Stokes' law and intrinsic viscosity coefficient in complex liquids

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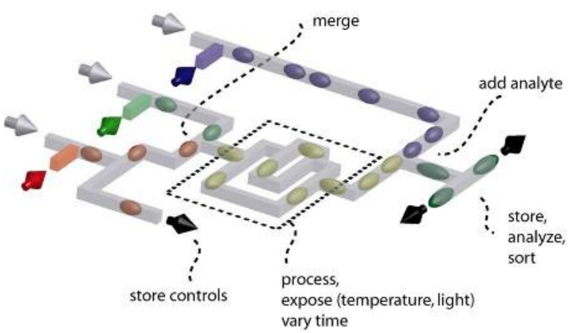
01.02.2017, Caltech

Motivation

December 2015

Piotr Garstecki



+ ~20 group members

Robert Hołyst

Diffusion in biological systems and complex liquids
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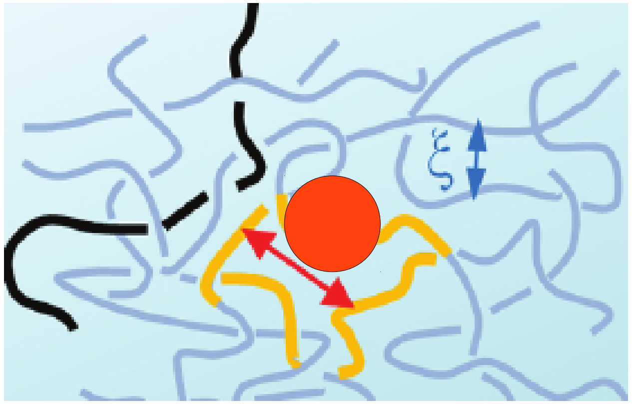
+ ~20 group members

Motivation – scaling with radius of particle

Observation in experiments with diffusion on complex liquids

$$D \neq \frac{k_B T}{6\pi\eta a}$$



In complex liquids scaling with a may be dramatically different!

Different scaling also observed at many systems, e.g.

Thomas Gisler and David A Weitz. PRL, 82(7):1606, 1999

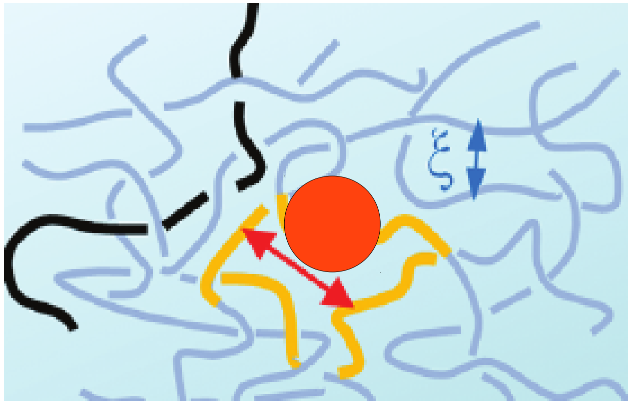
It happens when size of the particles is comparable to length characterizing complex liquid

Roseanna N Zia and John F Brady. Theoretical microrheology 113-157. Springer, 2015

Goal

What is the scaling of diffusion coefficient with size of the particle in complex liquid?

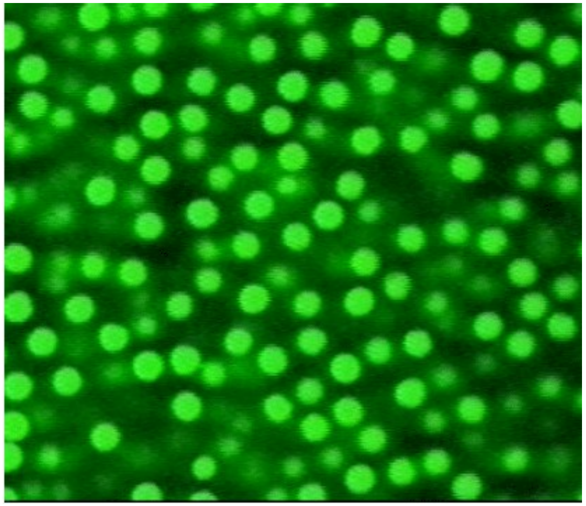
What is the relation between diffusion and viscosity of complex liquid?

