Collectivity in diffusion: from effective interactions to spatially correlated noise

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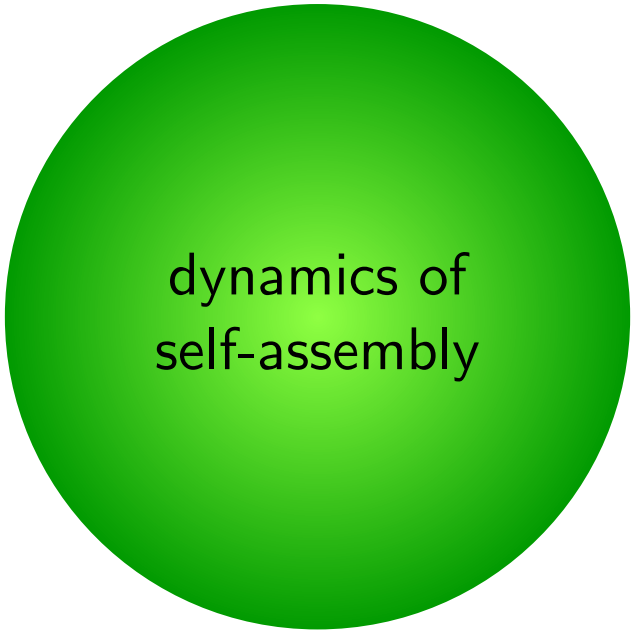
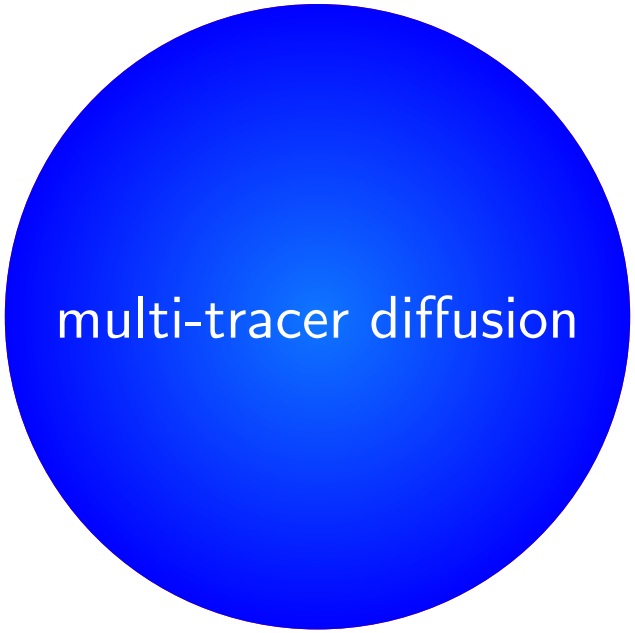
22.04.17

What is this talk about...

soft matter



stochastic processes



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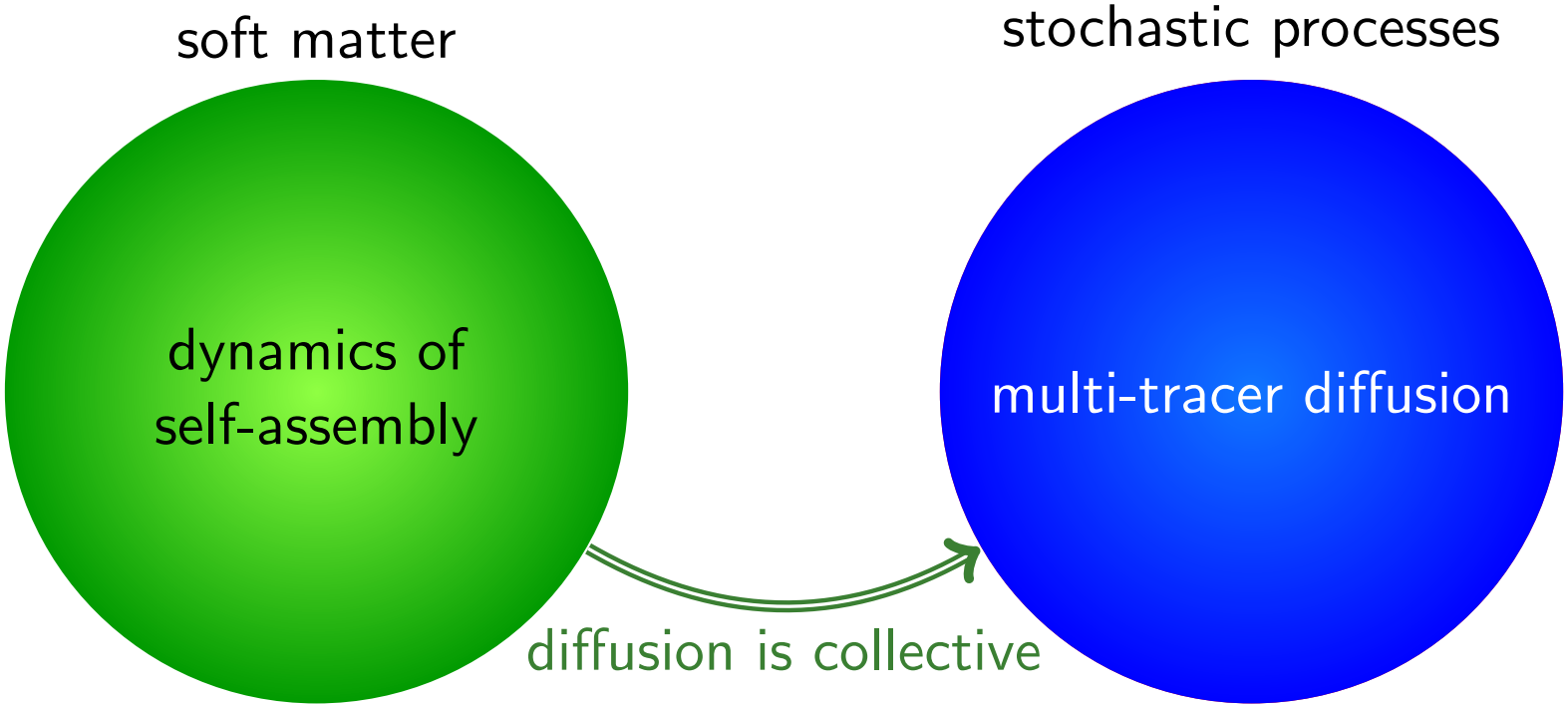

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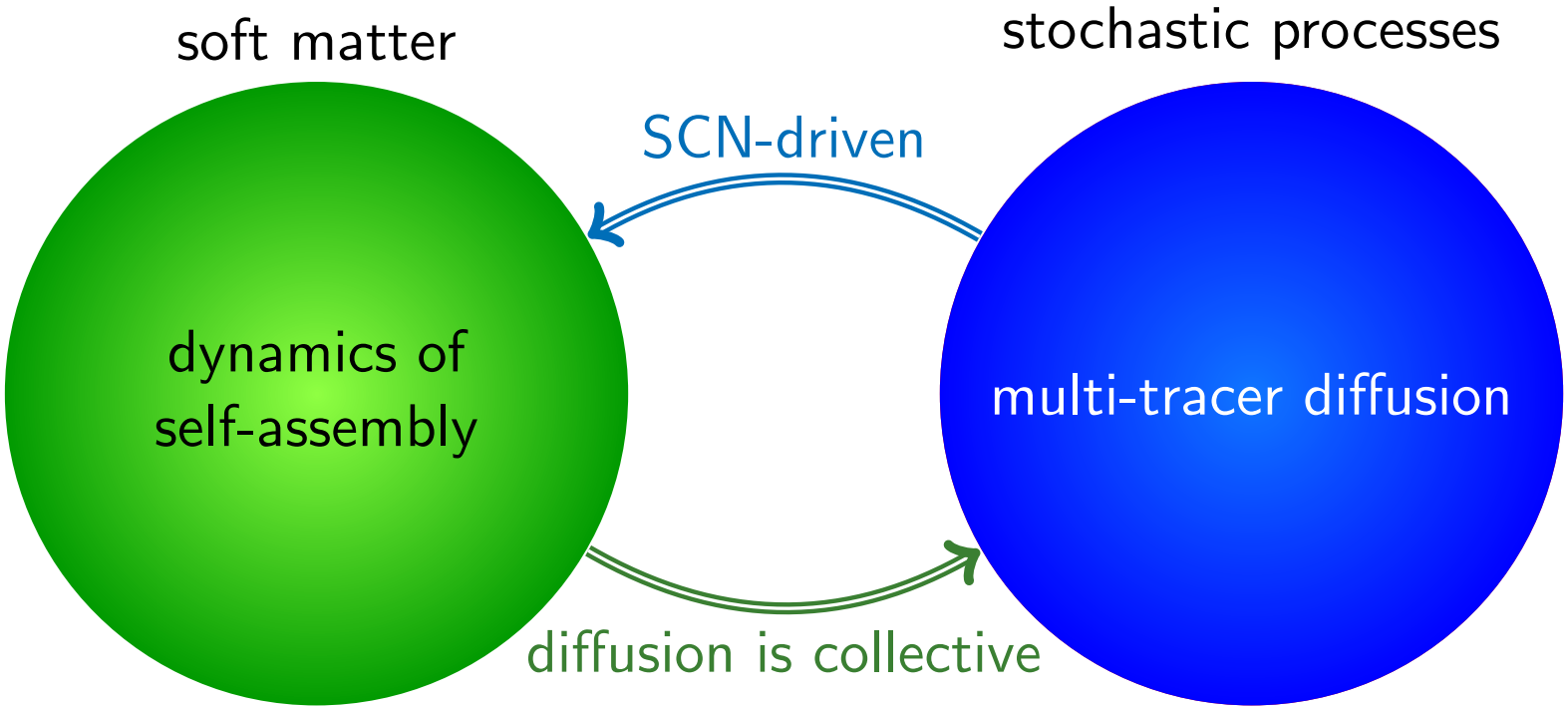
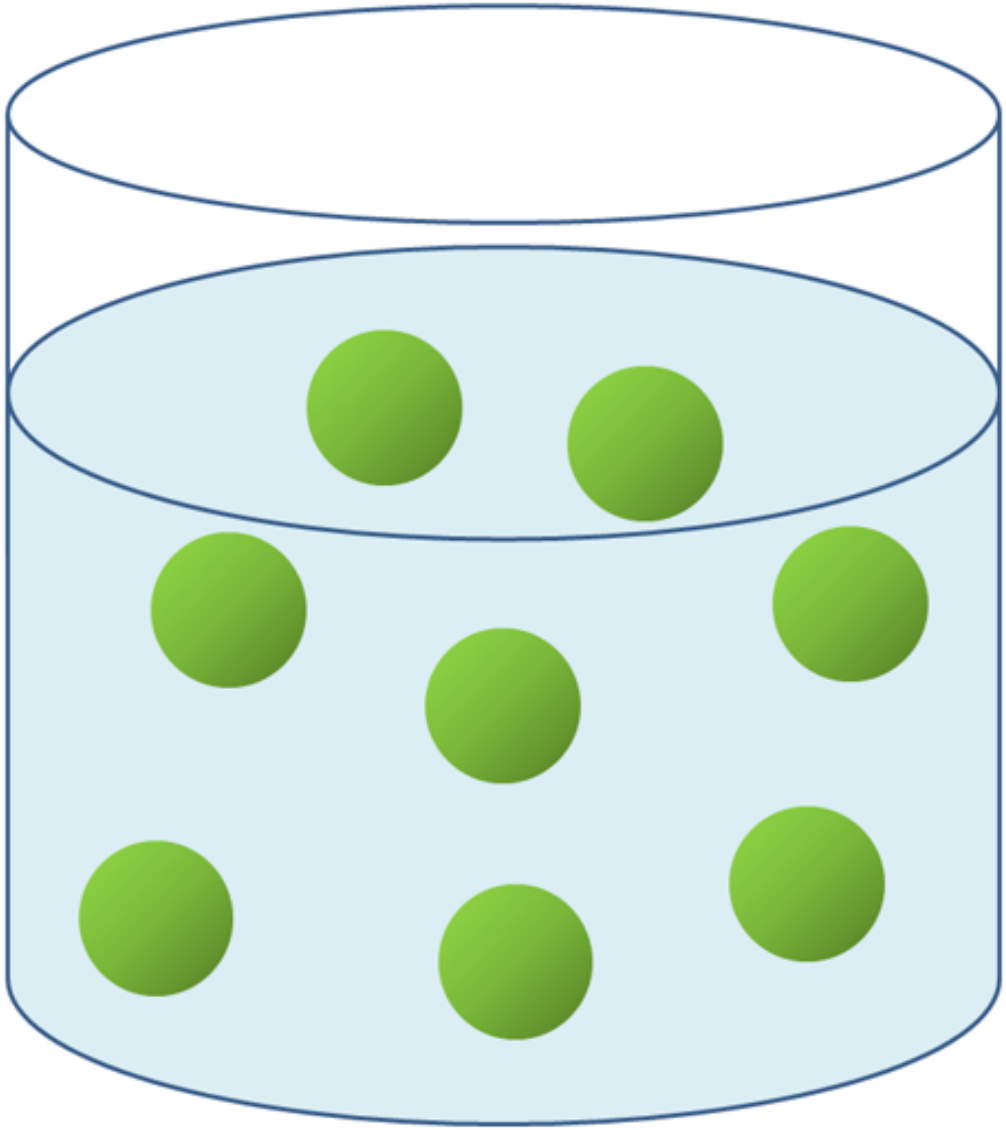


