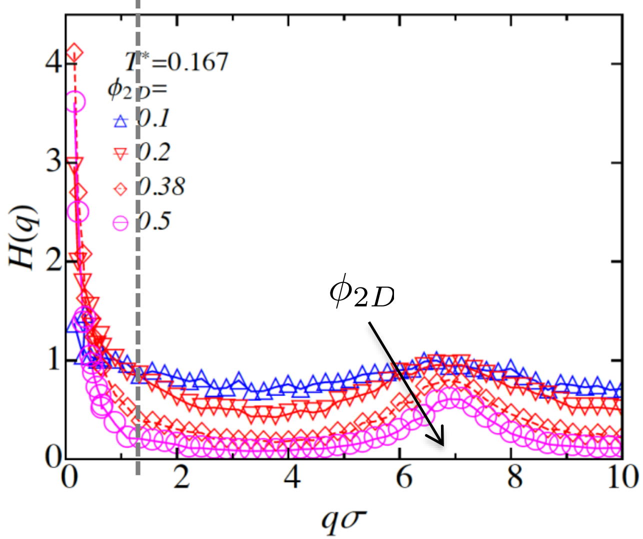
Static structure factor



Hydrodynamic function (MPC simul. with full HI)



Hydrodynamic function (MPC)



Hydrodynamic point – particles (Oseen) approximation of HI:

$$H(q) \approx \frac{3\phi_{2D}}{q\sigma} + 1 + \frac{9\phi_{2D}}{2\sigma}\int_0^\infty dr\,[g(r)-1] + \mathcal{O}(q\sigma)$$

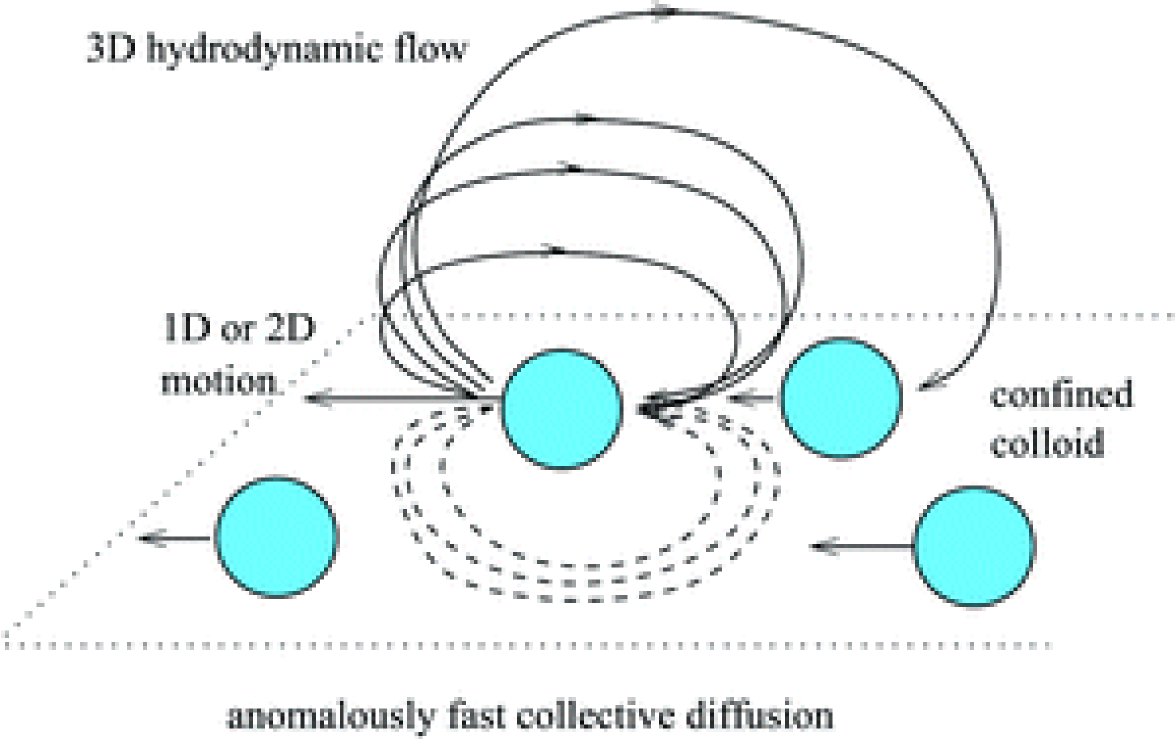
Low – q contribution independent of microstructure