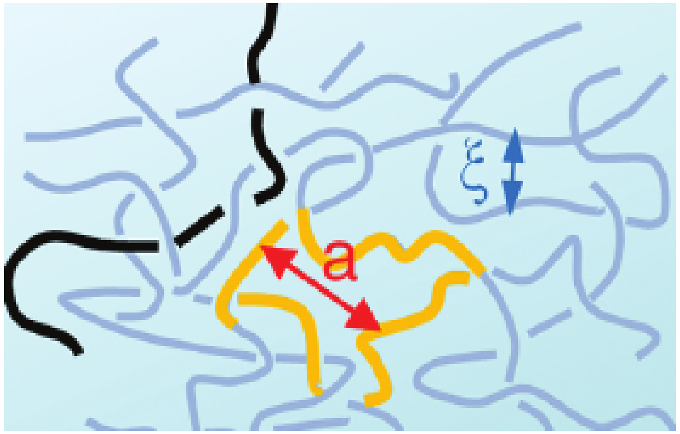


Complex liquids

Liquids with polyatomic structures

Examples: colloidal suspensions, polymer liquids, cell cytoplasm, ...





Frequency and wave-vector-dependent viscosity

Difference between simple and complex liquids:

simple liquid

$$\eta = \text{const}$$

complex liquid

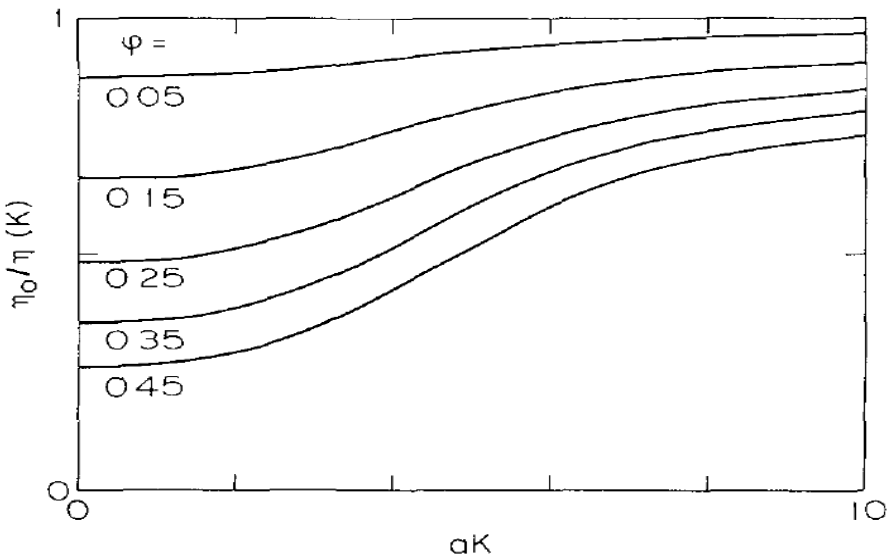
$$\underline{\eta(\omega, k)}$$

Smoluchowski dynamics with hydrodynamic interactions and direct interactions between particles suspended in fluid

+

linear response theory

Szymczak, P. & Cichocki, B. Journal of Statistical Mechanics: Theory and Experiment, 2008, P0102



Beenakker, C. W. J. Physica A: Statistical and Theoretical Physics, Elsevier, 1984, 128, 48-8

Consequences of linear response theory

Linear response:

$$V(\omega) = \zeta(\omega) F(\omega)$$

Fluctuation-dissipation theorem:

$$D(\omega) = \frac{k_B T}{\zeta(\omega)}$$

Assumption valid for big particles (bigger than all characteristic length scales of complex fluid):

