# Lattice Boltzmann simulations of soft–matter systems

Burkhard Dünweg
Max Planck Institute for Polymer Research
Ackermannweg 10
55128 Mainz

B. D. and A. J. C. Ladd, arXiv:0803.2826v2,
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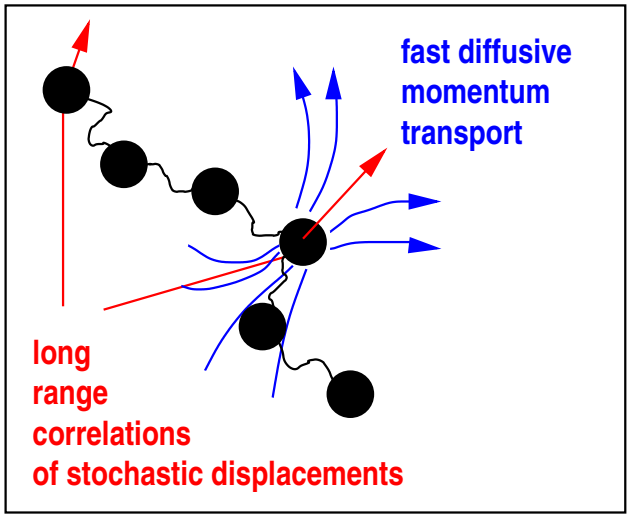
# Hydrodynamic interactions




Navier–Stokes equation
(Green's function)
solvent viscosity $\eta$

$$\langle \Delta\vec{r}_i \otimes \Delta\vec{r}_j \rangle = 2\, \overleftrightarrow{D}_{ij}\, \Delta t$$

Oseen tensor:

$$\overleftrightarrow{D}_{ij} = k_B T\, \overleftrightarrow{\mu}_{ij} = \frac{k_B T}{8\pi\eta} \frac{1}{|\vec{r}_i - \vec{r}_j|} \left( \overleftrightarrow{1} + \hat{r}_{ij} \otimes \hat{r}_{ij} \right)$$

# Oseen tensor

$\overleftrightarrow{\mu}_{ij}$ from hydrodynamics:

$$\eta\vec{\nabla}^2\vec{u} - \vec{\nabla}p + \vec{F}\delta(\vec{r}) = 0$$

$$\vec{\nabla}\cdot\vec{u} = 0$$

$$\vec{u}(\vec{r}) = \frac{1}{8\pi\eta r}\left(\overleftrightarrow{1} + \hat{r}_{ij}\otimes\hat{r}_{ij}\right)\vec{F}$$

# Schmidt number

Kinematic viscosity

$$\eta_{kin} = \eta/\rho \qquad (m^2/sec)$$

measures diffusion of momentum
Particle diffusion constant $D$
Schmidt number:

$$Sc = \eta_{kin}/D$$

Typically, $Sc = 10^2 \ldots 10^3$
$\Rightarrow$ Quasistatic approximation justified!

# Brownian Dynamics

$$\vec{r}_i(t+\Delta t) = \vec{r}_i(t) + \Delta t \sum_j \overleftrightarrow{\mu}_{ij}\, \vec{F}_j(t) + \Delta\vec{r}_i$$

$$\langle \Delta\vec{r}_i \otimes \Delta\vec{r}_j \rangle = 2\, \overleftrightarrow{D}_{ij}\, \Delta t$$

direct implementation on the computer.

**Problem:**

For many Brownian particles, the correlation matrix becomes huge and **very** unwieldy!

$\Rightarrow$ **Explicit** momentum transport desired.

# Is this argument still valid?

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## Accelerated Stokesian dynamics: Brownian motion

Adolfo J. Banchio[a] and John F. Brady[b]
*Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125*

(Received 21 November 2002; accepted 12 March 2003)

A new Stokesian dynamics (SD) algorithm for Brownian suspensions is presented. The implementation is based on the recently developed accelerated Stokesian dynamics (ASD) simulation method [Sierou and Brady, J. Fluid Mech. **448**, 115 (2001)] for non-Brownian particles. As in ASD, the many-body long-range hydrodynamic interactions are computed using fast Fourier transforms, and the resistance matrix is inverted iteratively, in order to keep the computational cost $O(N \log N)$. A fast method for computing the Brownian forces acting on the particles is applied by splitting them into near- and far-field contributions to avoid the $O(N^3)$ computation of the square root of the full resistance matrix. For the near-field part, representing the forces as a sum of pairwise contributions reduces the cost to $O(N)$; and for the far-field part, a Chebyshev polynomial approximation for the inverse of the square root of the mobility matrix results in an $O(N^{1.25} \log N)$ computational cost. The overall scaling of the method is thus roughly of $O(N^{1.25} \log N)$ and makes possible the simulation of large systems, which are necessary for studying long-time dynamical properties and/or polydispersity effects in colloidal dispersions. In this work the method is applied to study the rheology of concentrated colloidal suspensions, and results are compared with conventional SD. Also, a faster approximate method is presented and its accuracy discussed.
 [DOI: 10.1063/1.1571819]

# Mesoscopic methods: General considerations

Disadvantage of Molecular Dynamics:

- Hard potentials, short time step, solvent motion on an uninteresting time scale
- Any solvent potential $\longrightarrow$ non–trivial potential of mean force between Brownian particles $\longrightarrow$ equilibration of *combined* system necessary!

$\Rightarrow$ **Desirable:**

- Mesoscopic method (coarse–grained length scale, *coarse–grained time scale*)
- with *structureless solvent* (i. e. solvent is *not* needed for statics)

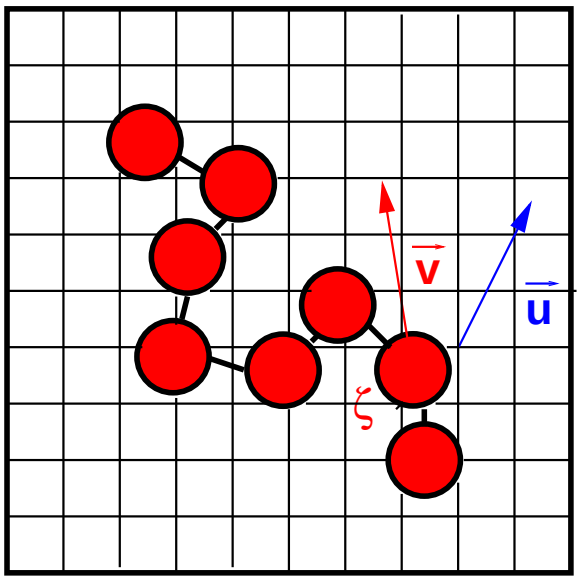
**Methods:**

- Dissipative particle dynamics
- Multi–particle collision dynamics
- Lattice Boltzmann + Molecular Dynamics

# Coupling lattice Boltzmann $\leftrightarrow$ Molecular Dynamics

(P. Ahlrichs & B. D. 1999)

- particle system: stochastic Molecular Dynamics
- solvent: stochastic lattice Boltzmann
- *dissipative* coupling:




- $\vec{F} = -\zeta(\vec{v} - \vec{u})$
- $\vec{u}$: interpolation from surroundings
- momentum conservation
- fluctuation–dissipation theorem

yields hydrodynamic interactions on large scales

# Equations of motion, continuum limit

$$\vec{u}_i \equiv \int d^3\vec{r}\sigma_i(\vec{r}_i,\vec{r})\vec{u}\left(\vec{r}\right)$$

$$\begin{aligned}\frac{d}{dt}\vec{r}_i &= \frac{1}{m_i}\vec{p}_i \\ \frac{d}{dt}\vec{p}_i &= \vec{F}_i - \zeta_i\left(\frac{1}{m_i}\vec{p}_i - \vec{u}_i\right) + \vec{f}_i\end{aligned}$$

$$\partial_t\rho + \partial_\alpha j_\alpha = 0$$

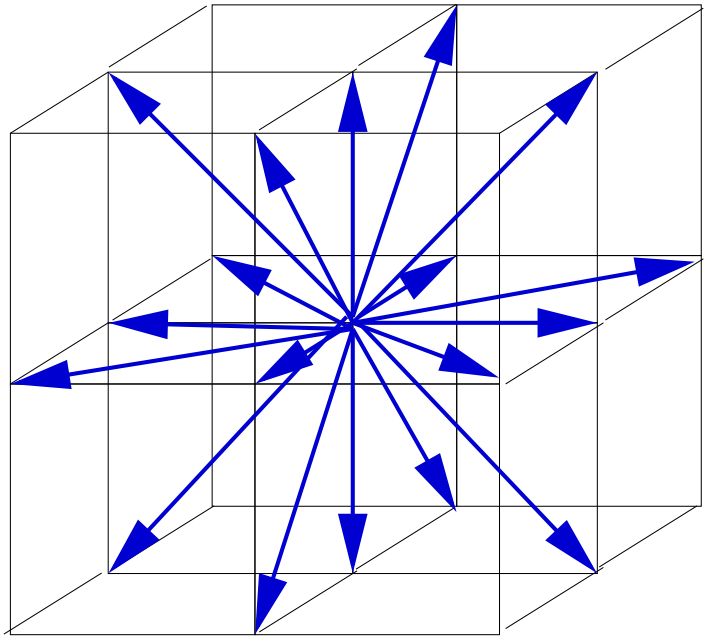
$$\partial_t j_\alpha + \partial_\beta\left(p\delta_{\alpha\beta} + \rho u_\alpha u_\beta\right) = \partial_\beta\eta_{\alpha\beta\gamma\delta}\partial_\gamma u_\delta + \partial_\beta Q_{\alpha\beta}$$

$$+\sum_i\left[\zeta_i\left(\frac{1}{m_i}p_{i\alpha} - u_{i\alpha}\right) - f_{i\alpha}\right]\sigma_i\left(\vec{r}_i,\vec{r}\right)$$

# Fluctuation–dissipation relations

$$
\begin{aligned}
\langle f_{i\alpha} \rangle &= 0 \\
\langle Q_{\alpha\beta} \rangle &= 0 \\
\left\langle f_{i\alpha}\left(t\right) f_{j\beta}\left(t'\right)\right\rangle &= 2k_B T \zeta_i \delta_{ij} \delta_{\alpha\beta} \delta\left(t - t'\right) \\
\left\langle Q_{\alpha\beta}\left(\vec{r}, t\right) Q_{\gamma\delta}\left(\vec{r}', t'\right)\right\rangle &= 2k_B T \eta_{\alpha\beta\gamma\delta} \delta\left(\vec{r} - \vec{r}'\right) \delta\left(t - t'\right)
\end{aligned}
$$

# Lattice Boltzmann



- linearized Boltzmann equation (kinetic theory of gases)
- fully discretized
- sites $\vec{r}$, lattice spacing $a$
- time t, time step $h$

- $\vec{c}_i$ small set of velocities
- $\vec{c}_i h$ connects two sites
- $n_i(\vec{r}, t)$: real number, mass density on site $\vec{r}$ corresponding to velocity $\vec{c}_i$

$$n_i(\vec{r} + \vec{c}_i h, t + h) = n_i^\star(\vec{r}, t) = n_i(\vec{r}, t) + \Delta_i(\vec{r}, t)$$

# Conservation laws, symmetries

$$n_i(\vec{r} + \vec{c}_i h, t + h) = n_i^\star(\vec{r}, t) = n_i(\vec{r}, t) + \Delta_i \{n_i(\vec{r}, t)\}$$

$$\rho = \sum_i n_i$$

$$\vec{j} = \rho \vec{u} = \sum_i n_i \vec{c}_i$$

$$\sum_i \Delta_i = \sum_i \Delta_i \vec{c}_i = 0$$

- 👍 mass conservation
- 👍 momentum conservation
- 👍 locality
- 👎 rotational symmetry (lattice!)
- 👎 Galilei invariance (finite number of velocities)

# Low Mach number physics

- only $u \ll c_i$
- only $u \ll c_s$
- $Ma = u/c_s \ll 1$
- low Mach number $\Rightarrow$
  compressibility does not matter $\Rightarrow$
  equation of state does not matter $\Rightarrow$
  choose ideal gas!

$m_p$ particle mass:

$$p = \frac{\rho}{m_p} k_B T$$

$$c_s^2 = \frac{\partial p}{\partial \rho} = \frac{1}{m_p} k_B T$$

$$p = \rho c_s^2$$

$$k_B T = m_p c_s^2$$

# Necessity of thermal fluctuations

- Ideal gas, temp. $T$, particle mass $m_p$, sound speed $c_s$:

$$k_B T = m_p c_s^2$$

- $c_s \sim a/h$ ($a$ lattice spacing, $h$ time step)
- $c_s$ as small as possible

Example (water):
mass density $\rho = 10^3 kg/m^3$
sound speed realistic: $1.5 \times 10^3 m/s$
sound speed artificial: $c_s = 10^2 m/s$
temperature $T \approx 300K$, $k_B T = 4 \times 10^{-21} J$
particle mass: $m_p = 4 \times 10^{-25} kg$

| | macroscopic scale | molecular scale |
|---|---|---|
| lattice spacing | $a = 1mm$ | $a = 1nm$ |
| time step | $h = 10^{-5} s$ | $h = 10^{-11} s$ |
| mass of a site | $m_a = 10^{-6} kg$ | $m_a = 10^{-24} kg$ |
| "Boltzmann number" | $Bo = (m_p/m_b)^{1/2} = 6 \times 10^{-10}$ | $Bo = (m_p/m_b)^{1/2} = 0.6$ |

# Lattice Boltzmann algorithm

- $\rho = \sum_i n_i$
- $\vec{j} = \sum_i n_i \vec{c}_i$, $\vec{u} = \vec{j}/\rho$
- $\overleftrightarrow{\Pi} = \sum_i n_i \vec{c}_i \otimes \vec{c}_i$
- $n_i^{eq}(\rho, \vec{u}) = w_i \rho \left(1 + \frac{\vec{u}\cdot\vec{c}_i}{c_s^2} + \frac{(\vec{u}\cdot\vec{c}_i)^2}{2c_s^4} - \frac{u^2}{2c_s^2}\right)$, such that
- $\sum_i n_i^{eq} = \rho$
- $\sum_i n_i^{eq} \vec{c}_i = \vec{j}$
- $\sum_i n_i^{eq} \vec{c}_i \otimes \vec{c}_i = \rho c_s^2 + \rho \vec{u} \otimes \vec{u}$
- linear relaxation: $\Delta_i^{det} = \sum_j L_{ij}(n_j - n_j^{eq})$
- addition of noise: $\Delta_i^{stoch}$
- streaming

# Modes

$$n_i^{neq} = n_i - n_i^{eq}$$

Theory of fluctuations (PRE 2007) $\Rightarrow$

$$\left\langle n_i^{neq\,2} \right\rangle = w_i \rho \mu$$

with $\mu = m_p/a^3 = k_B T/(a^3 c_s^2) \Rightarrow$ normalization:

$$\hat{n}_i^{neq} = \frac{n_i^{neq}}{\sqrt{w_i \rho \mu}}$$

modes via orthonormal transformation $\hat{e}_{ki}$:

$$\hat{m}_k^{neq} = \sum_i \hat{e}_{ki} \hat{n}_i^{neq}$$

- $m_0 \propto \rho$
- $(m_1, m_2, m_3) \propto \vec{j}$
- $m_4 \in \text{span}(\rho, \Pi_{\alpha\alpha})$ (bulk stress)
- $\text{span}(m_5, \ldots, m_9) = \text{span}(\bar{\Pi}_{\alpha\beta})$ (5 shear stresses)
- kinetic (or "ghost") modes $m_{10}, \ldots, m_{18}$

# Mode update: Relaxation and noise

$$P\left(\left\{\hat{m}_k^{neq}\right\}\right) \propto \exp\left(-\frac{1}{2}\sum_{k\geq 4}\hat{m}_k^{neq\,2}\right)$$

$$\hat{m}_k^{\star neq} = \gamma_k \hat{m}_k^{neq} + \left(1-\gamma_k^2\right)^{1/2} r_k$$

$r_k$ Gaussian with

$$\langle r_k \rangle = 0 \qquad\qquad \left\langle r_k^2 \right\rangle = 1$$

satisfies detailed balance!

