Brownian motion at various length scales with hydrodynamic and direct interactions

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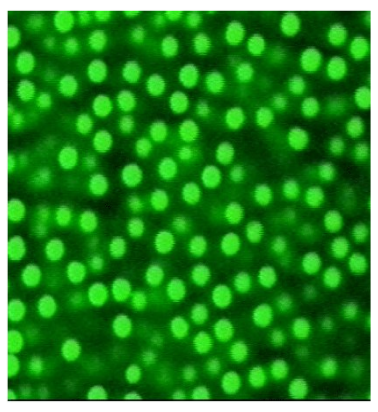
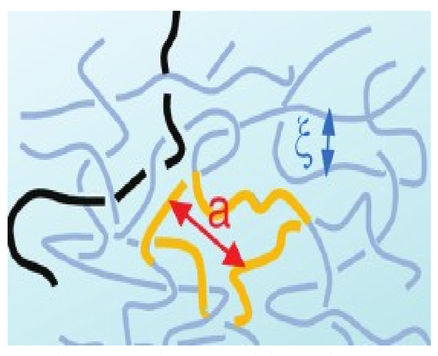
Motivation and goals

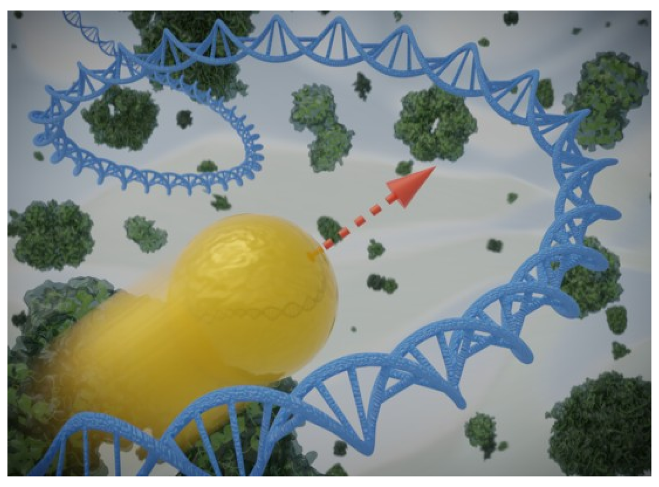
Example of complex liquids: suspensions, polymer solutions





Cai, Panyukov, Rubinstein, Macromolecules, 2011, 44, 7853-7863

Drag force on a spherical particle moving in a complex liquid:



$$\mathbf{F} = \zeta\,(a)\,\mathbf{U}$$

Friction coefficient

Stokes' law in simple liquids:

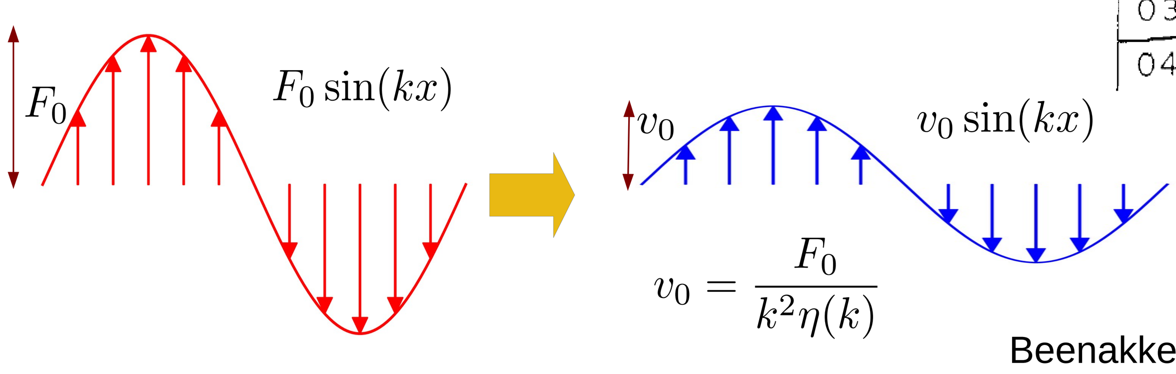
$$\zeta\,(a) = 6\pi\eta_0 a$$

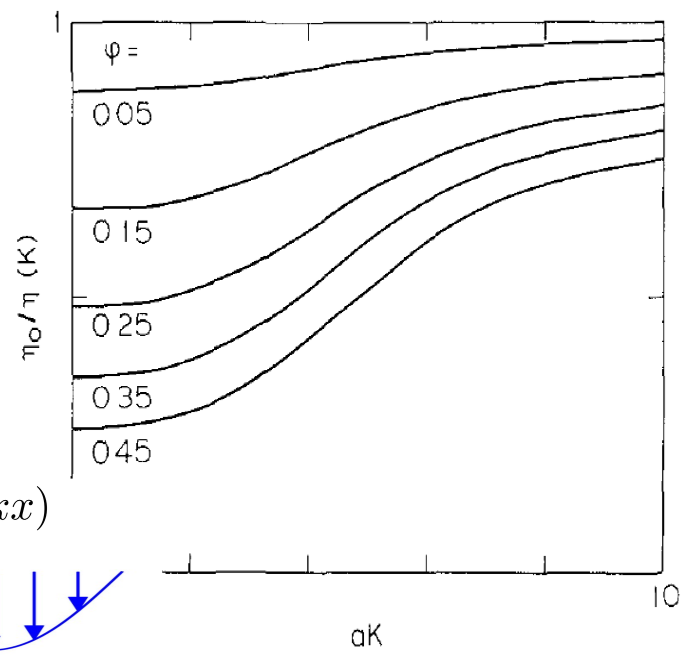
What is the friction experienced by a particle moving in complex liquid?

Simple and complex liquids

simple liquid: complex liquid:

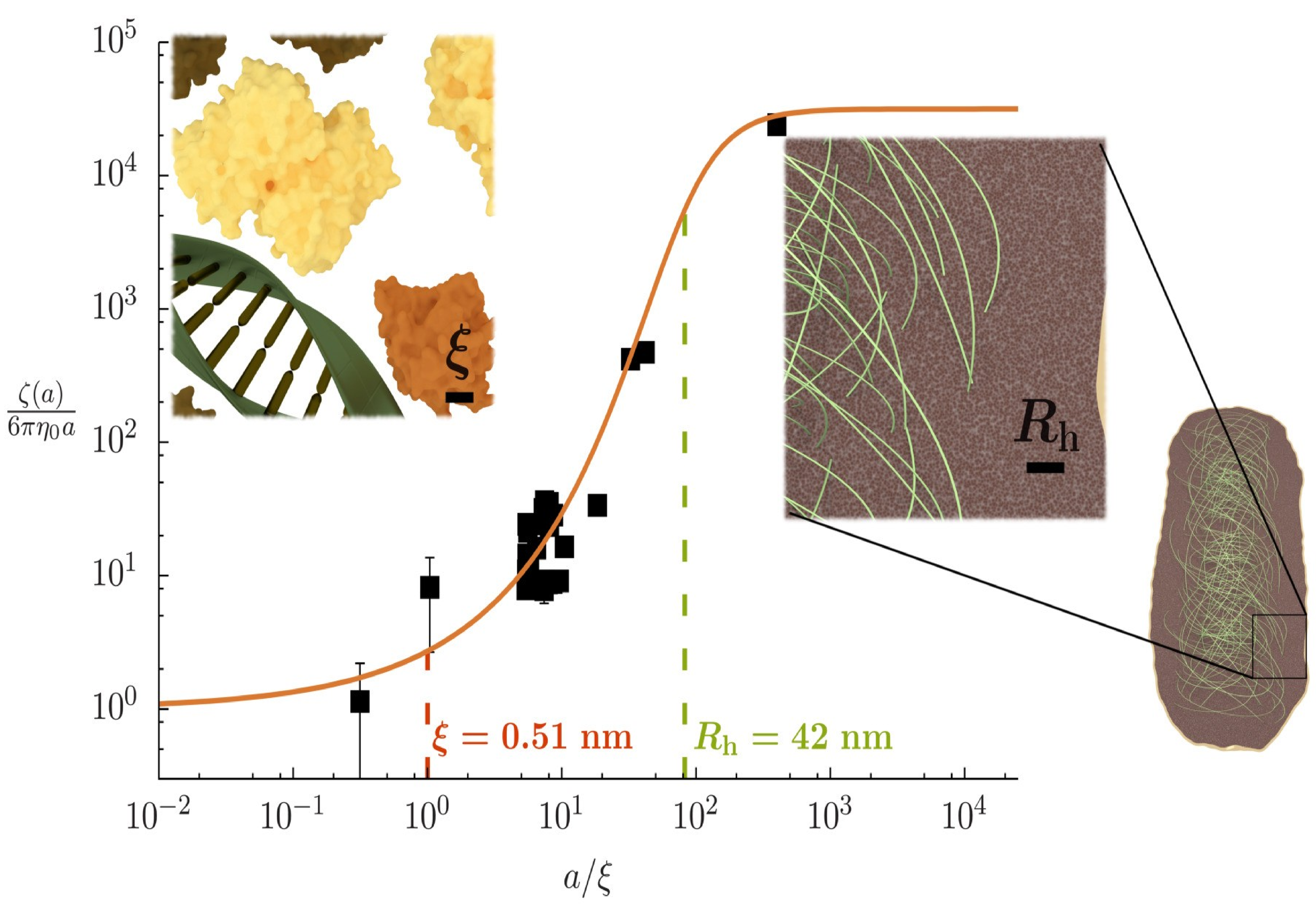
$\eta = \mathrm{const}$ $\eta(k)$





Beenakker C., Physica A, 128, 48 (1984)

Motion in complex liquids



Experimental data from the literature on diffusion inside Escherichia Coli cell cytoplasm. Normalized friction coefficient as a function of radius of the probe particle [Kalwarczyk et al., *Nano Lett.* 2011, 11, 2157–2163].

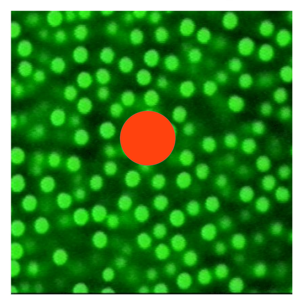
Size of a probe particle is crucial in order to determine the friction experienced by the particle.

Theory

Average velocity field around the probe particle in complex liquid

[Szymczak, P. Cichocki, B. Journal of Statistical Mechanics: Theory and Experiment, 2008, P01025]

$$\langle \mathbf{v}(\mathbf{r})\rangle = \int d^3r'\,\mathbf{G}_{\mathrm{eff}}(\mathbf{r}-\mathbf{r}')\mathbf{t}^{\mathrm{irr}}(\mathbf{r}')\mathbf{F}$$



Effective Green function, does not depend on the probe particle:

$$\hat{\mathbf{G}}_{\mathrm{eff}}(\mathbf{k}) = \frac{1}{\eta\,(k)\,k^2}\left(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}}\right)$$

Gives forces in complex liquid induced by the probe particle. Also contains all 'interactions' between complex liquid and the probe particle.

Boundary conditions on the surface of the probe particle: $\mathbf{v}\,(a\hat{\mathbf{r}}) = \mathbf{U}$

$$\eta\,(k) = \frac{1}{6\pi k^2}\left[\int_0^\infty da\,a^2\frac{j_0\,(ak)}{\zeta\,(a)}\right]^{-1}$$

K. Makuch, R. Holyst, T. Kalwarczyk, P. Garstecki, J. F. Brady, Soft Matter, 2020, 16, 114

Idea of our approach

Assume that the viscosity function is given and investigate the response of the probe to the external force in order to determine the diffusion coefficient of the probe