Stokes' law

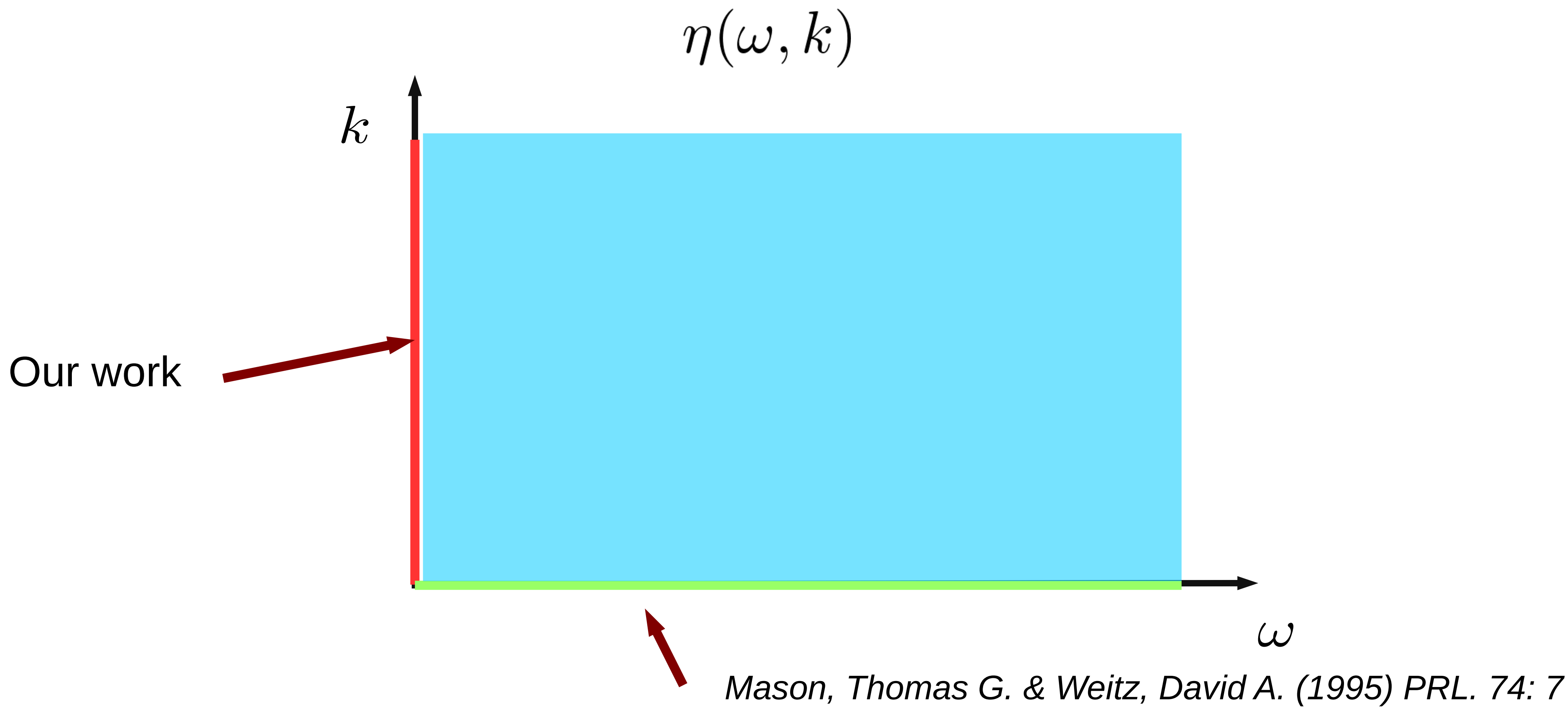
$$\zeta(\omega) = 6\pi\eta(\omega)a$$

Active microrheology

Passive microrheology

Invalid for small particles

Current stage of microrheology in complex liquids

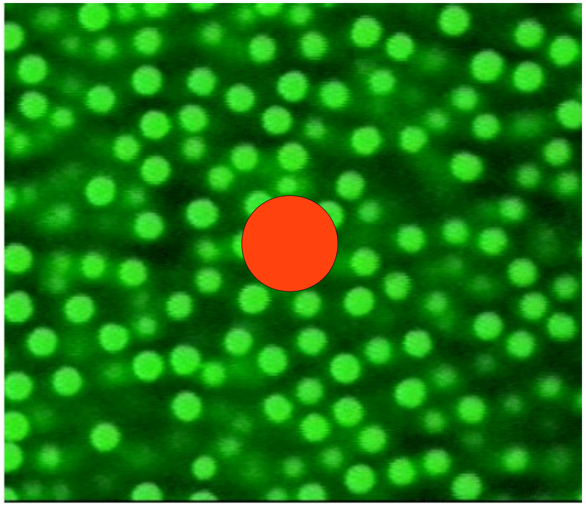


Current stage of knowledge – in the literature there is no generalization of the Stokes' law for wave-vector-dependent viscosity. Therefore there is no theoretical foundation for microrheology with small particles.