Tan, Calandrini, Dhont, and **Nägele**, to be submitted (2025)

Nägele et al., Molec. Phys. **100** (2002)

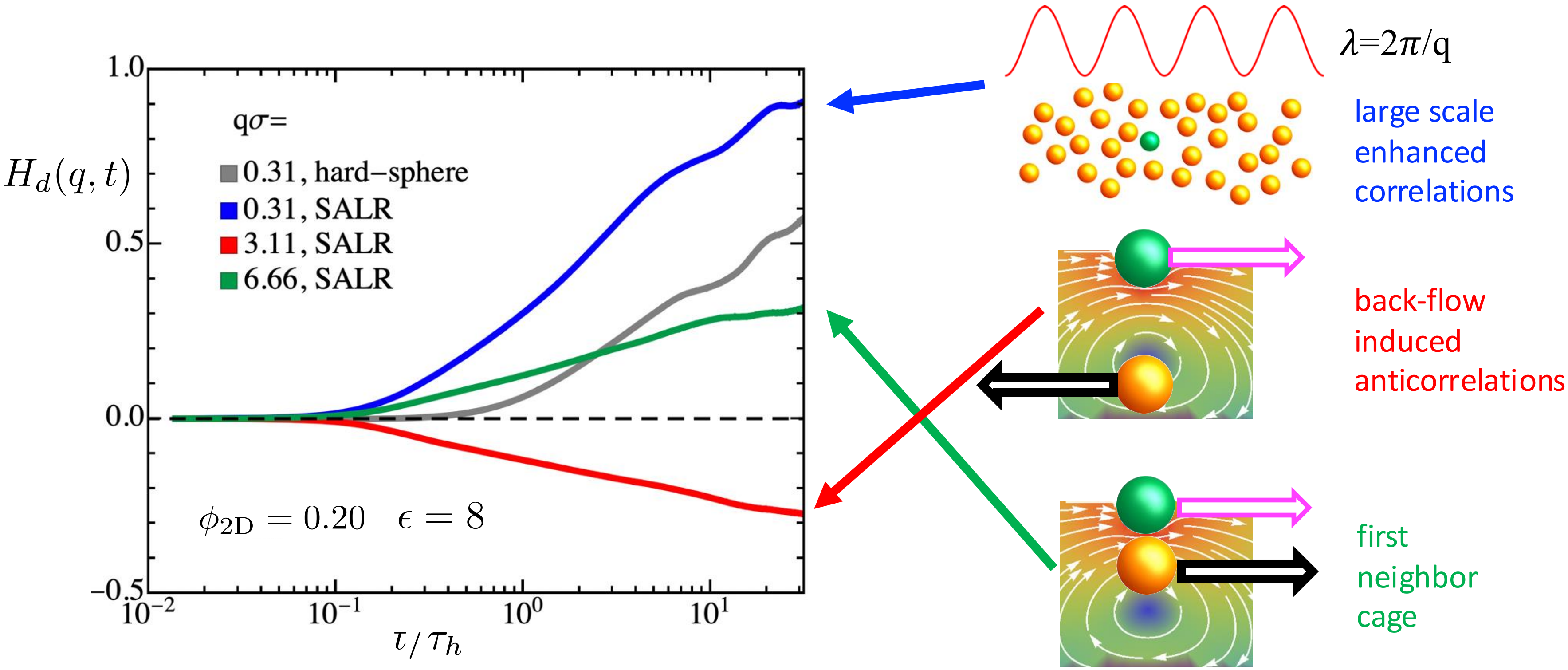
Dominguez, Phys. Rev. E **90** (2014)

- **Cluster peak** of *H(q)* visible in 3D systems, but masked in Q2D due to low - *q* **collective diffusion enhancement**



- Diffusion (sedimentation) along in - plane concentration gradient creates **out - of - plane backflow**
- In - plane flow appears **compressible** even though fluid actually incompressible