- $\gamma_4 \rightarrow$ bulk viscosity
- $\gamma_5 = \ldots = \gamma_9 \rightarrow$ shear viscosity
- $\gamma_{10} = \ldots \gamma_{18} = 0$ easiest choice

# Chapman–Enskog expansion

Multi–time scale analysis: $\varepsilon \ll 1$ (e. g. $\varepsilon = 10^{-3}$):

$$\vec{r}_1 = \varepsilon \vec{r}$$

interpretation: "coarse–grained ruler":
$1\mu m$ instead of $978nm$

$$t_1 = \varepsilon t$$

interpretation: "coarse–grained clock":
$1ns$ instead of $837ps$

$$t_2 = \varepsilon^2 t$$

interpretation: "yet more coarse–grained clock":
$1\mu s$ instead of $976ns572ps$

- $t_1$ to capture wave–like phenomena
- $t_2$ to capture diffusive phenomena
- location in space and time: read off $\vec{r}_1$, $t_1$, $t_2$

Macroscopic limit is obtained for $\varepsilon \longrightarrow 0$.

$$\vec{r} = \varepsilon^{-1}\vec{r}_1$$

$\vec{r}_1$ fixed $\Rightarrow$ $\vec{r}$ varies with $\varepsilon$ $\Rightarrow$

$$\begin{aligned} n_i &= n_i^{(0)} + \varepsilon n_i^{(1)} + O(\varepsilon^2) \\ \Delta_i &= \Delta_i^{(0)} + \varepsilon \Delta_i^{(1)} + \varepsilon^2 \Delta_i^{(2)} + O(\varepsilon^3) \end{aligned}$$

LBE:

$$n_i(\vec{r}_1 + \varepsilon \vec{c}_i h, t_1 + \varepsilon h, t_2 + \varepsilon^2 h) - n_i(\vec{r}_1, t_1, t_2) = \Delta_i(\vec{r}_1, t_1, t_2)$$

- Taylor expansion wrt $\varepsilon$
- truncate after 2nd order
- hierarchy of LBEs
- moments: $\sum_i \ldots$, $\sum_i \vec{c}_i \ldots$, $\sum_i \vec{c}_i \otimes \vec{c}_i \ldots$
- hierarchy of moment equations
- transform back to $\vec{r}, t$
- $\equiv$ (fluctuating) Navier–Stokes

# "Bare" vs. effective friction constant

$D_0$: long–time diffusion coefficient
$D_0 > k_B T/\zeta_{bare}$ (due to long time tail)
$\vec{F} = \text{const.}$, $\vec{V} = \text{const.}$

$$\vec{V} = \frac{1}{\zeta_{bare}}\vec{F} + \vec{u}_{av}$$

$$\vec{u} \approx \frac{1}{8\pi\eta r}\left(\overleftrightarrow{1} + \hat{r}\otimes\hat{r}\right)\vec{F}$$

$$\vec{u}_{av} = \frac{1}{g\eta a}\vec{F}$$

$$\frac{1}{\zeta_{eff}} = \frac{1}{\zeta_{bare}} + \frac{1}{g\eta a}$$

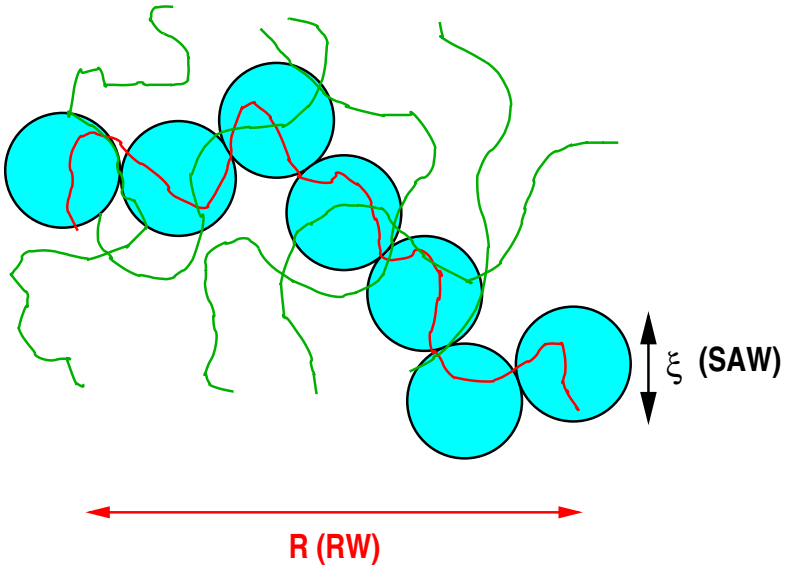
Stokes contribution from lattice discretization

Lattice *regularizes* theory (no point particles in nature!)

$\zeta_{bare}$: no physical meaning!

# Blob picture of semidilute polymer solutions

monomer concentration $c \to 0$, $N \to \infty$, strong overlap

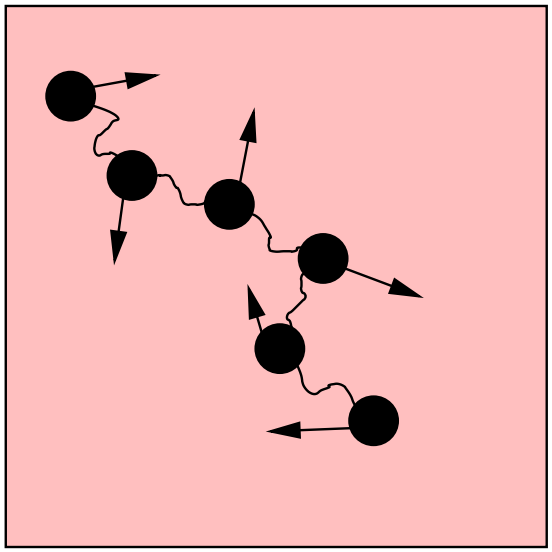



"blob size"

$$\xi \propto c^{-\frac{\nu}{3\nu-1}} = c^{-0.77}$$

$\xi \sim bn^{\nu}$, $c \sim n/\xi^3$ ($n$ number of monomers in a blob)