There is also no generalization for arbitrary frequency and wave-vector

Goals of our work

Spherical particle immersed in complex liquid



$$\eta(k)$$

Mean-field

1) Drag force on spherical particle moving in complex liquid:

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

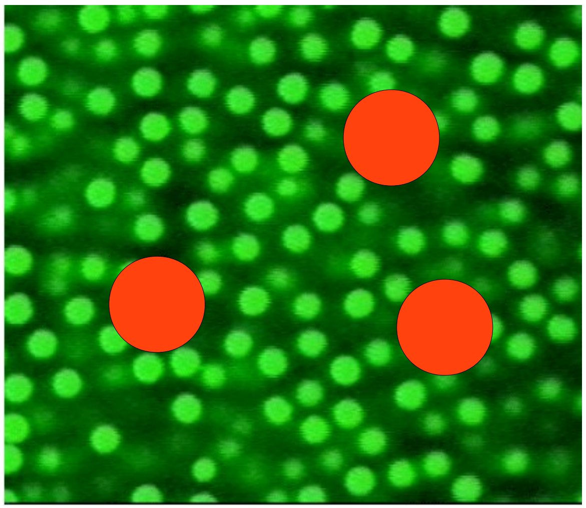
Friction coefficient

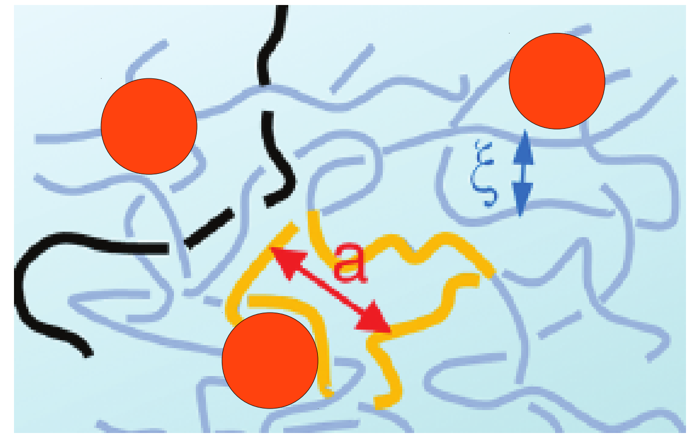
Stokes law in <u>simple liquids</u>:

$$\zeta\left(a\right) = 6\pi\eta a$$

Goals of our work

Add particles to complex liquids





2) Increase of viscosity

$$\eta_{\text{eff}} = \eta\left(0\right)\left(1 + E\left(a\right)\phi\right)$$

intrinsic viscosity coefficient

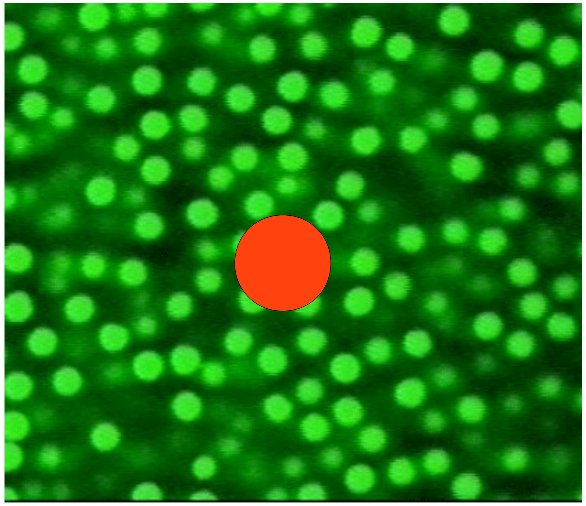
intrinsic viscosity coefficient
<u>(simple liquids)</u>:

$$E\left(a\right) = 5/2$$

Stokes law in complex liquids – formulation of the problem

Stokes equations in <u>complex liquids</u> viscosity depends on scale:

$$\begin{aligned} i\mathbf{k}p + k^2\eta(k)\,\hat{\mathbf{v}}(\mathbf{k}) &= 0, \\ \mathbf{k}\cdot\hat{\mathbf{v}}(\mathbf{k}) &= 0. \end{aligned}$$



