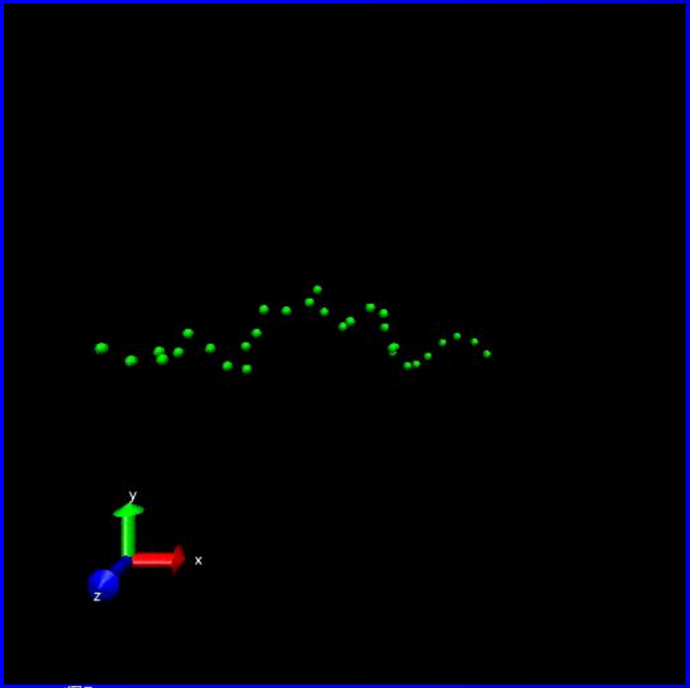
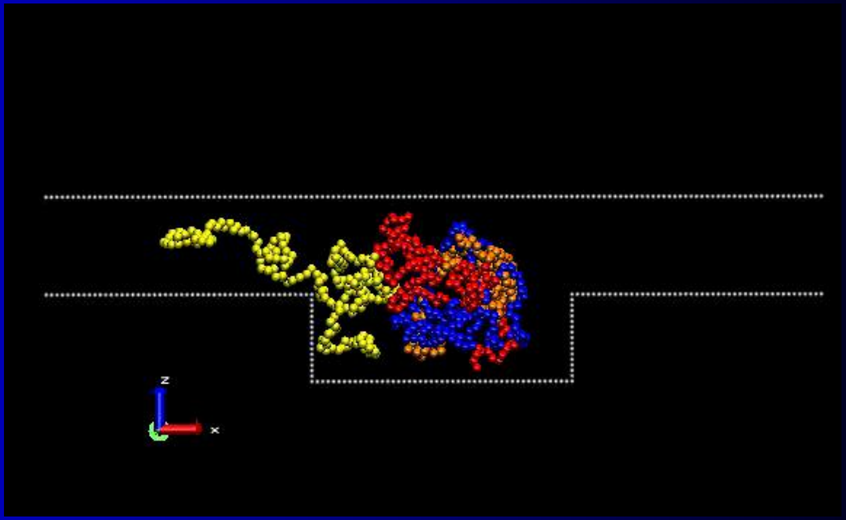
Coupling MD particles to a Lattice-Boltzmann Fluid through the use of Conservative Forces:

Noise, fluctuations, and polymer dynamics





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Outline

Model:

- Fluctuations in a lattice-Boltzmann (LB) model
- Particles coupled to a LB fluid

Examples:

- Polymer dynamics
- Polymer in a channel
- Conclusions

Thermal noise in a continuum fluid

- Navier-Stokes equations with thermal noise (Landau & Lifshitz):

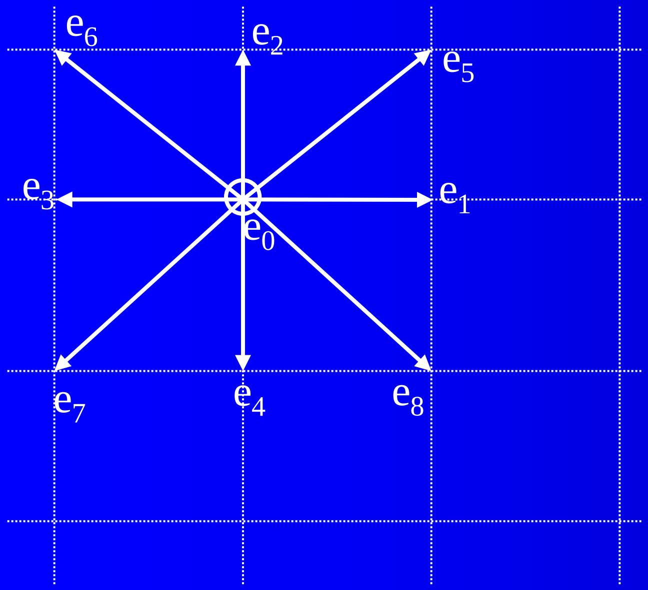
$$\left(\partial_t + \partial_\alpha u_\alpha\right)\rho = 0$$

$$\rho(\partial_t + u_\alpha \partial_\alpha)u_\beta = -\partial_\alpha(P_{\beta\alpha} + s_{\beta\alpha}) + \partial_\alpha\left(\eta_{\alpha\beta\gamma\nu}\,\partial_\gamma u_\nu\right)$$