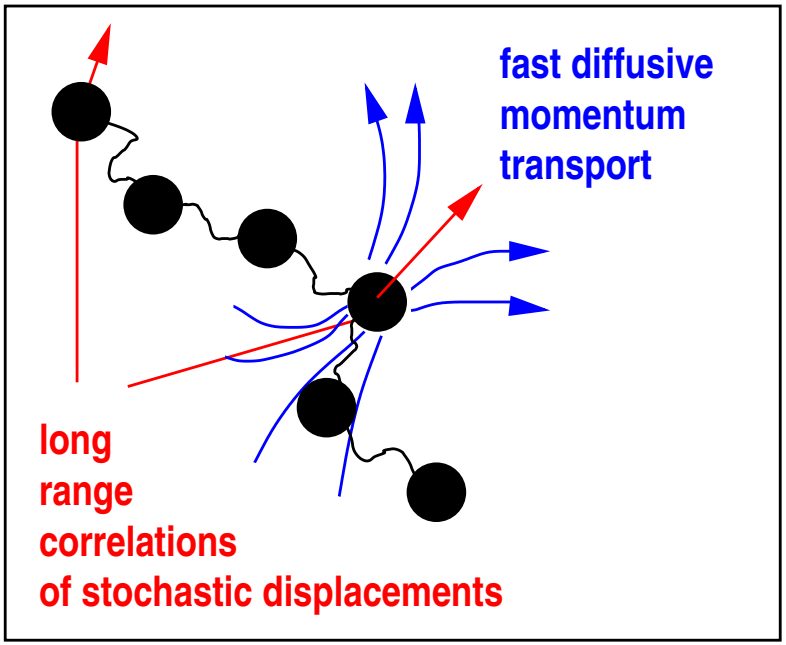
# Rouse model



- single chain with overdamped dynamics
- *uncorrelated* stochastic displacements
- $D$ diffusion constant
  $\tau_R$ relaxation time
  $z$ dynamic exponent

$$D \propto \frac{1}{N} \qquad \tau_R \propto \frac{R^2}{D} \propto R^2 N \propto R^4 \qquad z = 4$$

# Zimm model = Rouse model + hydrodynamic interaction

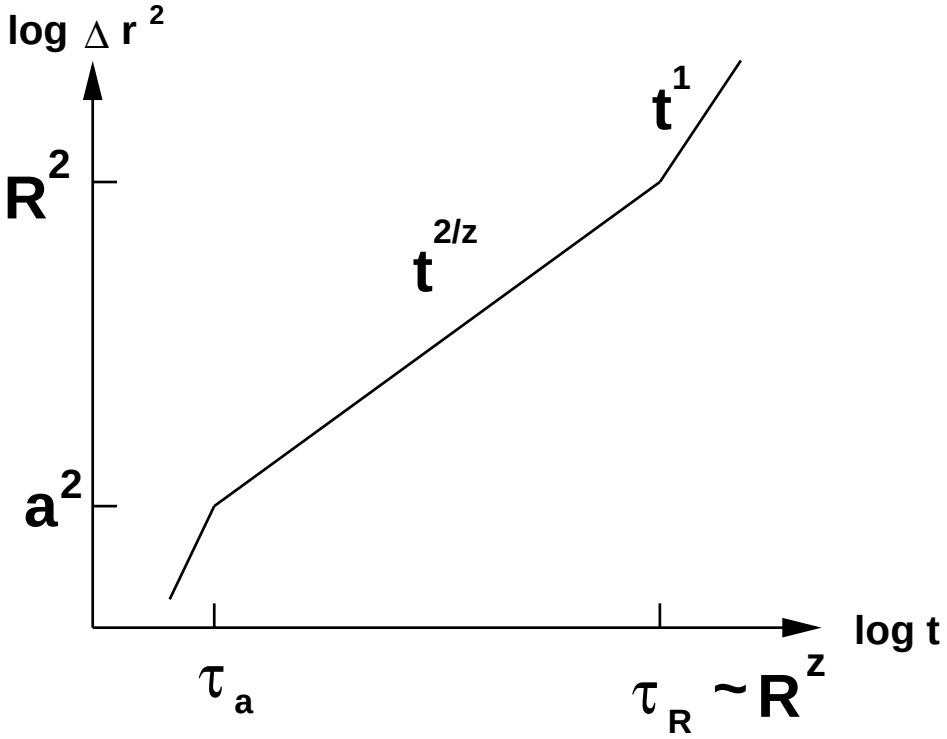


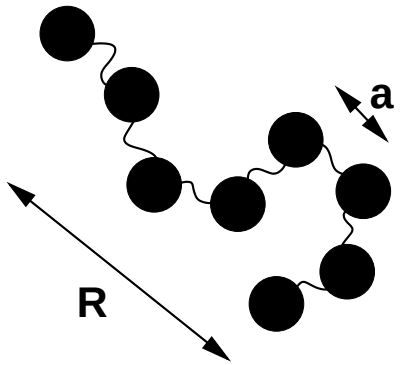

$$\langle \Delta\vec{r}_i \otimes \Delta\vec{r}_j \rangle \sim \frac{k_B T}{\eta} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$D \propto \frac{1}{R} \qquad \tau_R \propto \frac{R^2}{D} \propto R^3 \qquad z = 3$$

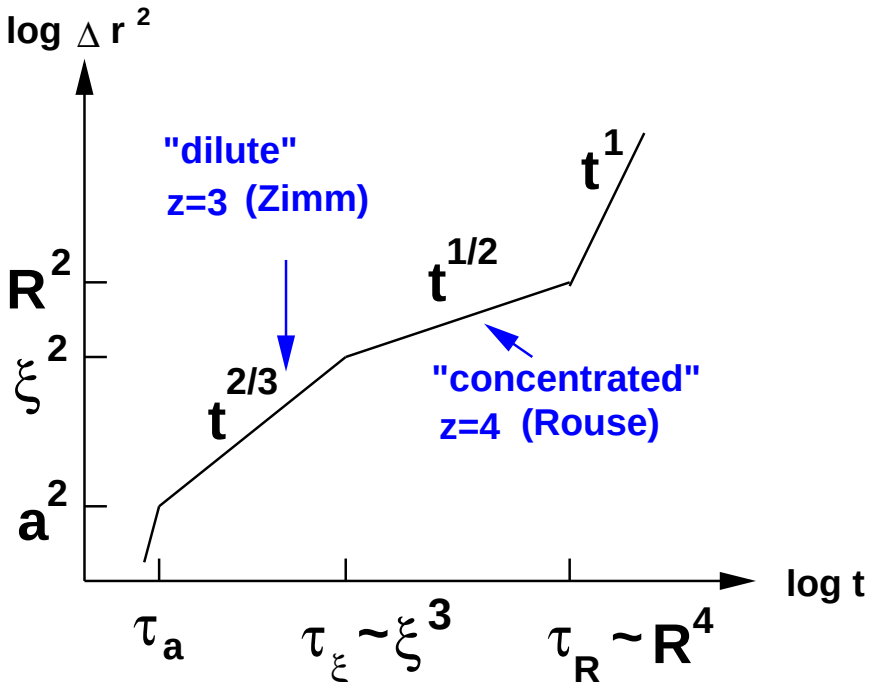
# Dynamic scaling

monomer mean square displacement:



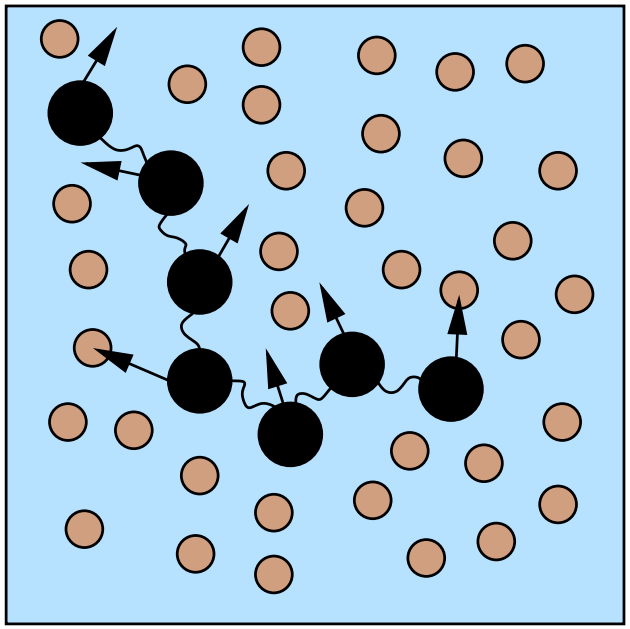
# Dynamic crossover for semidilute solutions




- assumption: $\xi$ controls both the static and the dynamic crossover
- mechanism?