Boundary conditions:

$\mathbf{v}(\mathbf{r}) = \mathbf{U}$ *for* $|r| = a$

$\mathbf{v}(\mathbf{r}) \to 0$ *for* $r \to \infty$

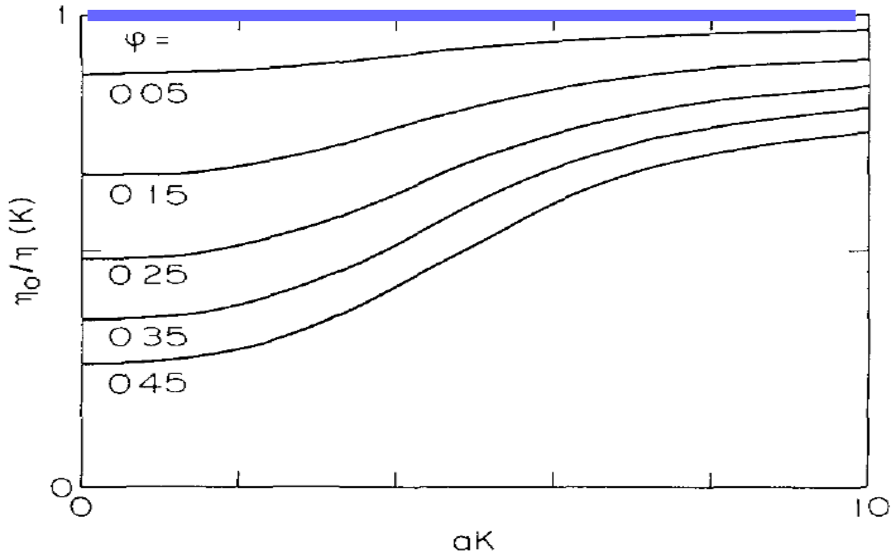
What is the friction coefficient $\zeta(a)$?

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

Stokes law in complex liquids – idea of derivation

Difference between simple and complex liquids:

simple liquid		complex liquid
$\eta\Delta$	$\longrightarrow$	$\eta(\Delta)\,\Delta$
$\eta = \text{const}$	$\longrightarrow$	$\eta(k)$



Linearity and spherical symmetry (isotropic fluid, spherical particle) strongly simplifies derivation in simple fluids, $\eta = \text{const}$

Idea: Derive the Stokes law in simple liquids in Fourier space and with use of spherical symmetry, and generalize it to the case of scale dependent viscosity

Stokes law in simple liquids – idea of derivation that uses symmetry and Fourier space

Ansatz for velocity field:

$$\hat{\mathbf{v}}\left(\mathbf{k}\right) = \hat{\mathbf{v}}_0\left(\mathbf{k}\right) + c\hat{\mathbf{v}}_1\left(\mathbf{k}\right)$$

$$\begin{aligned} i\mathbf{k}p_0 + k^2\eta\hat{\mathbf{v}}_0\left(\mathbf{k}\right) &= \mathbf{F}, \\ \mathbf{k}\cdot\hat{\mathbf{v}}_0\left(\mathbf{k}\right) &= 0. \end{aligned}$$

$$\hat{\mathbf{v}}_0\left(\mathbf{k}\right) = \frac{1}{\eta k^2}\left(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}\right)\mathbf{F}$$

$$\Delta\mathbf{v}_1\left(\mathbf{r}\right) = 0$$

$$\mathbf{v}_1\left(\mathbf{r}\right) = \frac{1}{4\pi r^3}\left(\mathbf{1} - 3\hat{\mathbf{r}}\hat{\mathbf{r}}\right)\mathbf{F}$$