- Note that the thermal noise appears in the stress tensor so will conserve mass and momentum. It should also obey the fluctuation-dissipation theorem (Landau & Lifshitz):

$$\left\langle s_{\alpha\beta}(\mathbf{r},t)\,s_{\gamma\nu}(\mathbf{r}',t')\right\rangle = 2k_B T\,\eta_{\alpha\beta\gamma\nu}\,\delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t')$$

Simple Lattice Boltzmann Algorithm



- f_i = partial densities (9 in 2d, 15 in 3d)
- $\{ f_i \}_i$ = a discrete probability distribution
- Moments of these distributions ***are*** the physical variables of interest:

$$\rho \equiv \sum_i f_i, \quad \rho \mathbf{u} \equiv \sum_i f_i \mathbf{e}_i,$$

- They evolve via the equation:

$$(\partial_t + \mathbf{e}_{i\alpha} \partial_\alpha) f_i = -\lambda_{ij} (f_j(\mathbf{x}, t) - f_j^{eq}(\mathbf{x}, t, \{f_k\}))$$

where

$$f_i^{eq} = A_i + B_i \mathbf{u} \cdot \mathbf{e}_i + C_i \mathbf{u} \cdot \mathbf{u} + D_i (\mathbf{u} \cdot \mathbf{e}_i)^2,$$

and A_i, B_i, C_i, and D_i are chosen so that

$$\sum_i f_i^{eq} = \rho, \quad \sum_i f_i^{eq} \mathbf{e}_i = \rho \mathbf{u}, \quad \sum_i f_i^{eq} \mathrm{e}_{i\alpha} \mathrm{e}_{i\beta} = -p \delta_{\alpha\beta} + \rho u_\alpha u_\beta, \cdots$$

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Implementing thermal noise in Lattice-Boltzmann method

- Add stochastic stress to pressure tensor[1]:

$$\langle s_{\alpha\beta}^2 \rangle \equiv \langle (\zeta^a)^2 \rangle \quad = 2\,\eta\, k_B T \frac{1}{\Delta x^3} \frac{1}{\Delta t} \frac{q_{\mathrm{OU}}^2}{q_{\mathrm{FD}}^2}, \qquad a = 7, 8, 9;$$

$$\langle s_{\alpha\alpha}^2 \rangle \equiv \langle (\zeta^a)^2 \rangle \quad = 4\,\eta\, k_B T \frac{1}{\Delta x^3} \frac{1}{\Delta t} \frac{q_{\mathrm{OU}}^2}{q_{\mathrm{FD}}^2}, \qquad a = 4, 5, 6.$$

- For simple fluids with viscous stress tensor:

$$\sigma_{\alpha\beta} = \eta\left(\partial_\alpha u_\beta + \partial_\beta u_\alpha - \frac{2}{3}\partial_\gamma u_\gamma \delta_{\alpha\beta}\right) + \Lambda \partial_\gamma u_\gamma \delta_{\alpha\beta}$$

the off-diagonal elements of *s* are independent but diagonal elements are not:

$$\begin{bmatrix} \langle s_{xx}^2 \rangle & \langle s_{xx} s_{yy} \rangle & \langle s_{xx} s_{zz} \rangle \\ \langle s_{xx} s_{yy} \rangle & \langle s_{yy}^2 \rangle & \langle s_{yy} s_{zz} \rangle \\ \langle s_{xx} s_{zz} \rangle & \langle s_{yy} s_{zz} \rangle & \langle s_{zz}^2 \rangle \end{bmatrix} = \begin{pmatrix} \frac{4[}{3} & \frac{2[}{3} & \frac{2[}{3} \\ \frac{2[}{3} & \frac{4[}{3} & \frac{2[}{3} \\ \frac{2[}{3} & \frac{2[}{3} & \frac{4[}{3} \end{pmatrix}$$

- Thermodynamic stability requires this matrix to be positive-definite so it can be Cholesky factorized (matrix “square root”) to generate the required correlated noise from 3 independent random variables[2].

1. Ladd, J. Fluid Mech. **271, 285 (1994)**

2. Ollila, CD, et al., J.C.P. **134**, 064902 (2011)

Implementing thermal noise in Lattice-Boltzmann method

- LB is not normally energy conserving so thermal noise can leak into higher moments and be dissipated there[1]. Higher moments must be thermalized too[1,2]:

$$\langle(\zeta^a)^2\rangle = \frac{18}{N^a} A_\eta = \frac{18}{N^a}\, \eta\, k_B T \frac{1}{\Delta x^3} \frac{1}{\Delta t} \frac{q_{\mathrm{OU}}^2}{q_{\mathrm{FD}}^2} \quad a > 3.$$