# Hydrodynamic screening

**fixed frictional obstacles**
**friction coeff.$\zeta$**
**concentration c**



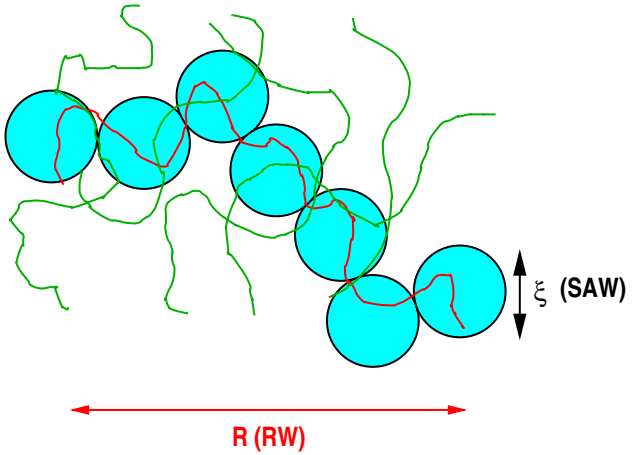
**solvent**

Darcy:

$$\begin{aligned} \rho\frac{\partial\vec{u}}{\partial t} &= \eta\nabla^2\vec{u} - \zeta c\vec{u} \\ \eta\xi_H^{-2} &= \zeta c \\ \xi_H &\propto c^{-1/2} \\ \frac{1}{r} &\rightarrow \frac{1}{r}\exp\left(-\frac{r}{\xi_H}\right) \end{aligned}$$

**short ranged**

- $\xi_H \propto c^{-1/2}$ vs. $\xi \propto c^{-0.77}$
- chains move




De Gennes (1976):
Picture is correct,
but the *blobs*
are the obstacles
("entanglements")

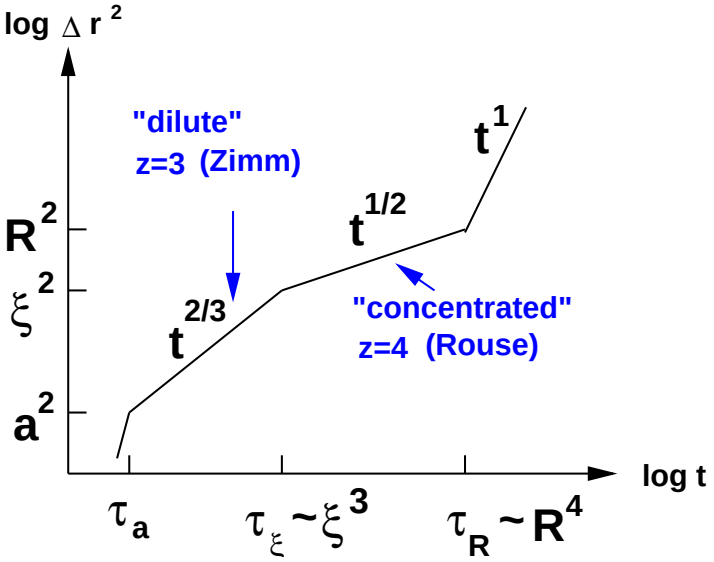
$$\eta \xi_H^{-2} = \zeta_{blob}\, c_{blob} \propto \eta\xi\, \xi^{-3}$$

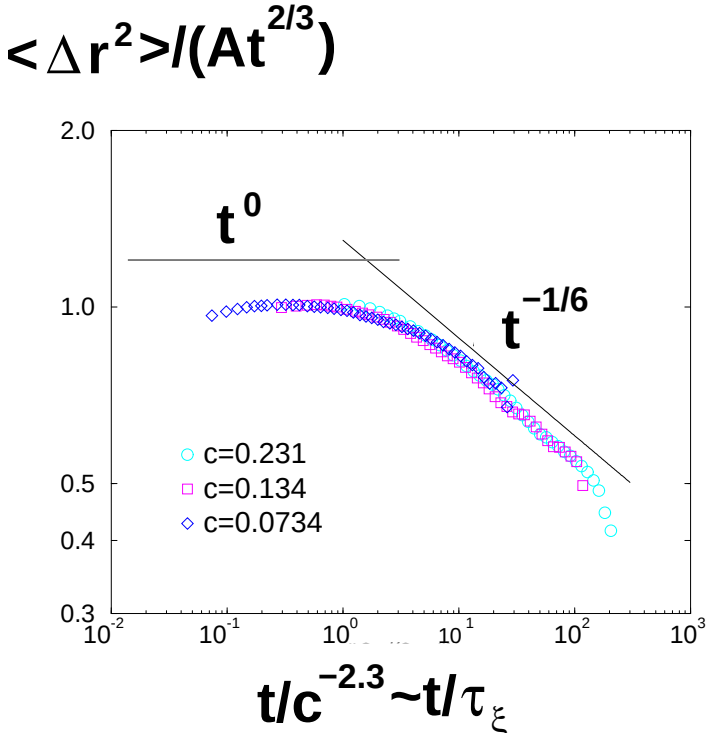
$$\xi_H \propto \xi$$

But:

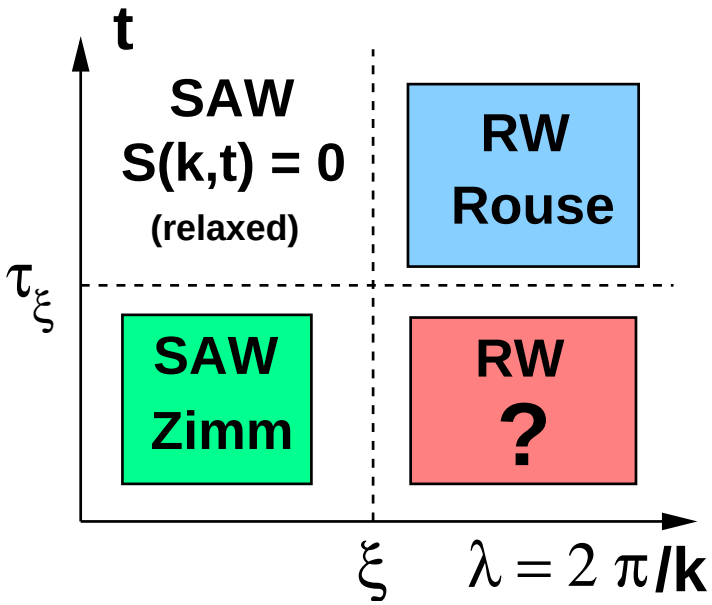
- Is a description in terms of length scales the whole story?
- What about time scales?

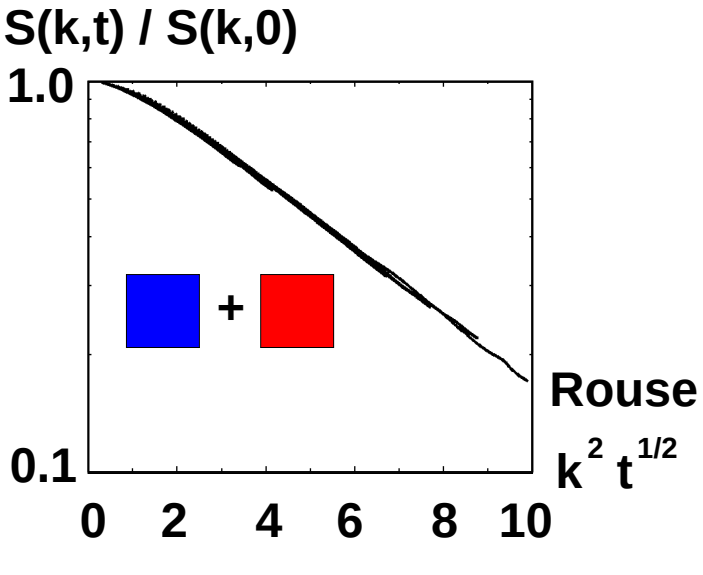
# Simulation results: Mean square displacements: Crossover Zimm $\longrightarrow$ Rouse