Boundary conditions on the surface of particle, $\mathbf{v}\left(a\hat{\mathbf{r}}\right) = \mathbf{U}$
applied to the above ansatz lead to $c, \mathbf{F}$

$$\mathbf{F} = 6\pi\eta a\mathbf{U}$$

Stokes law – generalization to the case of complex liquids

Ansatz for velocity field:

$$\hat{\mathbf{v}}\left(\mathbf{k}\right) = \hat{\mathbf{v}}_0\left(\mathbf{k}\right) + c\hat{\mathbf{v}}_1\left(\mathbf{k}\right)$$

$$\begin{aligned} i\mathbf{k}p_0 + k^2\eta\left(k\right)\hat{\mathbf{v}}_0\left(\mathbf{k}\right) &= \mathbf{F}, \\ \mathbf{k}\cdot\hat{\mathbf{v}}_0\left(\mathbf{k}\right) &= 0. \end{aligned}$$

$$\hat{\mathbf{v}}_0\left(\mathbf{k}\right) = \frac{1}{\eta\left(k\right)k^2}\left(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}\right)\mathbf{F}$$

$$\eta\left(\Delta\right)\Delta\mathbf{v}_1\left(\mathbf{r}\right) = 0$$

$$\mathbf{v}_1\left(\mathbf{r}\right) = \frac{1}{4\pi r^3}\left(\mathbf{1} - 3\hat{\mathbf{r}}\hat{\mathbf{r}}\right)\mathbf{F}$$

Boundary conditions on the surface of particle, $\mathbf{v}\left(a\hat{\mathbf{r}}\right) = \mathbf{U}$
applied to the above ansatz lead to

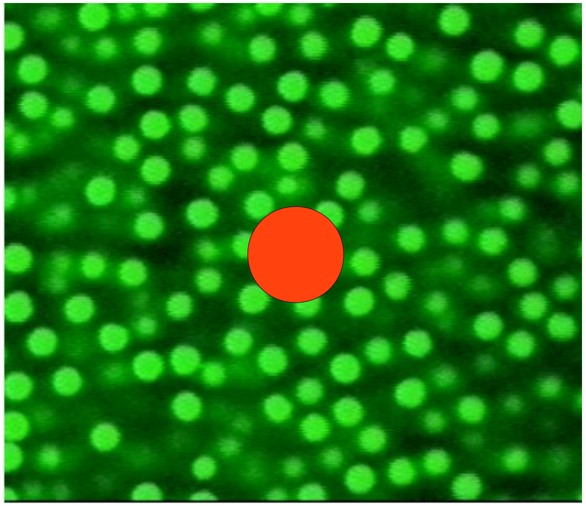
$$\mathbf{U} = \frac{1}{(2\pi)^3}\int d^3k\; e^{ia\hat{\mathbf{r}}\mathbf{k}}\frac{1}{\eta\left(k\right)k^2}\left(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}\right)\mathbf{F} + c\frac{1}{4\pi r^3}\left(\mathbf{1} - 3\hat{\mathbf{r}}\hat{\mathbf{r}}\right)\mathbf{F}$$

which yields...

Stokes' law in complex liquids

What is the friction coefficient?

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



$$\zeta(a) = \frac{3\pi^2}{\int_0^\infty dk\,\frac{j_0(ka)}{\eta(k)}}$$

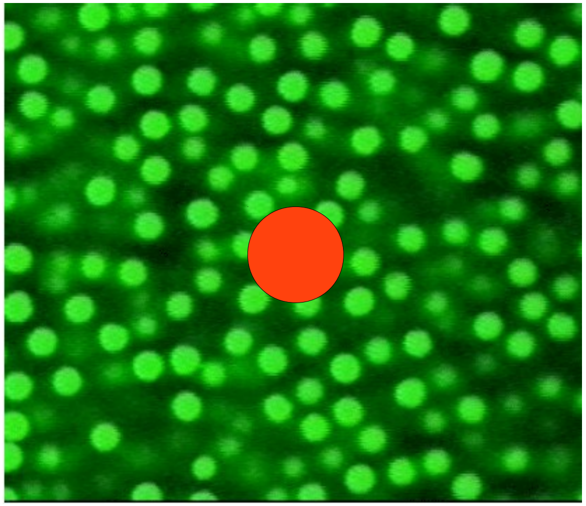
$$j_0(x) = \sin(x)/x$$

Application of the Stokes law in complex liquids
- from friction coefficient to scale dependent viscosity