SCN - Spatially Correlated Noise

Effective interactions and self-assembly

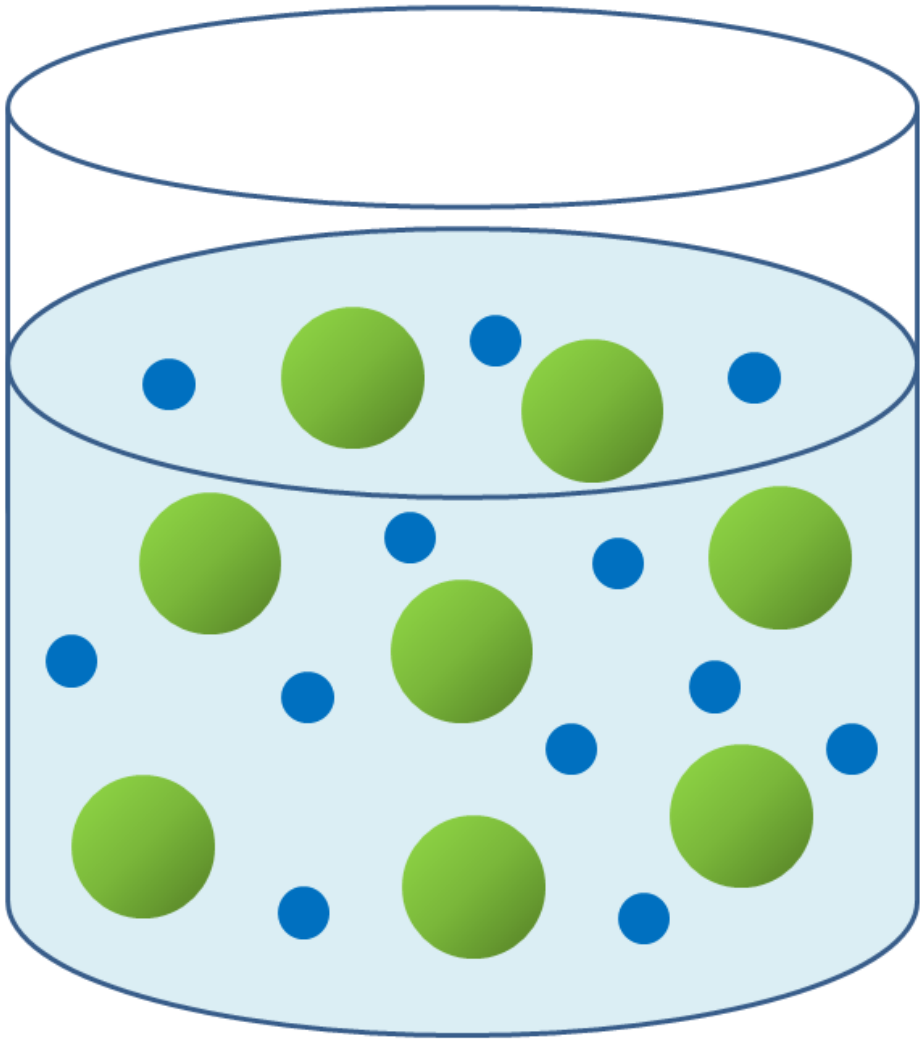
What are effective interactions?

A hard-sphere colloid, solvent density matches density of spheres...



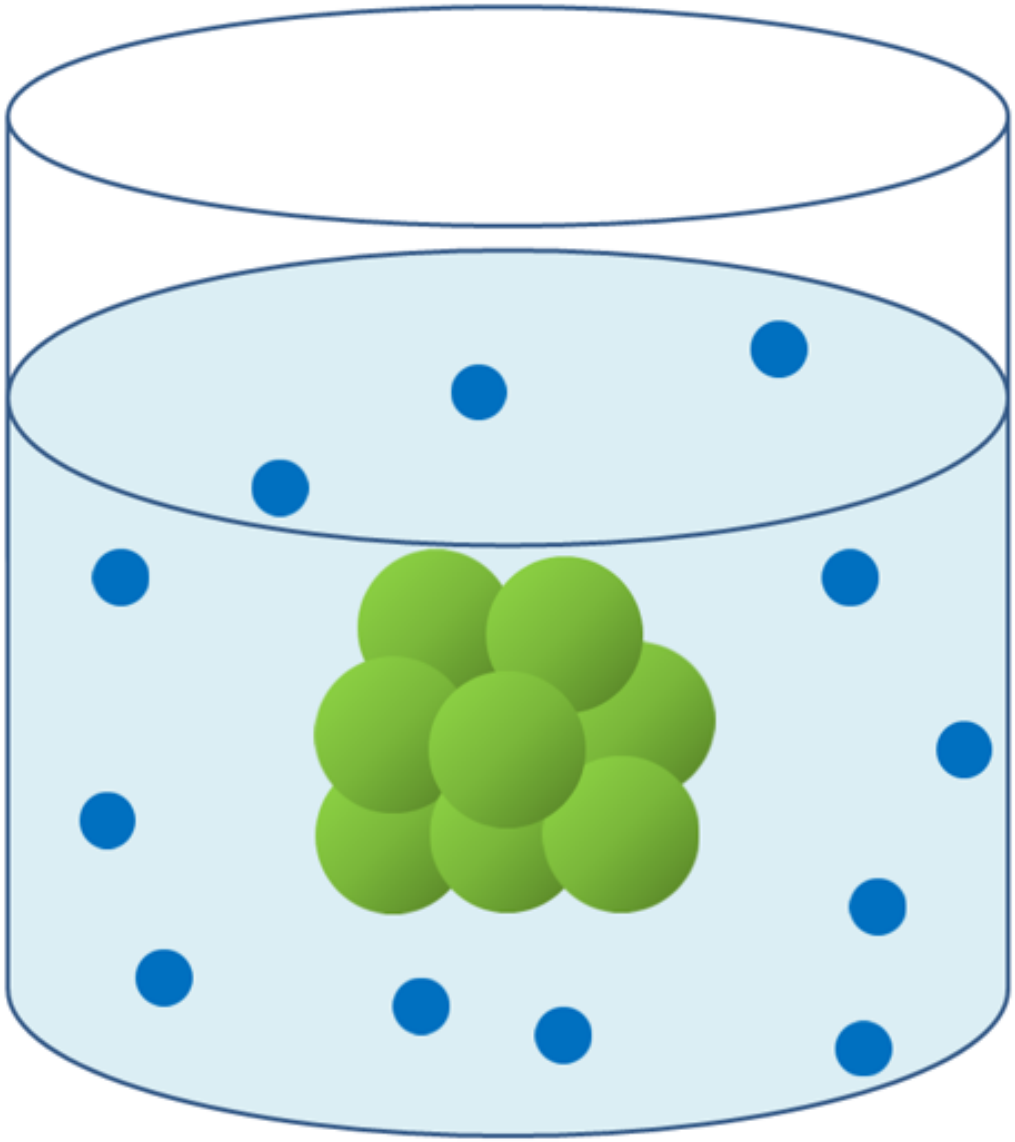
What are effective interactions?