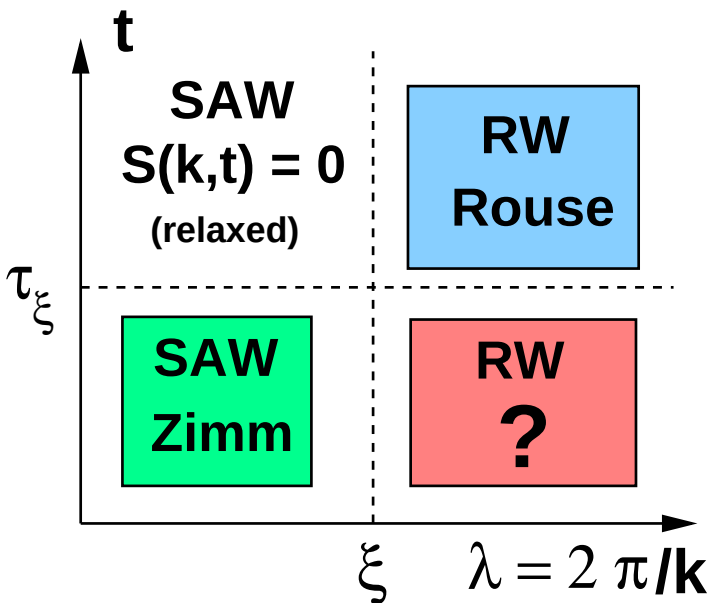



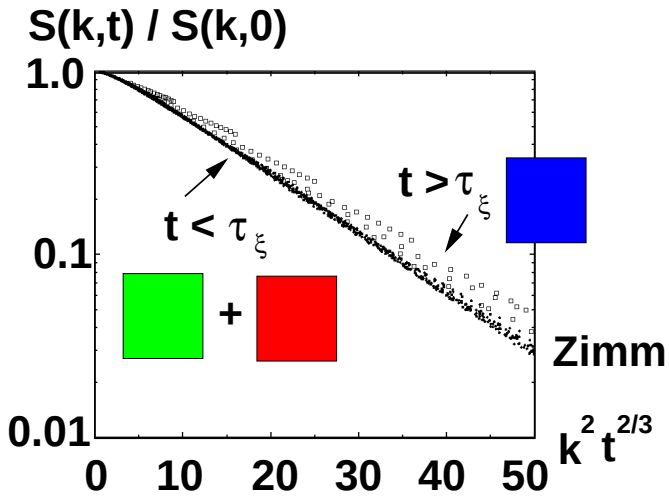
# Dynamic single–chain structure factor 1



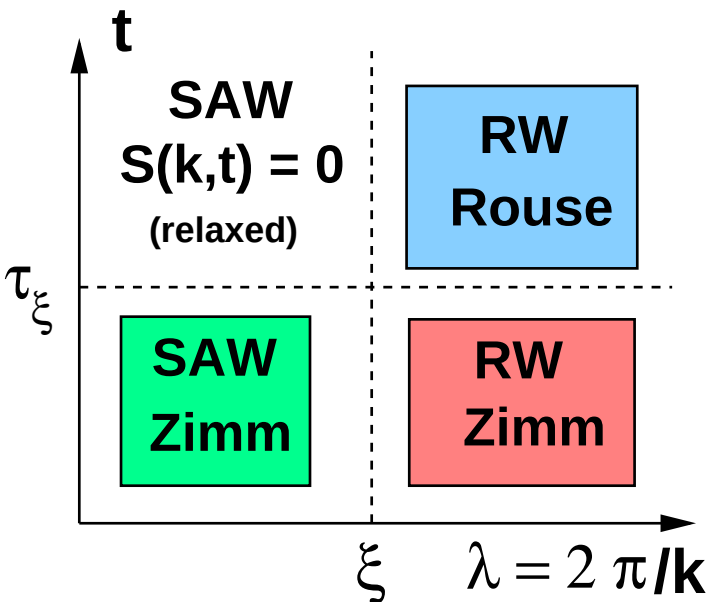



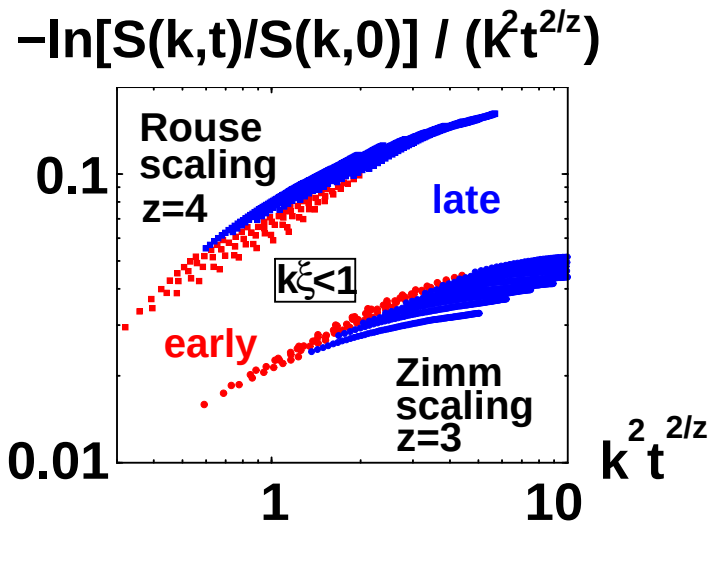
# Dynamic single–chain structure factor 2