Stokes law: from scale dependent viscosity to friction coefficient

$$\zeta(a) = 3\pi^2 / \left(\int_0^\infty dk\, j_0(ka) / \eta(k) \right)$$

Fourier transform



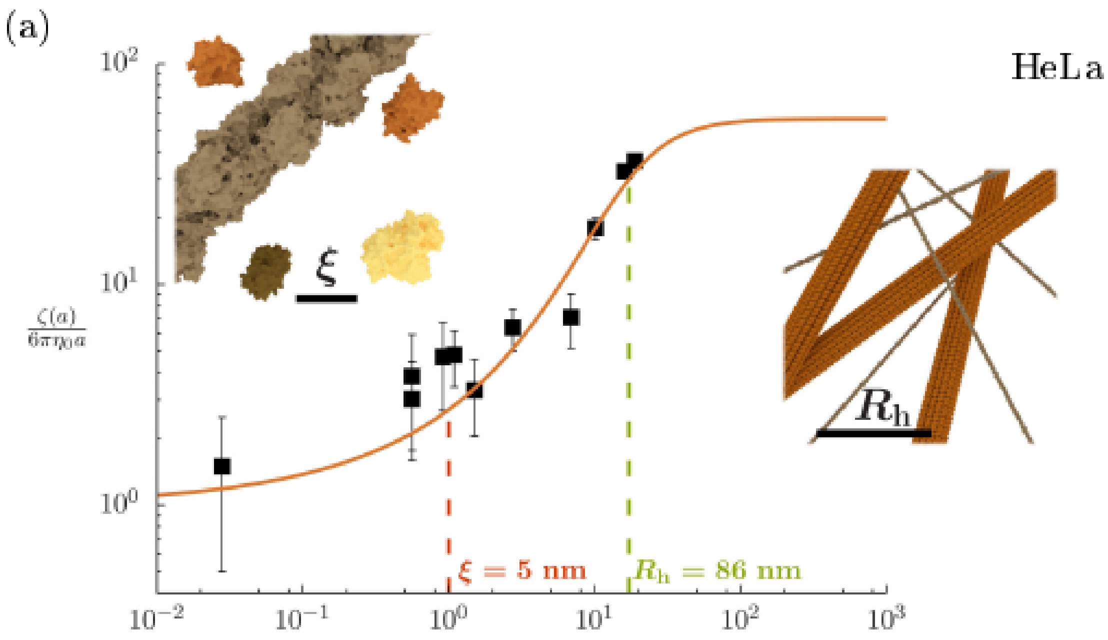
friction coefficient from scale dependent viscosity:

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

Friction from passive or active microrheological experiments

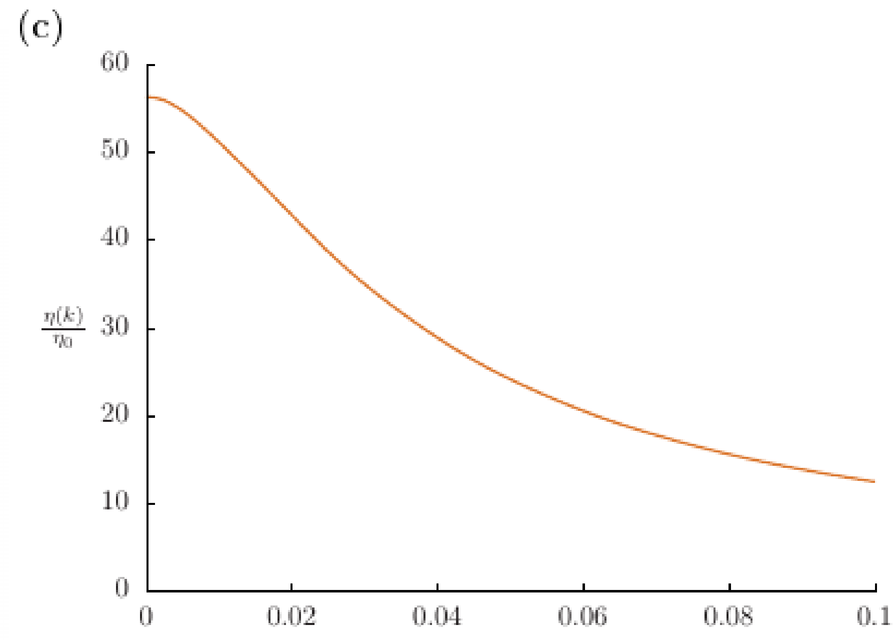
Application of the Stokes’ law in complex liquids
- from friction coefficient to scale dependent viscosity