...adding similar, but smaller spheres...



What are effective interactions?

...in result the bigger spheres self-organize.



Equilibrium self-assembly - entropic puzzle

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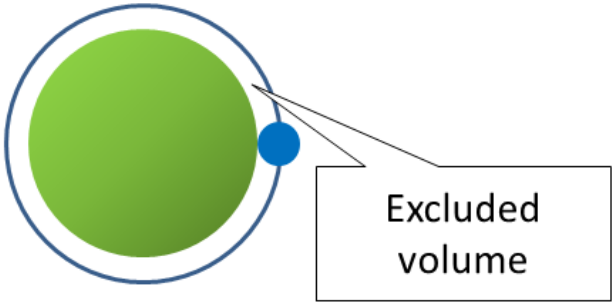

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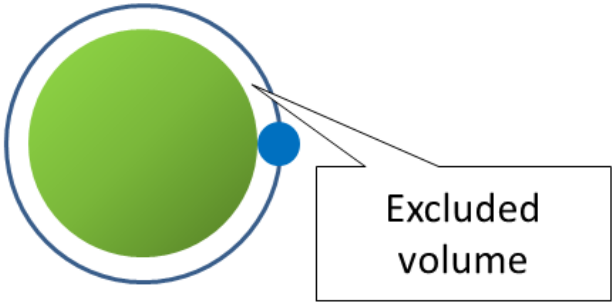

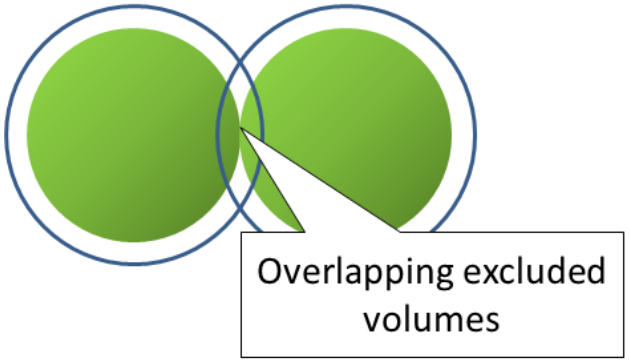

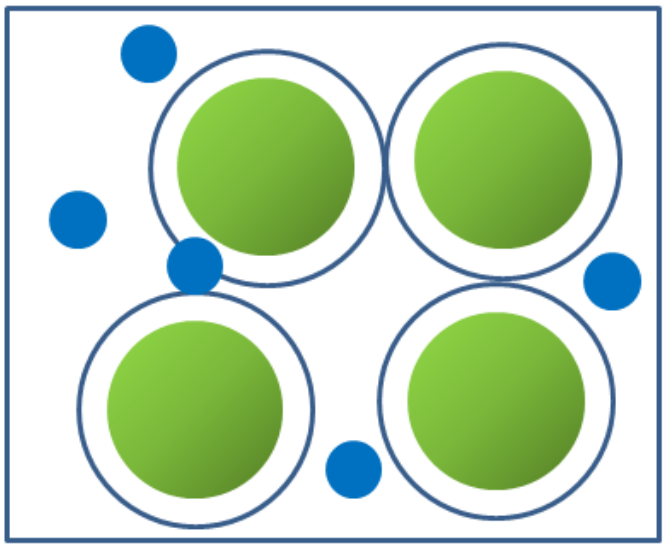

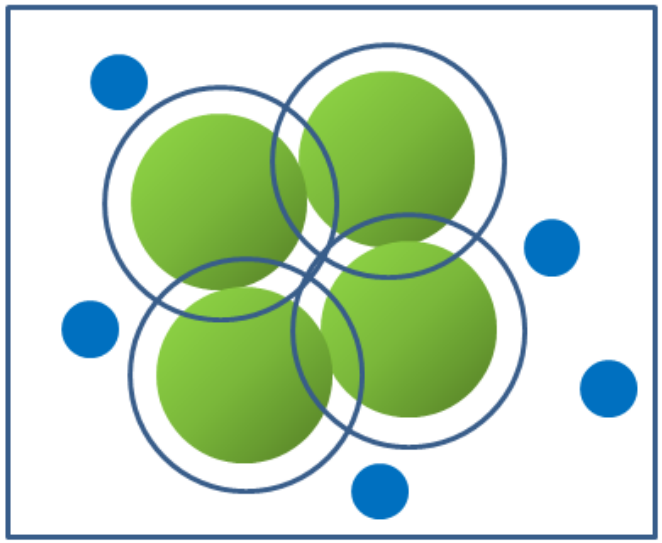

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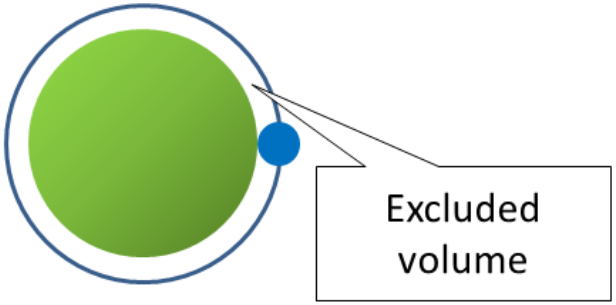
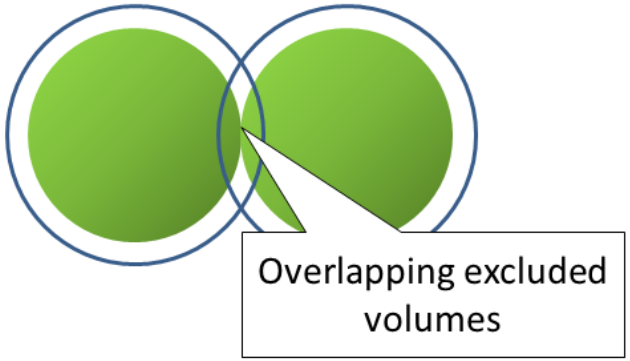
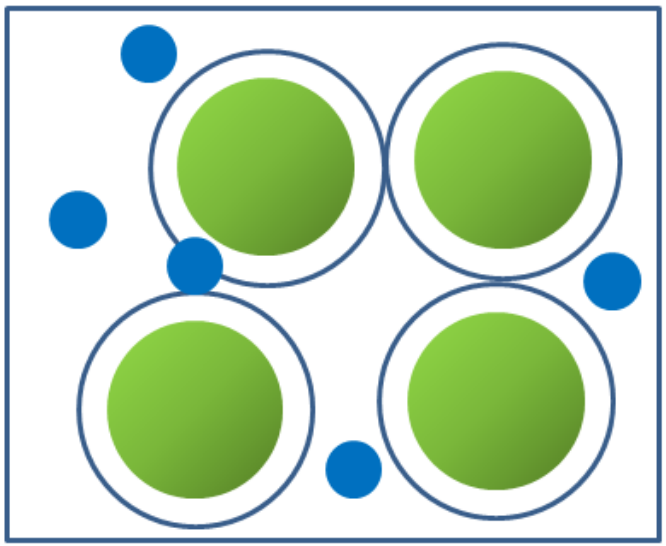
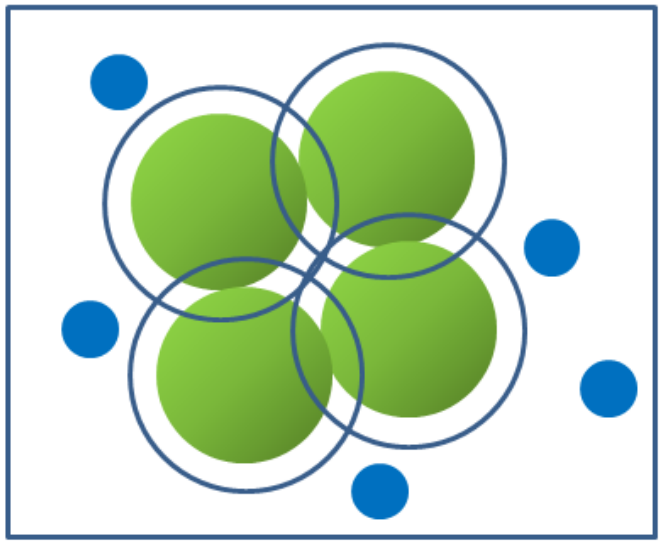








Left: less volume for smaller particles $\Rightarrow$ lower entropy

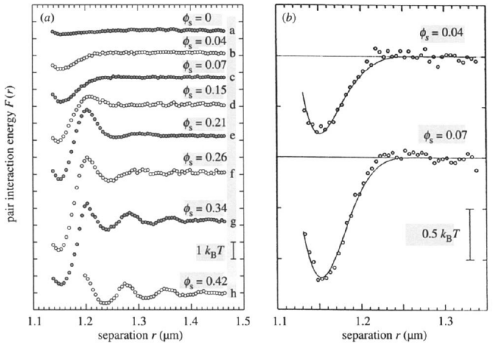
Right: more volume for small particles$\Rightarrow$higher entropy

Formal solution: Asakura-Oosawa model (1954)

Asakura-Oosawa-Vrij theory

For $\sigma_{big} < R < \sigma_{big} + \sigma_{small}$:

$$U_{eff}(R) \propto \left(1 - \frac{3R}{2(\sigma_{big} + \sigma_{small})} + \frac{3R^3}{2(\sigma_{big} + \sigma_{small})^3}\right)$$