# Dynamic single–chain structure factor 3

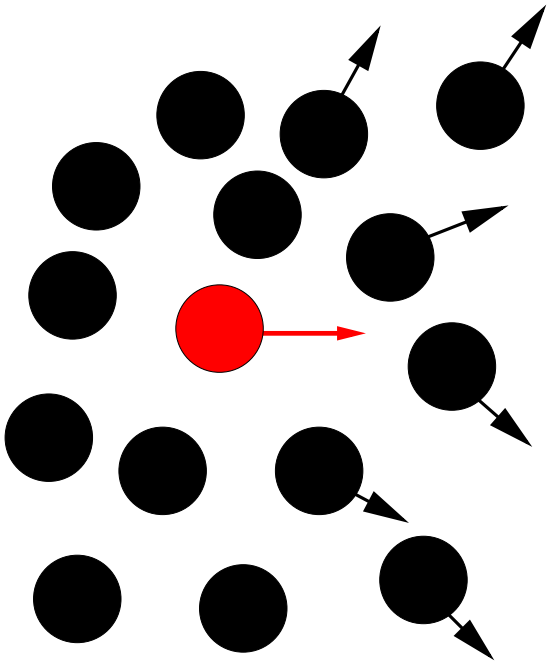


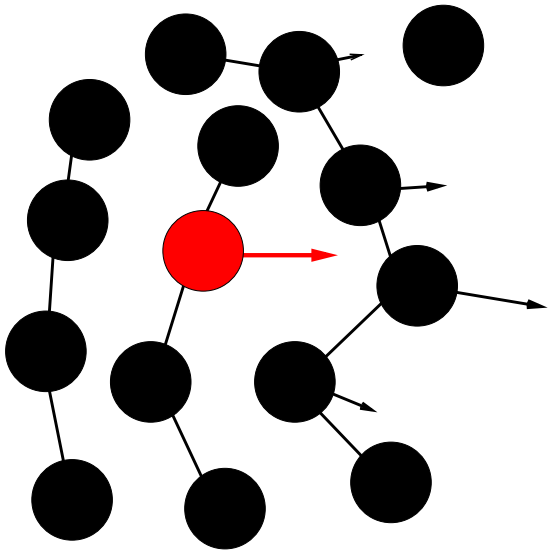

**"Incomplete screening" is a short–time effect!**
(P. Ahlrichs, R. Everaers , B. D., PRE 2001)

# Mechanism

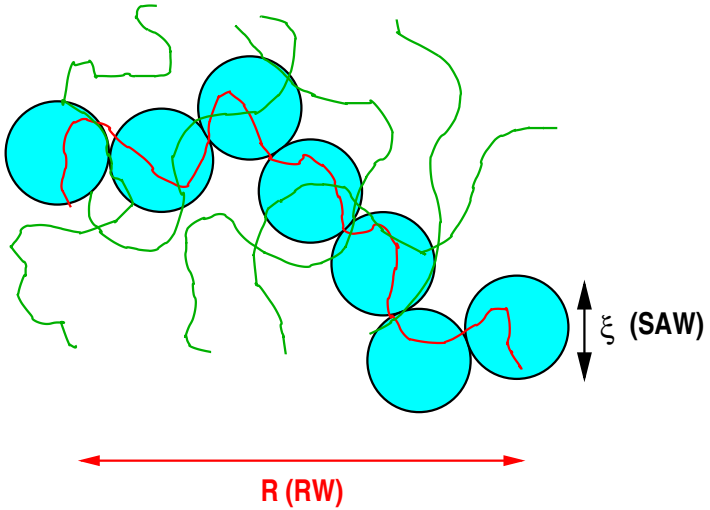
Simple fluid:
"Straight" propagation



Polymer melt:
Randomization of momentum



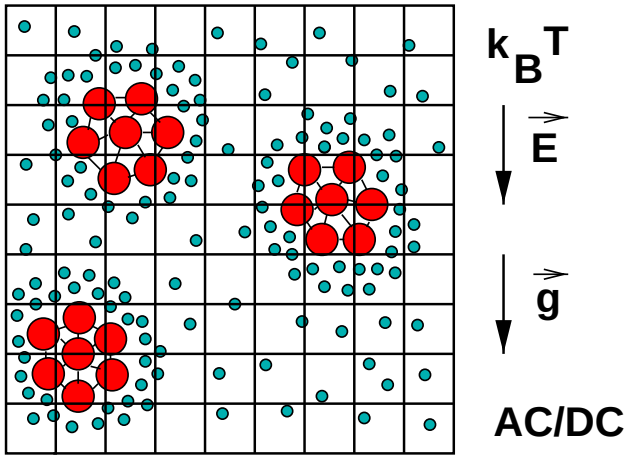
Semidilute solution:

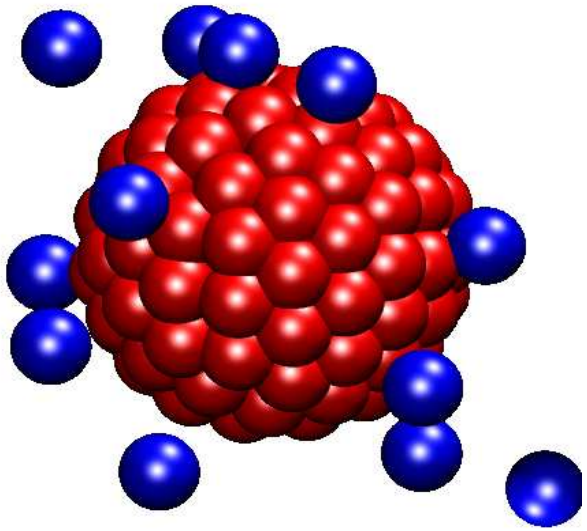



$t \ll \tau_\xi$:
Chains move with flow

$\tau_\xi \ll t \ll \tau_R$:
Chains in a temporary gel

# Raspberry model

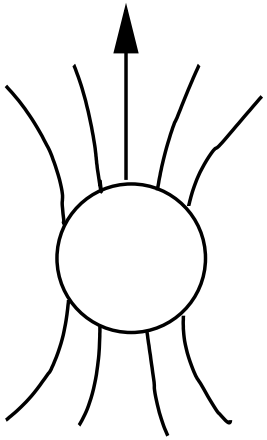


- particles via Molecular Dynamics
- solvent via Lattice Boltzmann
- coupling via particle–solvent friction

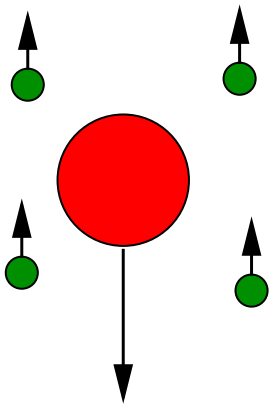
- single uncharged sphere: hydrodynamic behavior as expected (NJP 6, 54 (2004))

# Sedimentation / diffusion vs. electrophoresis



sedimentation:

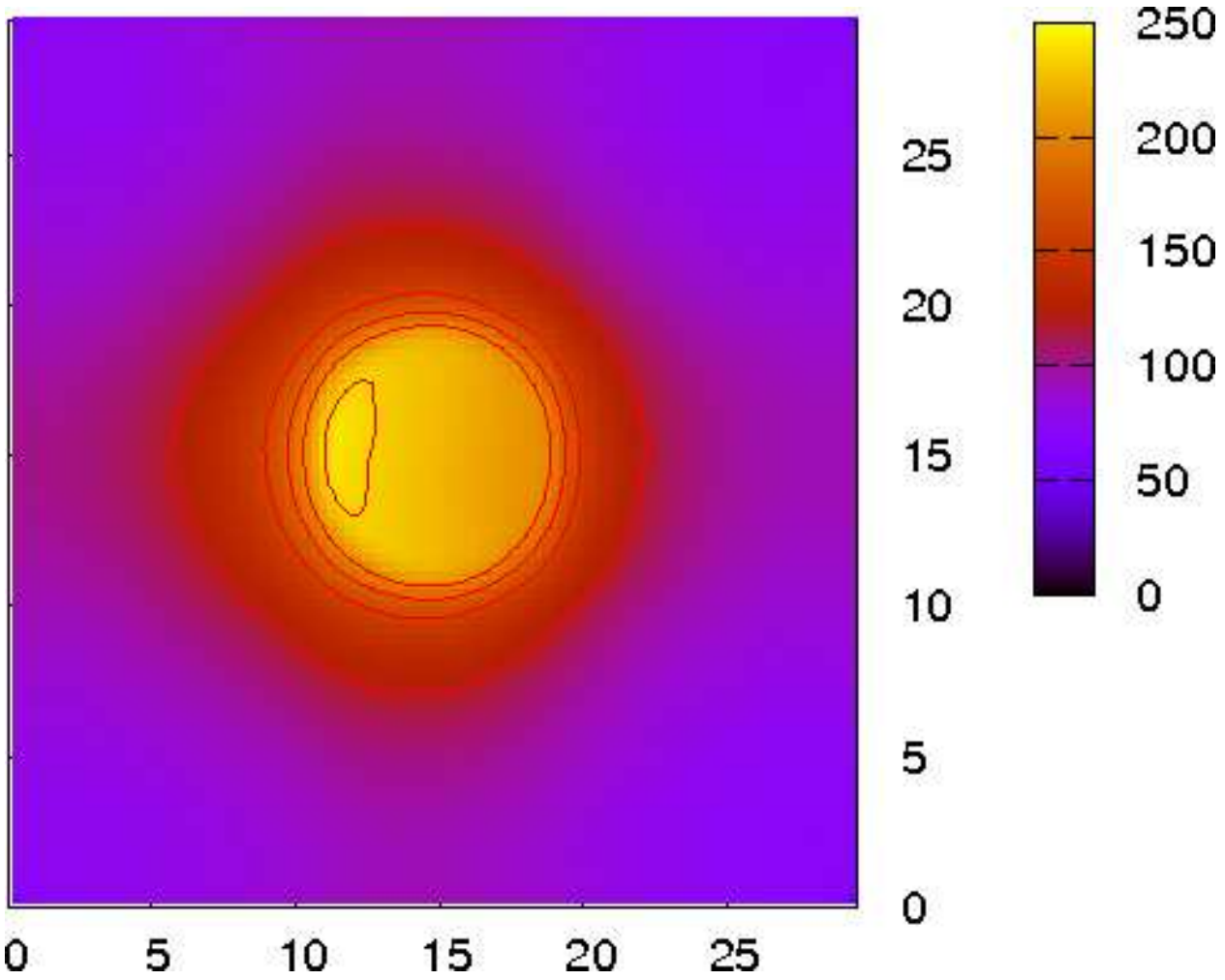
- force acts on the system in total
- flow field strongly influenced by boundary conditions
- large finite size effects



electrophoresis:

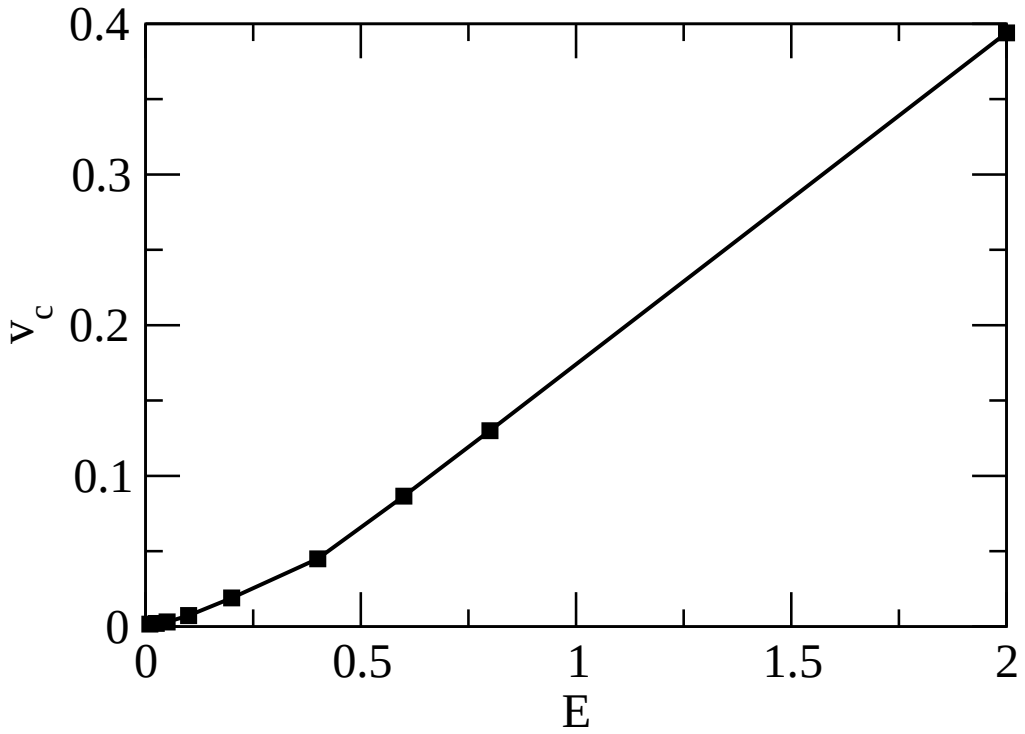
- total force ZERO
- flow fields compensate in leading order
- $\Rightarrow$ expect smaller finite size effects!
- $\Rightarrow$ single–colloid simulation permitted, corresponds to finite volume fraction

# Counterion density profile



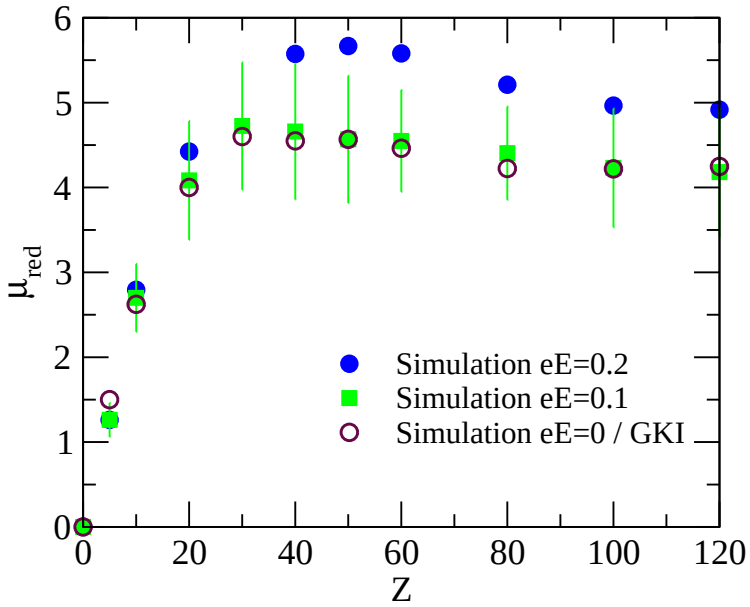
# Drift velocity vs. driving field

$v$




$eE$

# Reduced mobility



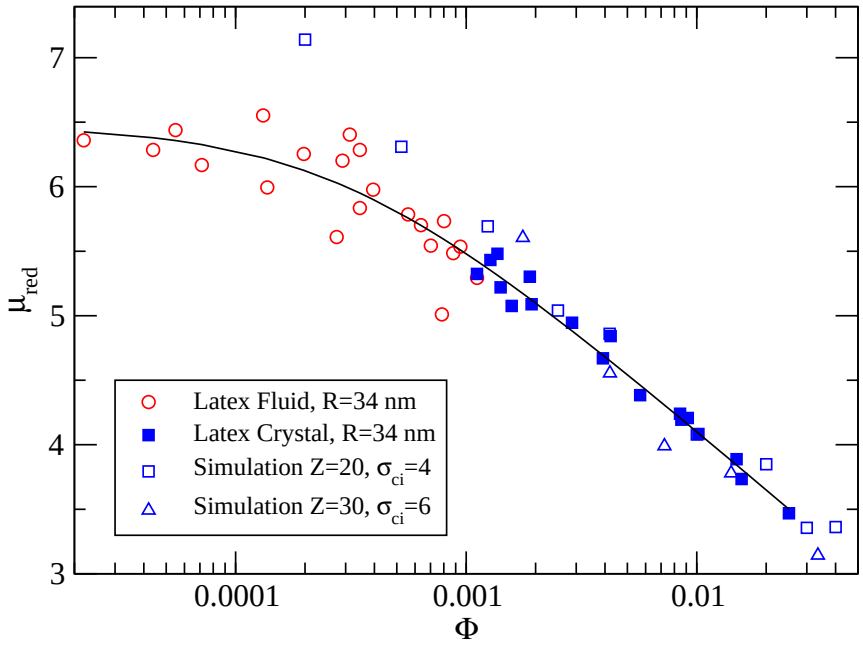

- $l_B = e^2/(4\pi\epsilon\epsilon_0 k_B T)$
- $\mu = v/(eE)$
- $\mu_{red} = 6\pi\,\eta l_B\,\mu$

Green–Kubo:

$$\mu = \frac{1}{3k_B T}\sum_i z_i \int_0^\infty dt\,\langle \vec{v}_c(t)\cdot\vec{v}_i(0)\rangle$$

# Simulation vs. experiment (T. Palberg)

- simulation: $Z_{eff} l_B / R_{eff} = 20 \times (1.3/3) = 8.7$
- experiment: $Z_{eff} l_B / R_{eff} = 450 \times (0.7nm/34nm) = 9.3$




- effective parameters from charge renormalization
- deviations at low Φ due to water dissociation

(V. Lobaskin et al., PRL 2007)

# Summary

- Hydrodynamic interactions via dissipative coupling MD / LB: Simple, versatile, efficient
- Hydrodynamic screening in polymer solutions: Result of chain–chain collisions which occur only *after* the blob relaxation time
- Electrophoresis: Good agreement with experiments in terms of effective dimensonless parameters

# Thanks!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