$\zeta(a)/6\pi\eta_0 a$



a/ξ

$\eta(k)/\eta_0$

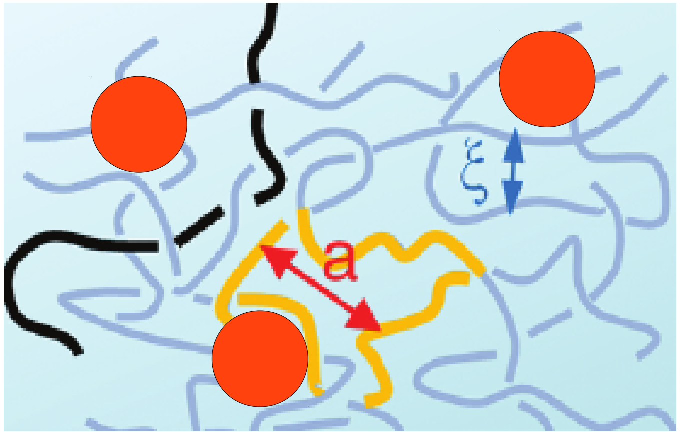


$k\xi$

Friction coefficient of different
particles inside HeLa cell cytoplasm

Intrinsic viscosity coefficient E(a) in complex liquids

$$\eta_{\text{eff}} = \eta(0)\left(1 + E(a)\,\phi\right)$$



$$E(a) = -\frac{5}{2}\frac{1}{\eta(0)}\left[\frac{10}{3\pi}a^2\frac{d}{da}\int_0^\infty dk\,\frac{j_0(ak)}{\eta(k)} + \frac{4}{\pi}a\int_0^\infty dk\,\frac{j_2(ak)}{\eta(k)} + \frac{4a^2}{3\pi}\frac{d}{da}\int_0^\infty dk\,\frac{j_2(ak)}{\eta(k)}\right]^{-1}$$

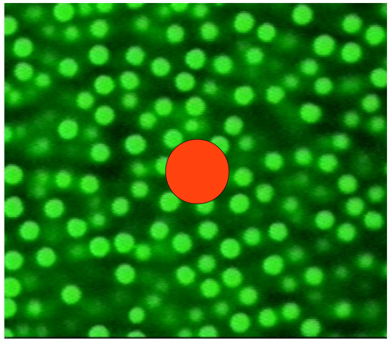
$$j_0(x) = \sin(x)/x$$

$$j_2(x) = -\sin(x)/x - 3\cos x/x^2 + 3\sin(x)/x^3$$

Intrinsic viscosity coefficient and Stokes' friction coefficient

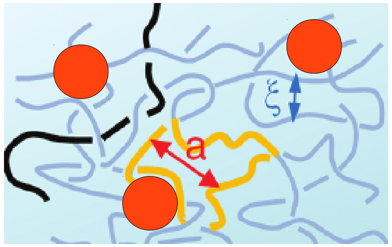
Stokes law in complex liquids:

$$\zeta\left(a\right)=3\pi^{2}/\left(\int_{0}^{\infty}dk\,j_{0}\left(ka\right)/\eta\left(k\right)\right)$$



Einstein viscosity coefficient in complex liquids:

$$E\left(a\right)=-\frac{5}{2}\frac{1}{\eta\left(0\right)}\left[\frac{10}{3\pi}a^{2}\frac{d}{da}\int_{0}^{\infty}dk\,\frac{j_{0}\left(ak\right)}{\eta\left(k\right)}+\frac{4}{\pi}a\int_{0}^{\infty}dk\,\frac{j_{2}\left(ak\right)}{\eta\left(k\right)}+\frac{4a^{2}}{3\pi}\frac{d}{da}\int_{0}^{\infty}dk\,\frac{j_{2}\left(ak\right)}{\eta\left(k\right)}\right]^{-1}$$



Universal relation between friction and intrinsic viscosity coefficient

$$E\left(a\right)=\frac{5}{12\pi\eta\left(0\right)a^{2}}\frac{\zeta\left(a\right)^{2}}{\frac{d\zeta\left(a\right)}{da}}$$

Summary

- Stokes law in complex liquids,
- Intrinsic viscosity coefficient,
- Universal relation between intrinsic viscosity coefficient and friction coefficient

… when viscosity is scale-dependent (depends on wave-vector) and does not depend on frequency