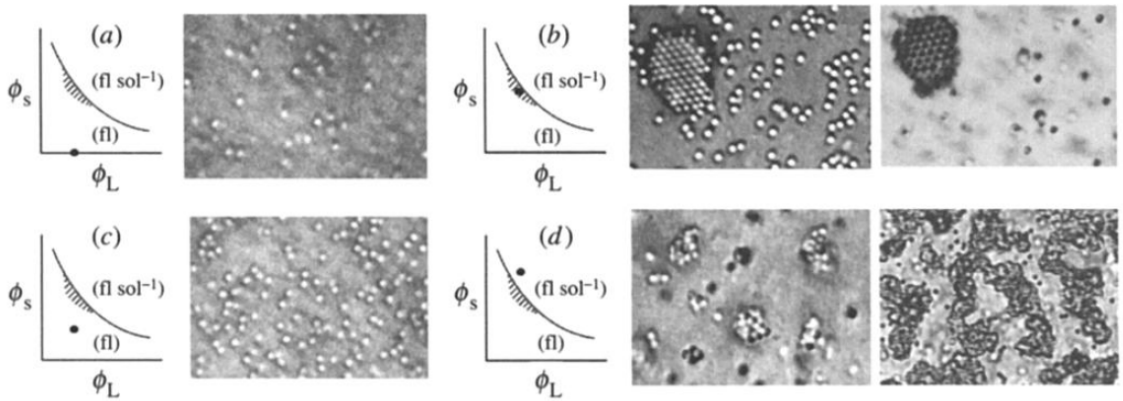


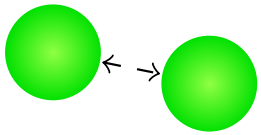
Figure 10. Microscope images of 0.825 μm/0.069 μm diameter binary particle suspensions as a function of small-ball volume fraction Φ_S. The large ball volume fraction is held constant at $\Phi_L = 0.02$, and only the large balls are apparent in the images. To the left of each photo we show the sample preparation volume fractions (the dots) along with the liquidus line. Parts (*a*)–(*c*) are imaged on the surface just below the cell wall, and part (*d*) is imaged *ca.* 20 μm into the bulk sample. (See text for further discussion.)

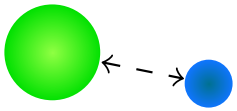
A. G. Yodh, K. Lin, J. C. Crocker, A. D. Dinsmore, R. Verma, P. D. Kaplan, Philos. T. R. Soc. A, 359, 1782 (2001)

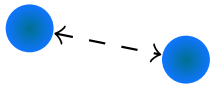
Effective interactions in binary mixtures - general case

Binary mixture: 3 **microscopic** potentials:

$$H_{TT} = \sum_{i>j}^{N} U_0(x_i - x_j) \qquad H_{bT} = \sum_{i}^{N} \sum_{j}^{\tilde{N}} V(x_i - \tilde{x}_j) \qquad H_{bb} = \sum_{i>j}^{\tilde{N}} v(\tilde{x}_i - \tilde{x}_j)$$







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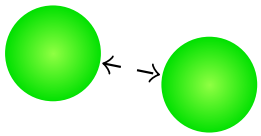
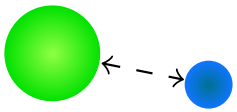
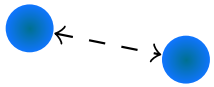

Partition function:

$$\Xi = \frac{z^N \tilde{z}^{\tilde{N}}}{N!\tilde{N}!} \int \{dx\} e^{-\beta H_{TT}} \int \{d\tilde{x}\} e^{-\beta(H_{bT}+H_{bb})}$$

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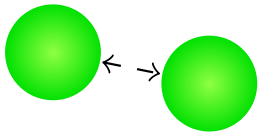
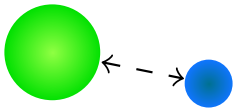
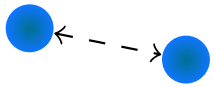

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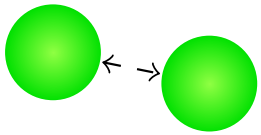
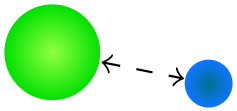
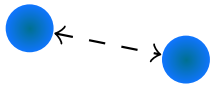

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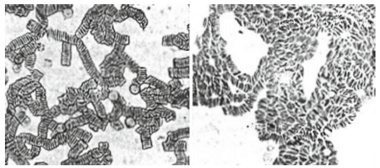
$$= \frac{z^N \tilde{z}^{\tilde{N}}}{N!\tilde{N}!} \int \{dx\} e^{-\beta(H_{TT}+U_{eff})}$$

$$U_{eff} = -\frac{1}{\beta} \ln \tilde{\Xi}$$

Effective interactions are important and ubiquitous

- medicine, e.g. inflamatory stacking of red blood cells



- industry: stabilizing mixtures/inducing sedimentation

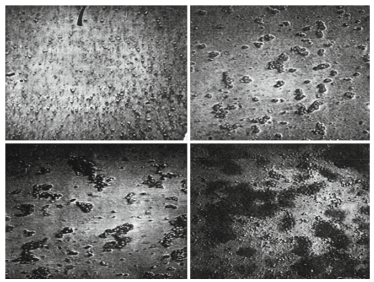
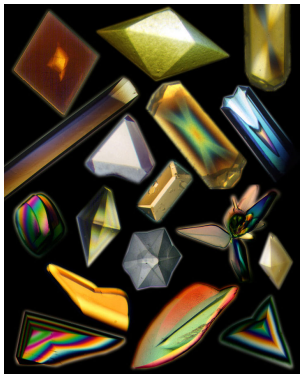
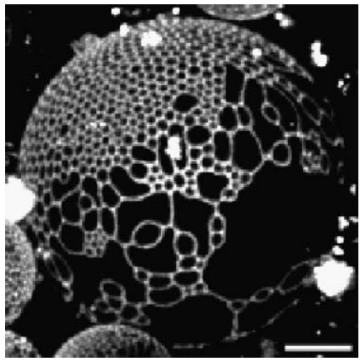


Fig. 1.12 Microscopic images of a rubber latex dispersion [81]. **a** 1% suspension without polymer; **b** 2 min after addition of 0.2% polysaccharide; **c** 10 min after addition of 0.2% polysaccharide; **d** image of the creaming layer. Size of the images are about 130 by 100 μm. Picture reprinted from H. C. Baker, *Inst. Rubber Ind.*, 13:70, 1937

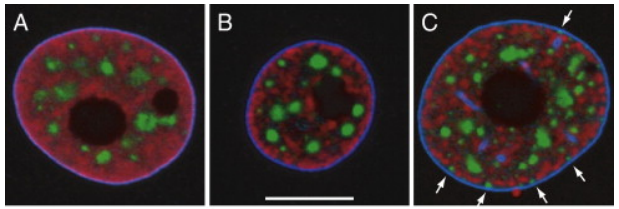
- protein crystallization



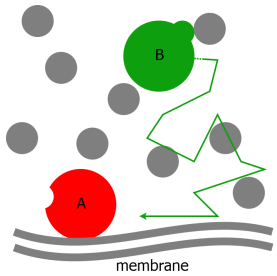
- domains in membranes



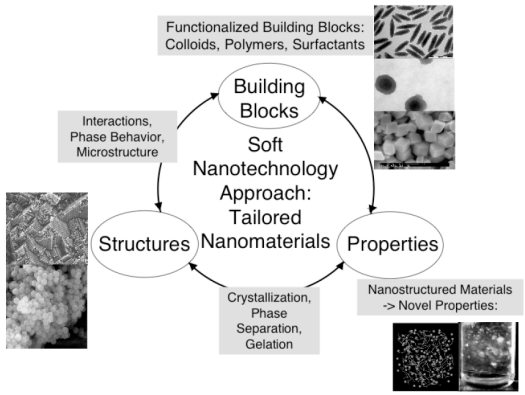
- chromosome formation



- protein complexation



- soft nano-technology



Self-assembly: statical picture

- we understand the **steady-state/equilibrium** picture of self-assembly

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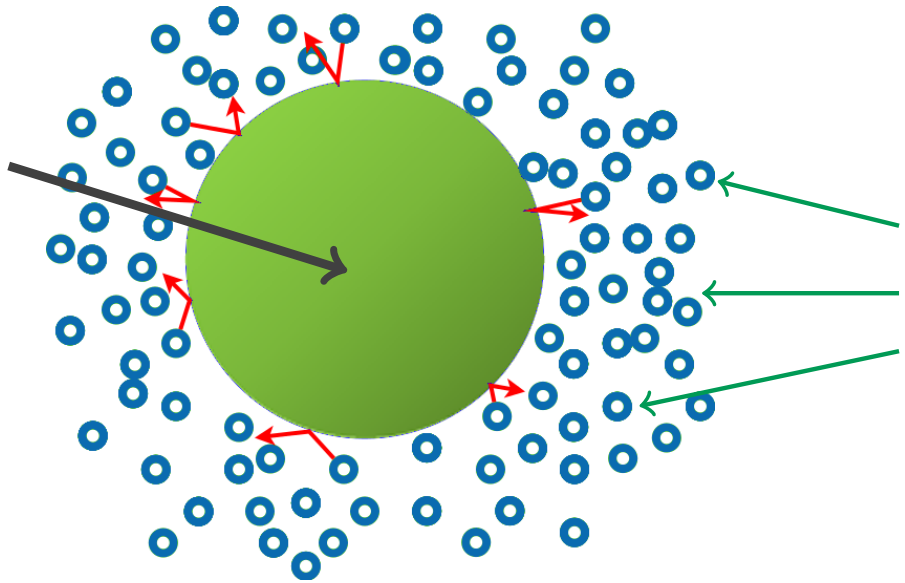
- ...but is it so in the dynamic picture?