- **Development of HI by diffusive spreading of solvent vorticity (MPC simulations)**



$$H(q,t) = \frac{\langle r^2 \rangle (t)}{4 d_0 t} + H_d(q,t)$$

time – resolved Q2D hydrodynamic function (buildup of HI)

$$H_d(q,t) = \frac{1}{2N_p d_0 q^2 t} \left\langle \sum_{l,j=1}^{N} \mathbf{q} \cdot (\mathbf{r}_l(t) - \mathbf{r}_l(0)) \, (\mathbf{r}_j(t) - \mathbf{r}_j(0)) \cdot \mathbf{q} \, e^{i\mathbf{q}\cdot(\mathbf{r}_l(0)-\mathbf{r}_j(0))} \right\rangle, \; l \neq j$$

- Fully developed HI -> anomalously enhanced collective diffusion: $H(q, t \gg \tau_h) \sim \frac{3\phi_{2D}}{q\sigma}$ for $q\sigma \ll 1$

Tan, Calandrini, Dhont and **Nägele**, to be submitted (2025)

Summary

- Have explored: Quasi - 2D dispersions with SA-LR pair interactions
- Methods: Langevin Dynamics and MPC simulations (latter includes HI)
- Determined: State diagram, clustering behavior and dynamics
- Dynamics mostly studied in time regime where HI fully developed

  Hydrodynamic enhancement of collective diffusion occurs in Q2D only
- Studied dynamics on very short time scales where vorticity diffusion and sound wave propagation are resolved (in MPC): buildup of HI resolved

Many thanks to my collaborators

Theory & Simulation

- **Zihan Tan (Soft & Biological Physics, TU Berlin, Germany)**
- Jonas Riest (Viega GmbH & Co. KG., Germany)
- Roland G. Winkler (IAS-2, FZ Jülich, Germany)
- R. Castaneda - Priego (U of Guanajuato, Mexico)

3D Experiments

- Norman J. Wagner (U of Delaware, USA)
- P. Douglas Godfrin (MIT, USA)
- Yun Liu (NIST, USA)

Q2D Experiments (in progress)

- Peter Lang (IBI-4, FZ Jülich, Germany)