Results

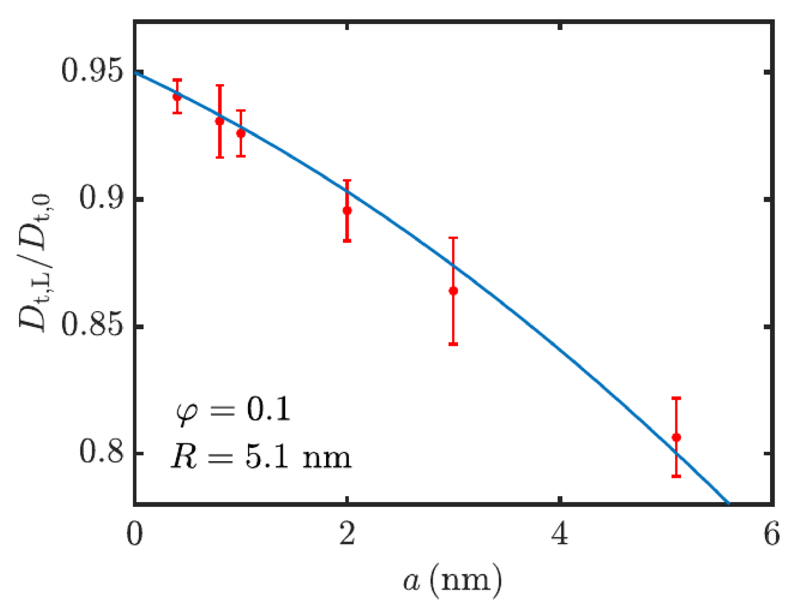
$$\mathbf{t}^{\mathrm{irr}}(\mathbf{r}')\mathbf{F} = \left\langle \sum_{i=1}^{N}\tilde{\mathbf{C}}_i^{\mathrm{t}}(\mathbf{r};\mathbf{R}^N)\cdot\left\{-\frac{\partial\Phi(\mathbf{R}^N)}{\partial\mathbf{R}_i}+\delta_{i1}\mathbf{F}-k_{\mathrm{B}}T\frac{\partial}{\partial\mathbf{R}_i}\ln[P_{\mathrm{F}}^{\infty}(\mathbf{R}^N)]\right\}\right\rangle^{irr}$$

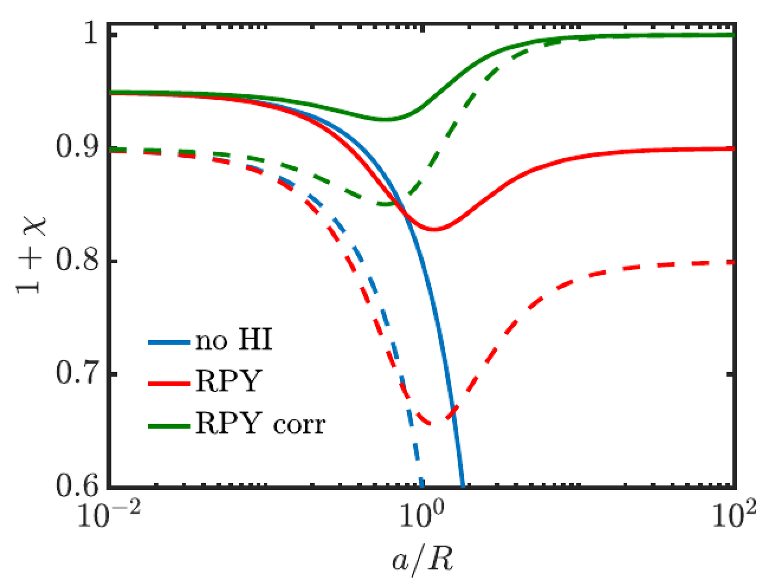
Assumptions:

- spherical probe (radius a)
- spherical host particles (radius R)
- small number of host particles (volume fraction φ)
- Hydrodynamic interactions in convective kernel neglected (but not in the viscosity function)

$$D_{\mathrm{t,L}} = \Delta^{(0)} + \Delta^{(1)} + \ldots$$

$$\Delta^{(0)} = \frac{k_{\mathrm{B}}T}{3\pi^2}\int_0^\infty dk\,\frac{j_0(ka)}{\eta^0(k)} \qquad \Delta^{(1)} = \frac{k_{\mathrm{B}}T}{3\pi^2}\int_0^\infty dk\,\frac{j_0(ka)}{\eta^0(k)}\chi(a)$$





Blue: our calculations. Red points:simularions (no hydrodynamic interactions) of E. Raczyłło, D. Gołowicz, T. Skóra, K. Kazimierczuk, and S. Kondrat, Nano Lett. 24, 4801 (2024).

Outlook

- Nonspherical particles
- Probe-host reactions in complex fluids

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