Single particle diffusion



'environment' particles (thermal bath)

Langevin dynamics:

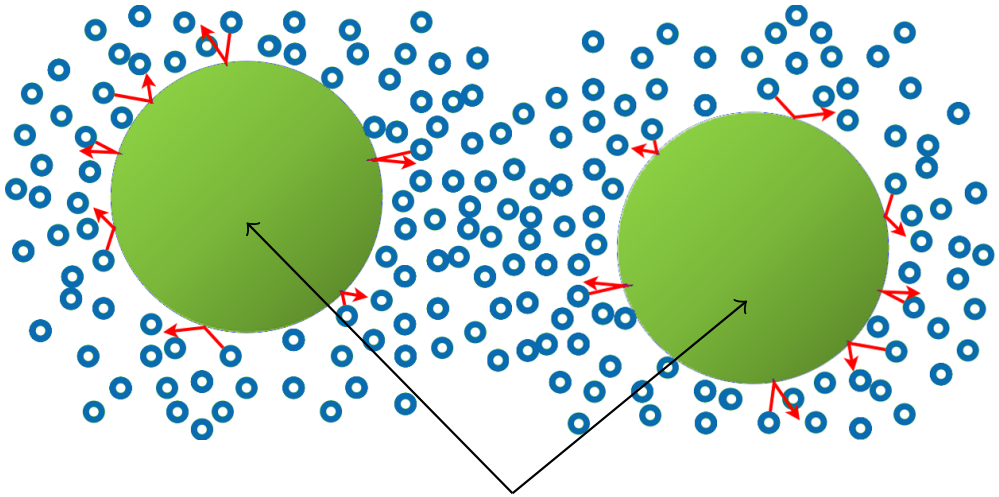
$$m\ddot{\vec{x}} = -\gamma\dot{\vec{x}} + \eta(t)$$

$\Leftarrow$ interaction with thermal bath replaced by noise+friction

some classical relations:

$$< \eta(t)\eta(t') >= \sigma^2\delta(t-t') \qquad \gamma = \frac{\beta\sigma^2}{2}$$

Multiple tracers



thermal bath induces effective interactions

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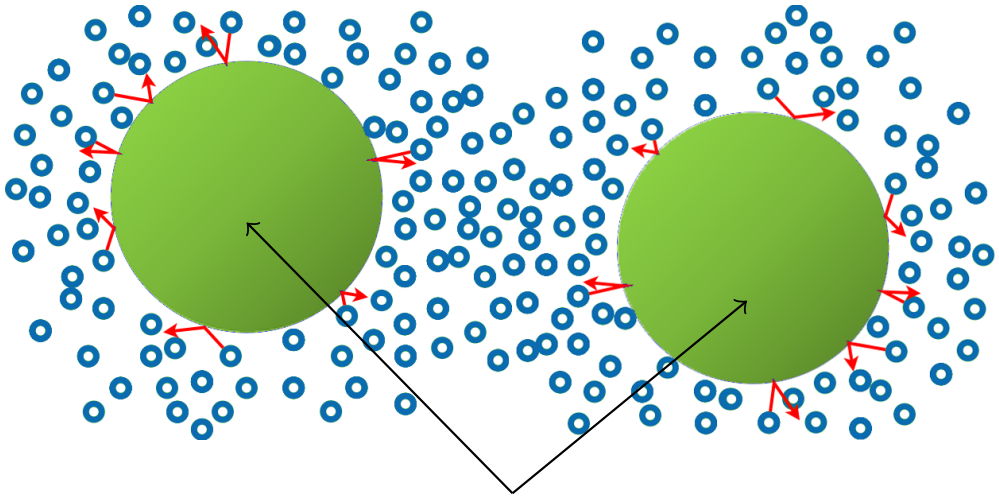
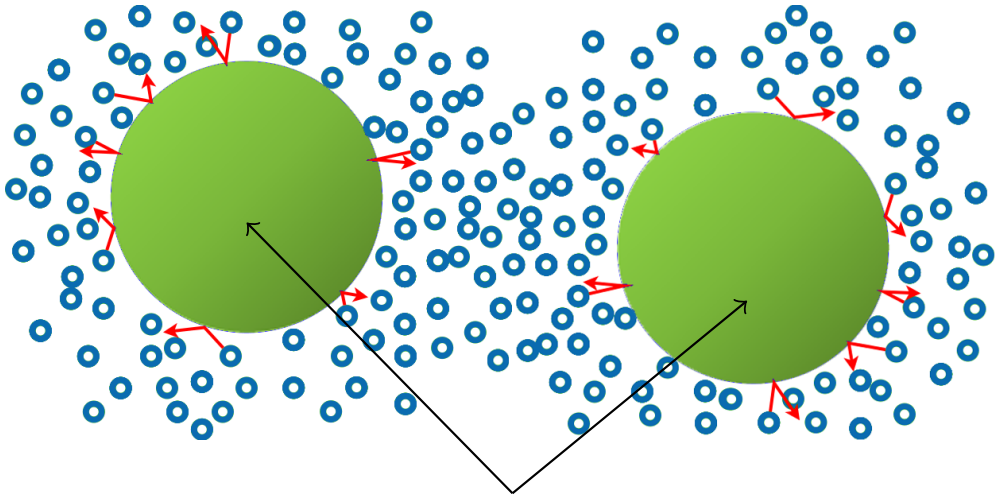


thermal bath induces effective interactions

$\Downarrow$

thermal bath acts in a spatially correlated way

Multiple tracers



thermal bath induces effective interactions

$\Downarrow$

thermal bath acts in a spatially correlated way

$\Downarrow$

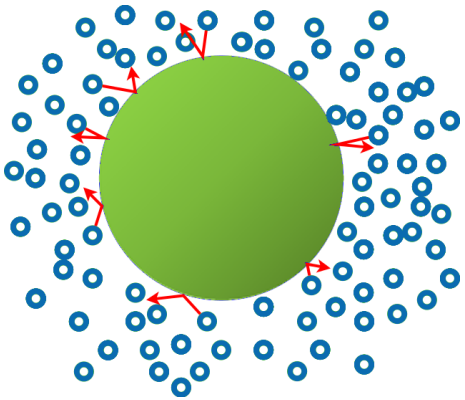
collectivity in diffusion
(thermal noise is not independent for different tracers)

Tracer-bath coupling: spatial correlation function

Tracer-bath coupling force is defined by:

$$\xi(x_i) = -\sum_{j}^{\tilde{N}} \partial_{x_i} V(x_i - \tilde{x}_j)$$

sum over environment particles



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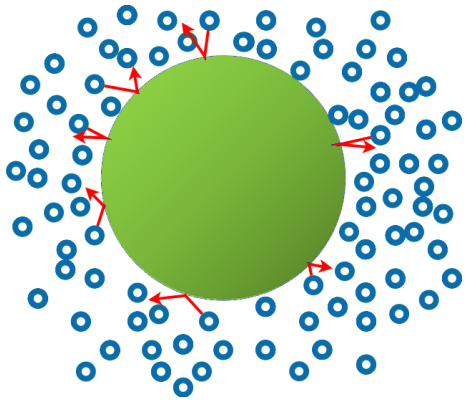


Spatial correlation function formally reads:

$$< \xi(0)\xi(r) > = \frac{z^N \tilde{z}^{\tilde{N}}}{N!\tilde{N}!\Xi} \int_{\Omega} \{dx\}\{d\tilde{x}\}\xi(x_i)\xi(x_i + r) \times$$
$$\times\, e^{-\beta\left(\sum_{k>l}^{N} U_0(x_k - x_l) + \sum_{k}^{N}\sum_{l}^{\tilde{N}} V(x_k - \tilde{x}_l) + \tilde{v}\right)}$$

this can be calculated via Density Functional approach etc...

Spatial correlation function

M. Majka, P.F. Góra, Phys, Rev. E, 94. 4, 042110 (2016)

Spatial correlation function

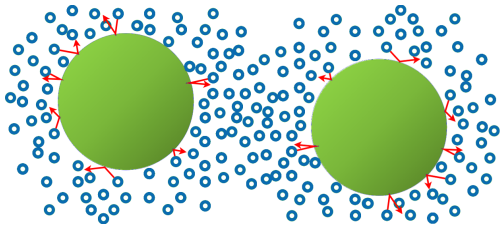
M. Majka, P.F. Góra, Phys, Rev. E, 94. 4, 042110 (2016)

Final result:

$$< \xi(0)\xi(r) > = < \sum_{j \neq i}^{N} F_{eff}(x_i - x_j) \sum_{k \neq i}^{N} F_{eff}(x_i - x_k + r) >$$

Tracer-bath coupling **is** spatially correlated as effective forces

What does it mean?



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- indeed, thermal bath acts on tracers in the spatially correlated manner
- even in equilibrium spatial correlations can be strong and long-ranged

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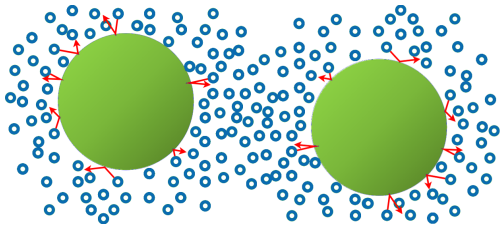

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new perspective on multi-tracer diffusion - we need formalism that accounts for collectivity

Langevin dynamics with Sptially Correlated Noise (SCN)

Stochastic processes in a nutshell...