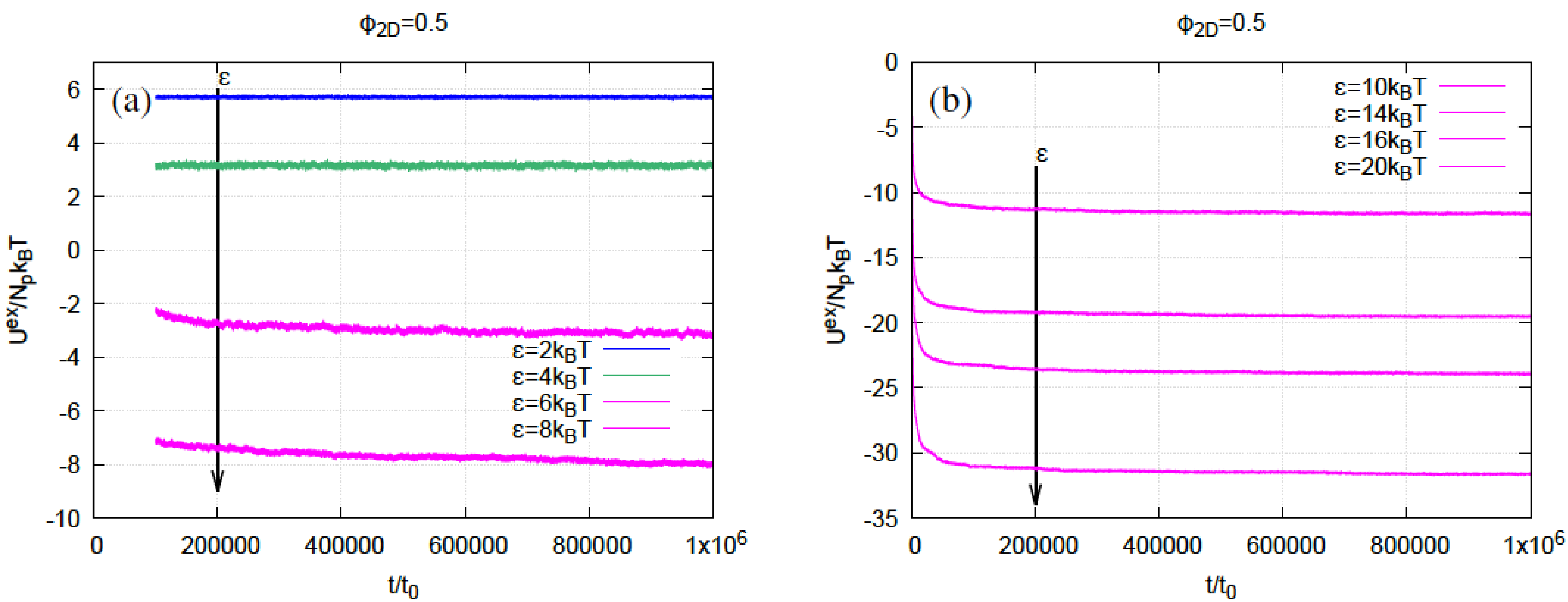
Thank you for your attention

Additional Slides

LD simulations: equilibration of internal energy

$$U^{\text{ex}}(t) = \left\langle \sum_{i<j}^{N_p} u(r_{ij}) \right\rangle(t)\,, \qquad N_p = 1014 - 4096$$

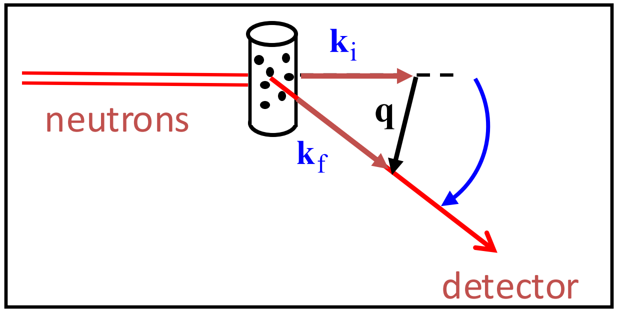
disperse fluid (DF)
equilibrium cluster (EC)
random percolation (RP)
cluster percolation (CP)



Q2D collective diffusion and hydrodynamic function

$$S(q, \tau_h \ll t \ll \tau_D) \propto \exp\{-q^2 D(q)\, t\}$$

↑ hydrodynamic interactions (HI) fully developed



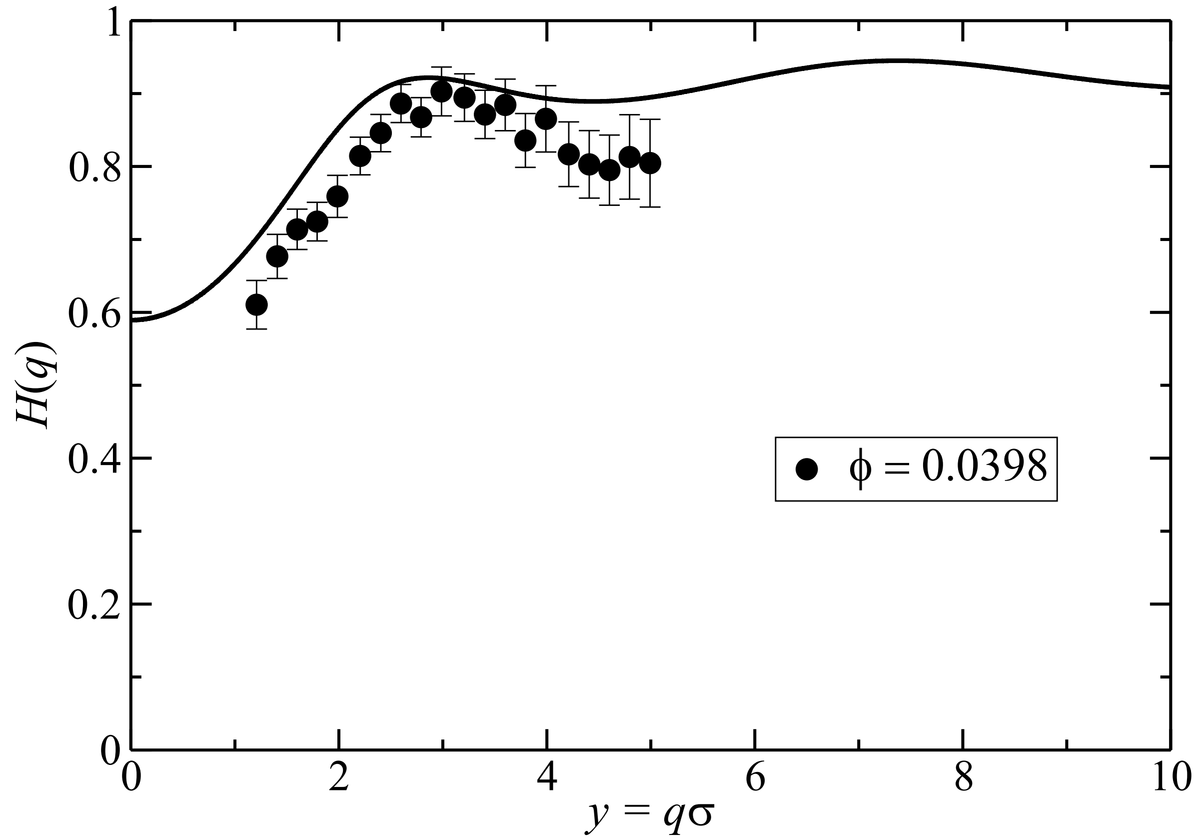
$$\tau_h = R^2/\nu$$ solvent vorticity diffusion time across protein radius *R* $(\tau_h \ll \tau_D)$