- Langevin eq. of motion $m\ddot{\vec{r}} + \gamma\dot{\vec{r}} = \vec{F}(r) + \vec{\eta}(t)$

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$$\partial_t P(x,t) = -\partial_x[A(x,t)P(x,t)] + \frac{1}{2}\partial_x\left[B(x,t)\partial_x(B(x,t)P(x,t))\right]$$

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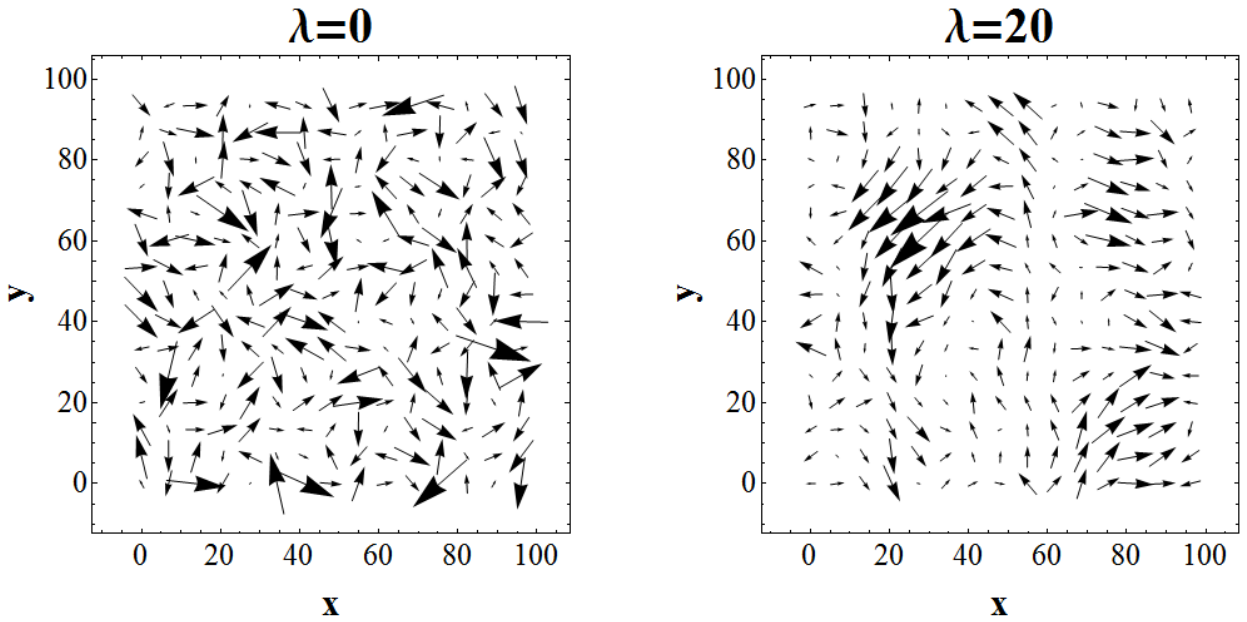
  under Stratonovich ($\circ$) interpretation (there are also other...)
- The **stationary** F-P eq. ($\partial_t P(x,t) = 0$) gives Boltzmann distribution $P_{st}(r) \propto e^{-\beta U(r)}$ where $-\partial_r U(r) = F(r)$

What is SCN?

Lets replace microscopic $\xi(x_i)$ with the Gaussian SCN:

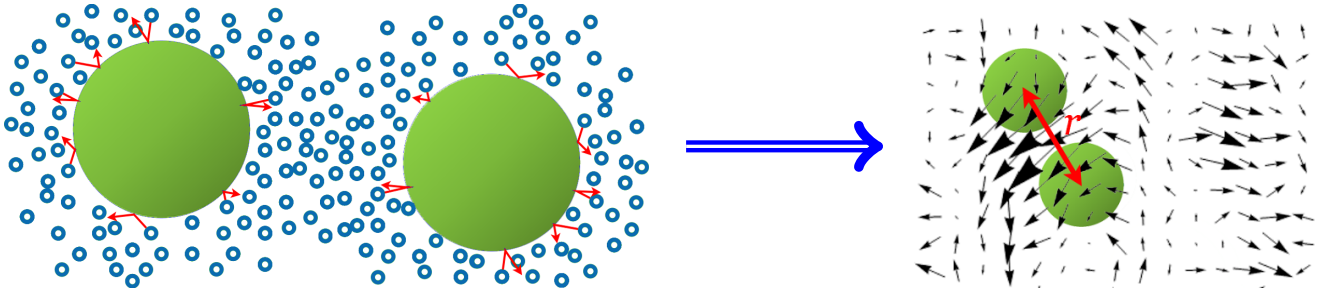
$$< \xi_i(t) >= 0 \quad < \xi_i^2(t) >= \sigma^2$$

$$< \xi_i(t)\xi_j(t') >= \sigma^2 \delta(t-t') h(x_i - x_j)$$



Simplest Langevin dynamics with SCN - assumptions

We want now to replace microscopic model with stochastic dynamics:



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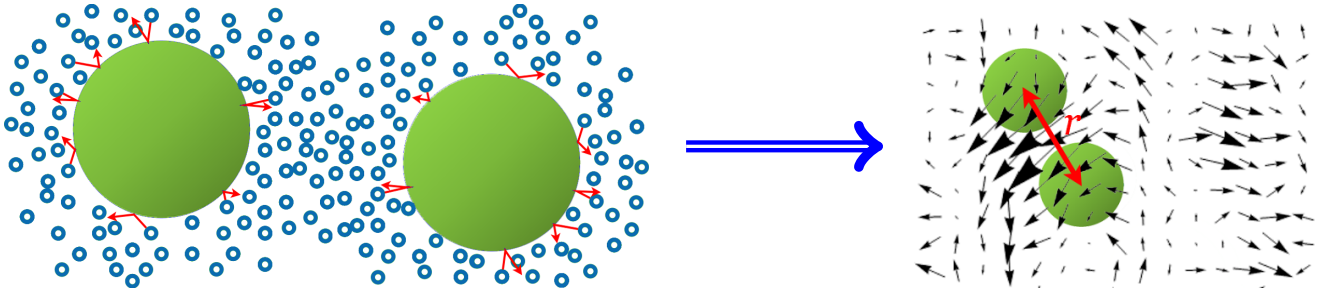

- From the microscopic theory for 2-tracers:

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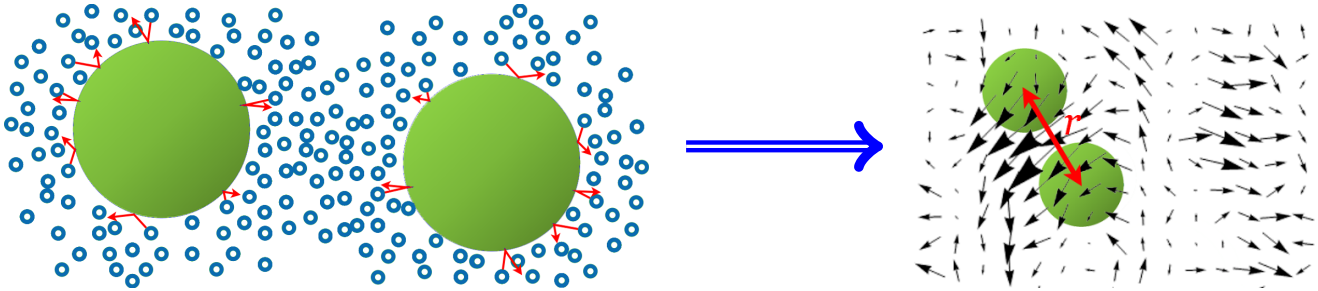

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- $h(r)$ is the equilibrium correlation function
- ...so our dynamics must reproduce the Boltzmann distribution in stationary state:

$$P_{Boltz}(r) = \mathcal{N}^{-1} \exp\left(-\beta(U_0(r) + U_{eff}(r))\right)$$

SCN-driven Langevin dynamics

- Over-damped eq. of motion, $F(r) = F_0(r) + F_{eff}(r)$ and γ is const:

$$\gamma \dot{x}_1 = F(x_1 - x_2) + \xi_1 \qquad \gamma \dot{x}_2 = -F(x_1 - x_2) + \xi_2$$

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- Change of variables: $R = (x_1 + x_2)/2$ and $r = (x_2 - x_1)/2$:

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Important trick

replace correlated noise with multiplicative non-correlated noise

$$\xi_2 \pm \xi_1 = \sqrt{2}\sigma\sqrt{1 \pm h(r)}\eta_\pm$$

where $\eta_\pm$ comes from the normal distribution and:

$$< \eta_+(t)\eta_-(t') >= 0 \quad < \eta_+(t)\eta_+(t') >=< \eta_-(t)\eta_-(t') >= \delta(t - t')$$

SCN-driven Langevin dynamics

Assigning $g_{\pm}(r) = \sqrt{1 \pm h(r)}$, we get:

$$\gamma \dot{r} = 2F(r) + \sqrt{2}\sigma g_{-}(r)\eta_{-}$$

$$\gamma \dot{R} = \frac{\sigma}{\sqrt{2}} g_{+}(r)\eta_{+}$$

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Under the Stratonovich interpretation the **stationary** Fokker-Planck Equation (FPE) for this set reads:

$$-\partial_r \left(\frac{2F(r)}{\gamma} \tilde{P}_{st} \right) + \sigma^2 \partial_r \left[\frac{g_{-}(r)}{\gamma} \partial_r \left(\frac{g_{-}(r)}{\gamma} \tilde{P}_{st} \right) \right] + \frac{\sigma^2}{4} g_{+}^2(r) \partial_{RR} \tilde{P}_{st} = 0$$

we can solve it...

Solution reads:

$$\tilde{P}_{st}(r,R) = \exp\left(\frac{2\gamma}{\sigma^2}\int_0^r dr' \frac{F(r')}{g_-^2(r')} - \ln\frac{g_-(r)}{\gamma} + \tilde{C}\right)$$

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Problem!

For SCN this solution cannot be equal to Boltzmann distribution.

No thermodynamical consistency!

Spatially Variant Friction Coefficient (SVFC)

Postulate:

Thermodynamical consistency for SCN requires friction coefficient that depends on the distance r

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now, our equations of motion read:

$$K(r)\dot{r} = 2F(r) + \sqrt{2}\sigma g_-(r)\eta_-$$
$$\frac{\gamma}{2}\dot{R} = \frac{\sigma}{\sqrt{2}} g_+(r)\eta_+$$

write down FPE, solve it:

$$P_{st}(r,R) = \exp\left(\frac{2}{\sigma^2}\int_0^r dr' \frac{F(r')K(r')}{g_-^2(r')} - \ln\frac{g_-(r)}{K(r)} + C\right)$$

$K(r)$ can compensate for $g_-(r) \Rightarrow$ we can restore Boltzmann dist.

SVFC cnd.

We use $P_{Boltz}(r)$ as a 'constraint' and demand $P_{st}(r) = P_{Boltz}(r)$. This is equivalent to:

$$K'(r) - \left(\beta F(r) + \frac{g'_-(r)}{g_-(r)}\right) K(r) = -\frac{2}{\sigma^2}\frac{F(r)}{g_-^2(r)} K^2(r)$$

which is the Bernoulli differential equation and can be solved analytically with boundary condition $K(r \to +\infty) = \gamma$:

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SVFC

$$K(r) = \frac{g_-(r) e^{-\beta U(r)}}{\frac{1}{\gamma} - \frac{2}{\sigma^2}\int_r^{+\infty} dr' \frac{F(r')}{g_-(r')} e^{-\beta U(r')}}$$

SCN-driven Langevin dynamics - basic properties

$$K(r)\dot{r} = 2F(r) + \sqrt{2}\sigma g_-(r)\eta_-$$

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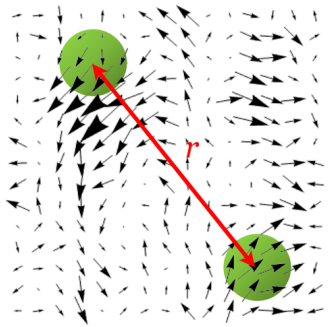
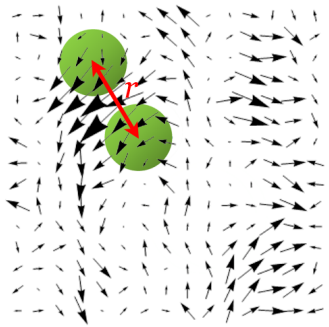
- classical relation $\gamma = \frac{\beta\sigma^2}{2}$ holds
- for non-correlated case $K(r) = \gamma$, as expected
- for huge r, $K(r) \to \gamma \Rightarrow$ ordinary Langevin dynamics



$r \to 0$ limit

- for $r \to 0$ we have $g_-(r) \to 0$ noise is (seemingly) attenuated:



- however, $K(r) \to 0$, so over-damped dynamics is **unstable**:

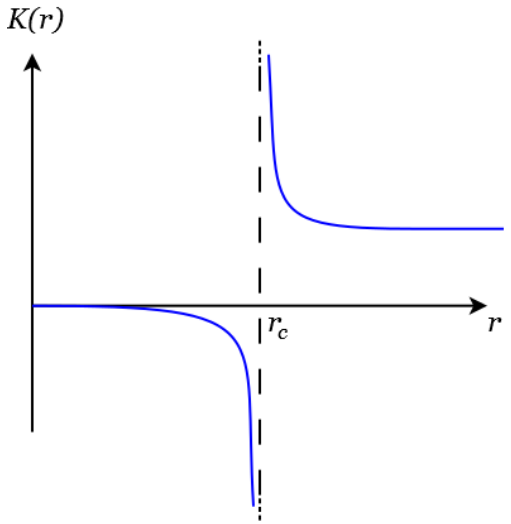
$$\dot{r} = 2\frac{F(r)}{K(r)} + \sqrt{2}\sigma\frac{g_-(r)}{K(r)}\eta_-$$

- in fact, $r \to 0$ is the inertial limit (confirmed by the short-range microscopic models)

K(r) - singular behavior

$K(r)$ can become singular for certain critical $r = r_c$ satisfying:

$$\beta \int_{r_c}^{+\infty} dr' \frac{F(r')}{g_-(r')} e^{-\beta U(r')} = 1$$



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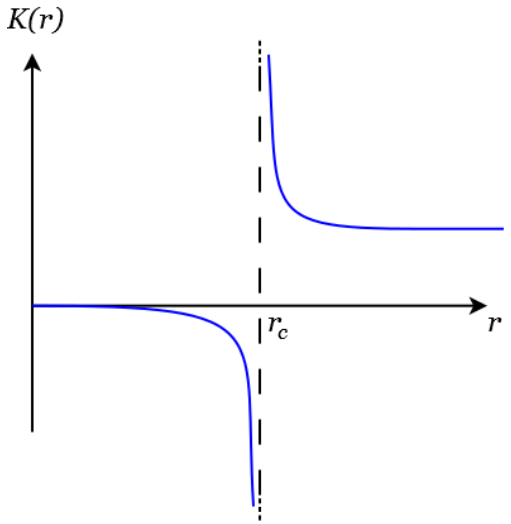

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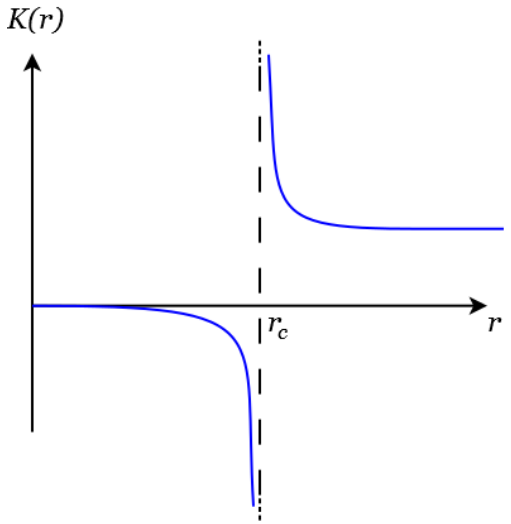

- a region of propulsion emerges
- linearized dynamics in the vicinity of r_c gives:

$$< r(t) >= r_c + (r_0 - r_c) \exp\left(\frac{4\beta F^2(r_c)}{\gamma g_-^2(r_c)} t\right)$$

This result bifurcates, for $r_0 < r_c$ we get **decreasing** $< r(t) >$

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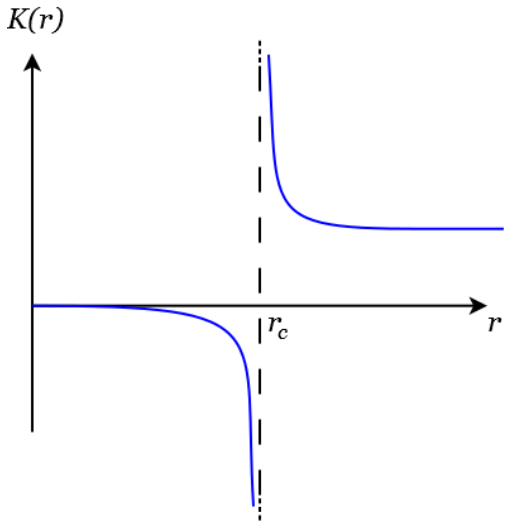

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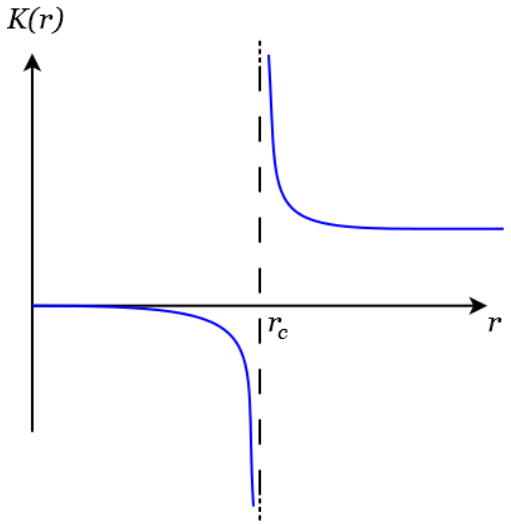

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- ergodicity breaking (for $r_0 < r_c$ system will not equilibrate)
- this effect must be confronted with full inertial dynamics

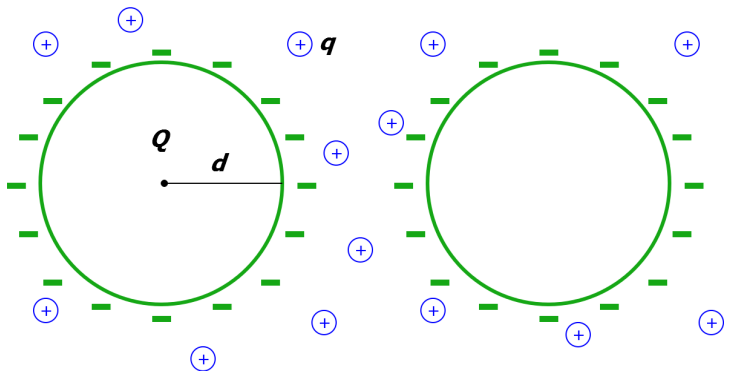
Surface-charged spheres and counter-ions

Screened-charge Yukawa potential is an effective potential:

$$U(r) = \begin{cases} \dfrac{Q^2}{\epsilon(1+\kappa d/2)^2}\dfrac{e^{-\kappa(r-d)}}{r} & r > d \\ +\infty & 0 < r < d \end{cases}$$

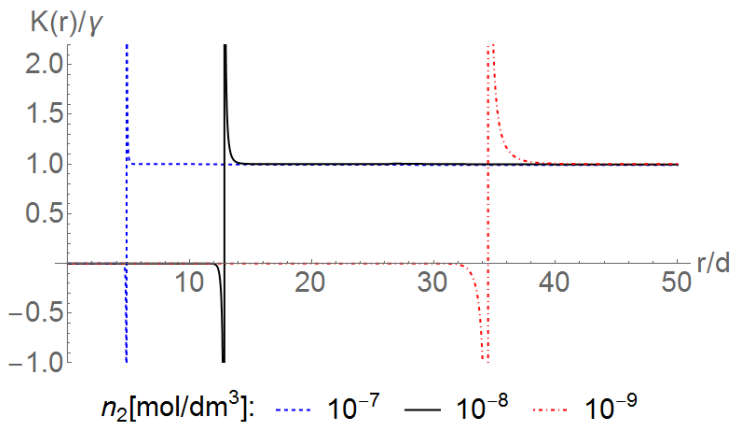
$$\kappa^2 = \beta\frac{4\pi}{\epsilon}(n_1 Q^2 + n_2 q^2)$$

- $Q = 2000e$, $q = 1e$ - charges
- sphere radius $d = 600nm$
- κ Debye-Huckle screening constant
- $n_1 = 2mm^{-3}$ sphere's concentration
- n_2 - **ion concentration** (control parameter)