$$D(q) = d_0 \frac{H(q)}{S(q)}$$ short - time diffusion function

In – plane hydrodynamic function w/o HI: ***H(q) = 1***

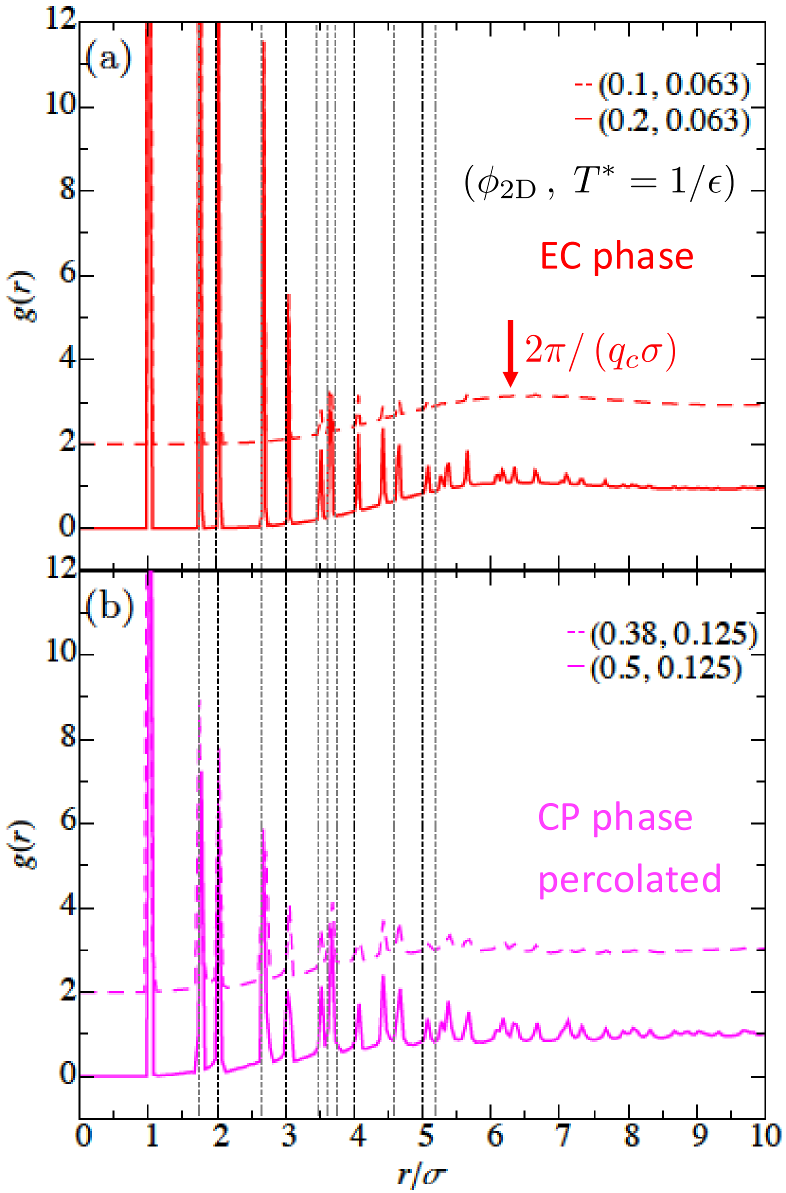
Comparison:
Theory vs. NSE (Lysozyme in D_2O)