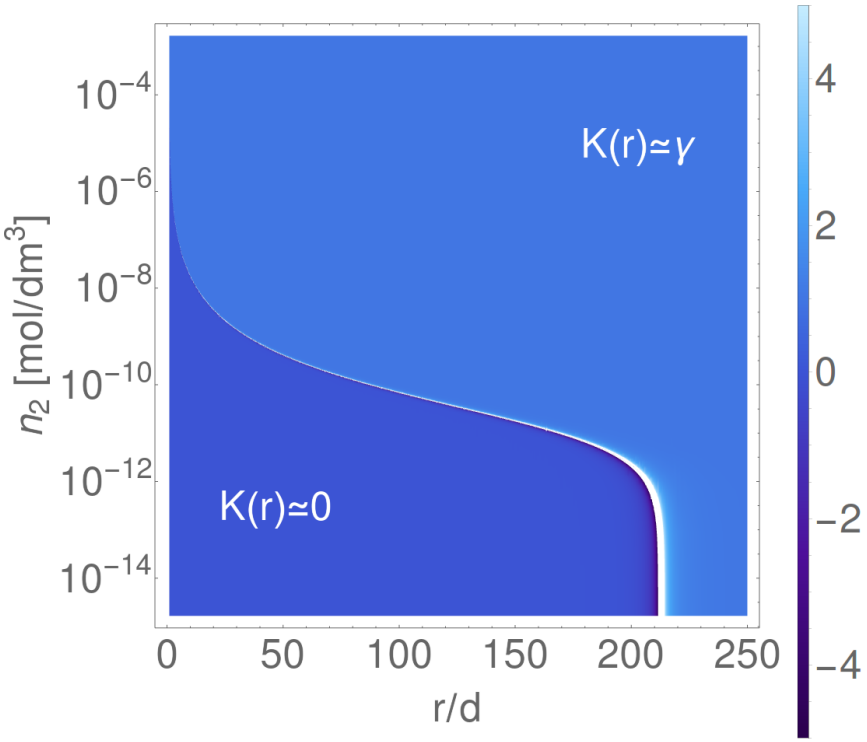


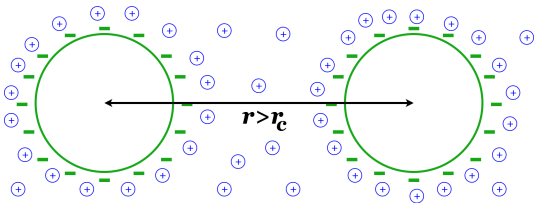
- $T = 300K$
- $m = 4.5 \times 10^{-16}kg$
- $\gamma = 4.5 \times 10^{-9}kg/s$

Surface-charged spheres and counter-ions

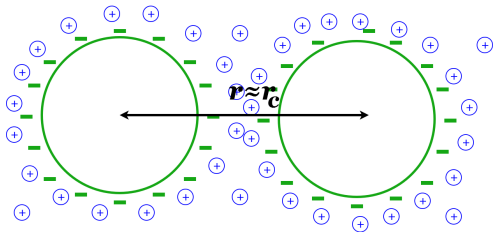


$K(r)$ for different concentrations n_2

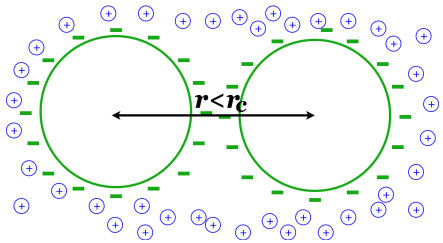




$r > r_c$, each particle has its own layer of ions



$r \simeq r_c$, layers see each other, peak in friction



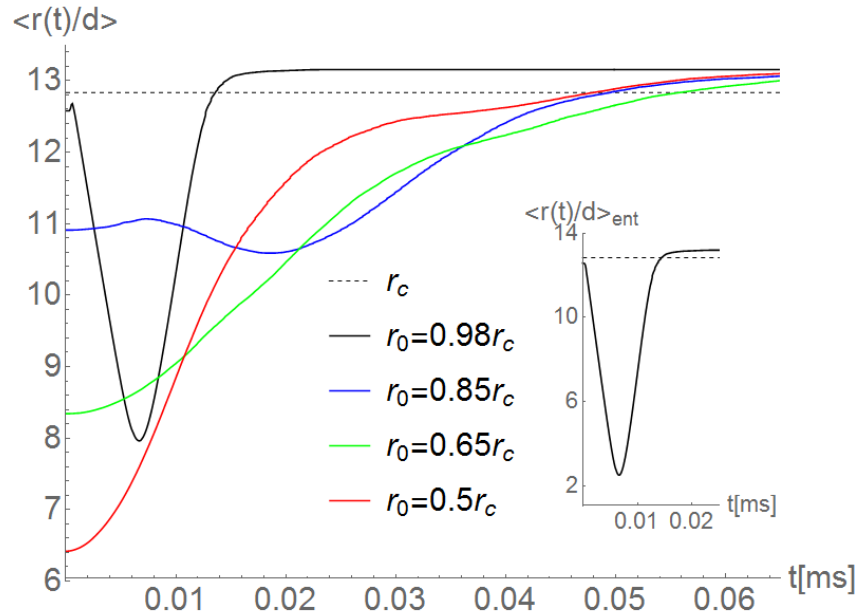
$r < r_c$, layers reorganize into single layer?

...and what if we combine $K(r)$ with inertial terms?

Numerical solution to:

$$m\ddot{r} + K(r)\dot{r} = 2F(r) + \sqrt{2}\sigma g_{-}(r)\eta_{-}$$

However $K(r)$ from the **over-damped** theory (no compatibility guaranteed!) in the regime of singular behavior.



transient attraction effect (non-equilibrium effect!) of like-charged spheres

Experimental confirmation?

Study of transient effects is rare, but ⇒ E. Nagornyak, H. Yoo, and G. H. Pollack, Soft Matter 5, 3850 (2009)

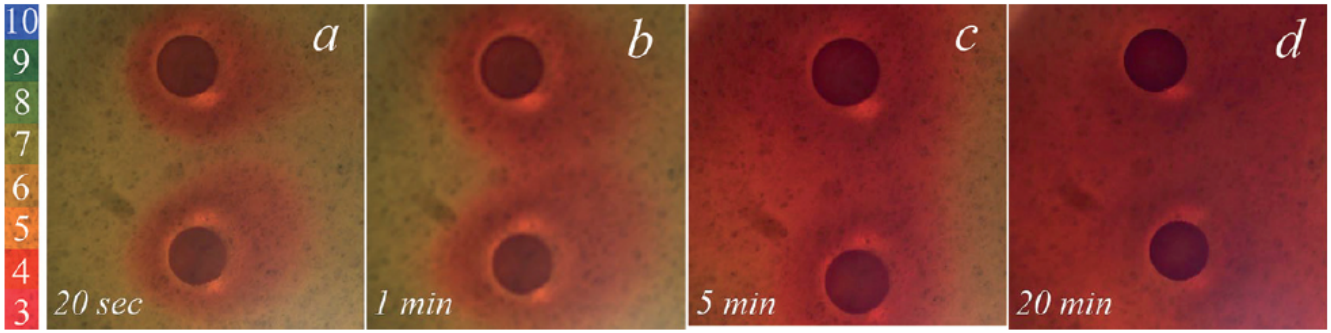
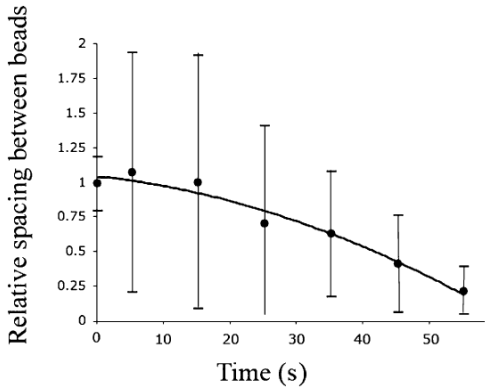


Fig. 3 Growth and propagation of low pH zone formed around negatively charged beads. pH scale shown in left panel.



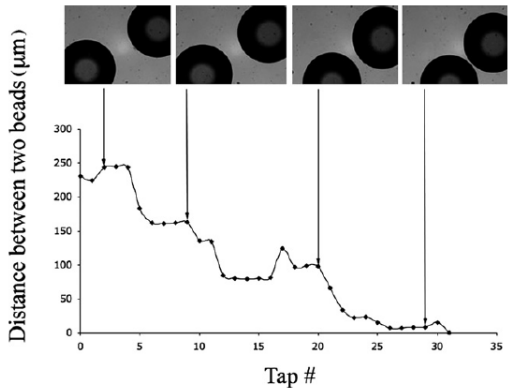


Fig. 1 Surface-to-surface distance between two beads following a series of taps, imparted every 2–3 seconds.

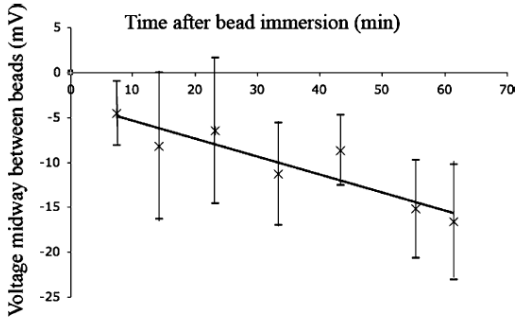


Fig. 5 Time dependence of electrical potential midway between beads. Standard deviations are shown as vertical lines. $n = 3$ experiments.

conclusions

tracer-bath coupling force is spatially correlated:

$$< \xi(0)\xi(r) > = < F_{eff}(0)F_{eff}(r) >$$

- we can mimic this correlations with SCN-driven Langevin dynamics
- SCN requires **spatially variant** friction coefficient
- over-damped dynamics predicts:
  - response forces
  - singularity in friction
  - transient attraction of like-charge spheres

Articles:

- M. Majka, P. F. Góra, Collectivity in diffusion of colloidal particles: from effective interactions to spatially correlated noise, J. Phys. A: Math. Theor., 50, 054004 (2017)
- M. Majka, P.F. Góra, Thermodynamically consistent Langevin dynamics with spatially correlated noise predicts frictionless regime and transient attraction effect, Phys, Rev. E, 94, 4, 042110 (2016)