$$H(q) = D(q)\,S(q)/D_0$$

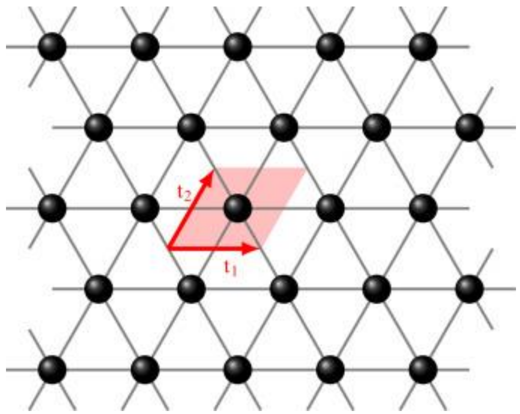


J. Riest, **G. Nägele**, Y. Liu, N. J. Wagner, and P.D. Godfrin, J. Chem Phys. **148**, 065101 (2018)

Radial distribution function



Triangular (hexagonal) lattice



$$\mathbf{t}_1 = \hat{\mathbf{x}}$$

$$\mathbf{t}_2 = \frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}$$

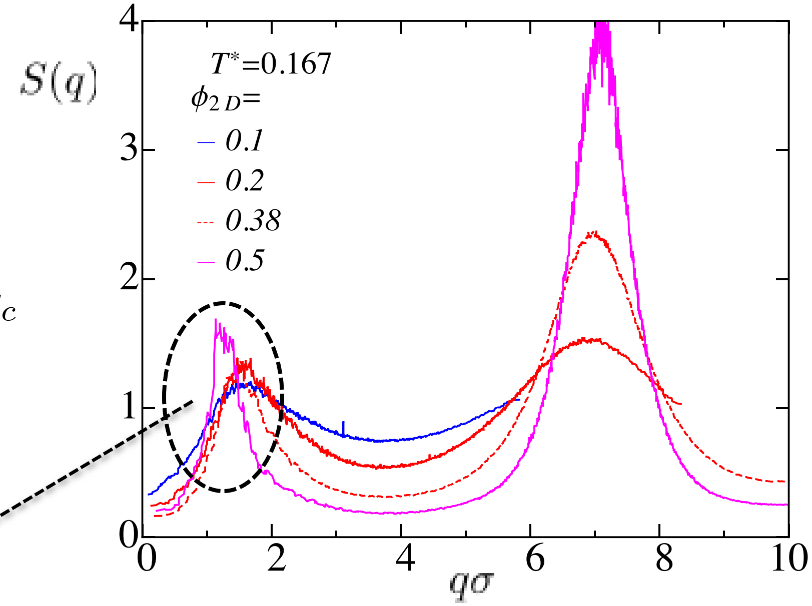
$$\mathbf{t}_1 \cdot \mathbf{t}_2 = \cos(60^o)$$

{Next, overnext, … } neighbor distances:

$$r/\sigma = \{1, \sqrt{3}, 2, 3, 2\sqrt{3}, \sqrt{13}, \sqrt{14}, 4, \sqrt{21}, 5, 3\sqrt{3}, \cdots\}$$

2D and 3D clusterpeak fitted by :

$$S(q) = 1 + n\,h(q) \;\approx\; \frac{S(q_c)}{1+\xi_T^2\,(q-q_c)^2}\,, \quad q \approx q_c$$



$r \gg \xi_T$

$$h(r) \;\sim c_1 S(q_c)\frac{\exp\{-r/\xi_T\}}{r}\left[\cos(q_c r) + q_c\xi_T \sin(q_c r)\right] + c_2\, q_c\, S(q_c)\frac{1}{r^4} \qquad \text{(D = 3)}$$

$$h(r) \;\sim c_1' S(q_c)\frac{\exp\{-r/\xi_T\}}{\sqrt{r}}\left[\cos(q_c r) + \frac{\pi + 2\psi}{4}\right] + c_2'\, q_c\, S(q_c)\frac{1}{r^3} \qquad \text{(D = 2)}$$

modulated pair structure on intercluster scale $\sim 1/q_c$

Envelope akin to fluid near gas - liquid critical point as described by mean - field Ornstein - Zernike theory