- Also, the 14th moment directly influences stress dissipation (Dellar) so needs to be chosen carefully[2]:

$$\frac{2}{3}\nabla\cdot\begin{bmatrix} \rho(u_y^2+u_z^2)/2 & P_{xy}+\rho u_x u_y & P_{xz}+\rho u_x u_z \\ P_{xy}+\rho u_x u_y & \rho(u_x^2+u_z^2)/2 & P_{xy}+\rho u_y u_z \\ P_{xz}+\rho u_x u_z & P_{yz}+\rho u_y u_z & \rho(u_x^2+u_y^2)/2 \end{bmatrix} + \frac{2}{9}\nabla\left(\mathrm{Tr}\,P - \rho + \frac{K^{\mathrm{eq}}}{\sqrt{2}}\right) = -\frac{1}{\tau}\mathbf{J}^{(1)},$$

1. Adhikari, Europhys. Lett. **71**, 473 (2005)

2. Ollila, CD, et al., J.C.P. **134**, 064902 (2011)

How do we know this works?

- In MD we are familiar with using equi-partition to measure T based on kinetic energy.

$$\langle \delta u_\alpha(\mathbf{r}_1)\delta u_\beta(\mathbf{r}_2)\rangle = \frac{k_B T}{\rho}\delta_{\alpha\beta}\delta(\mathbf{r}_1 - \mathbf{r}_2)$$

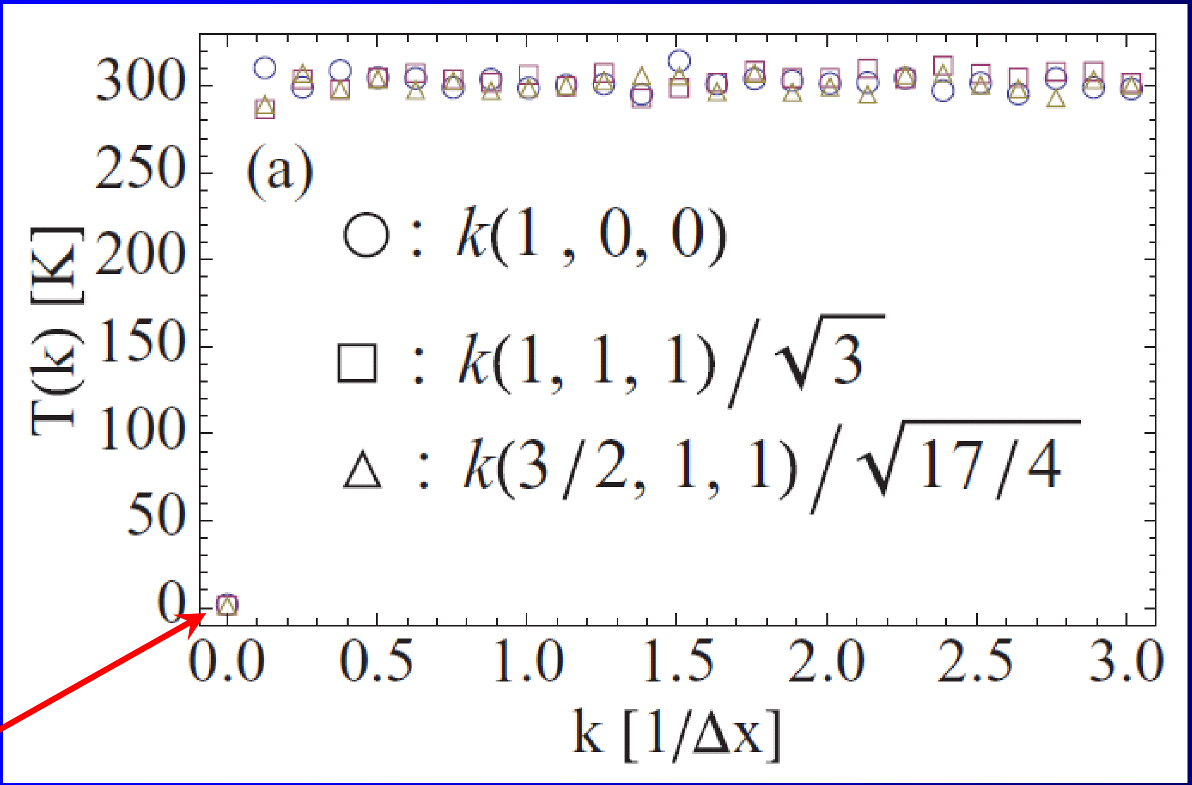
- In continuum we are measuring over a finite volume so the analogous idea is:

$$\frac{1}{2}\sum_\alpha \left\langle \frac{\left(\sum_{\mathbf{x}\in V_s}\rho(\mathbf{x})u_\alpha(\mathbf{x})\right)^2}{\sum_{\mathbf{x}\in V_s}\rho(\mathbf{x})}\right\rangle = \frac{3}{2}k_\mathrm{B}T(L_s)$$

- NOTE: Vs = volume. What volume should we use?

- Alternatively, we can also Fourier transform the local momentum flux ($\delta\mathbf{j}=\rho\delta\mathbf{u}$) and look at

$$T(\mathbf{k}) = \langle|\delta\mathbf{j}(\mathbf{k},t)|^2\rangle_t/(3k_\mathrm{B}\rho_0).$$



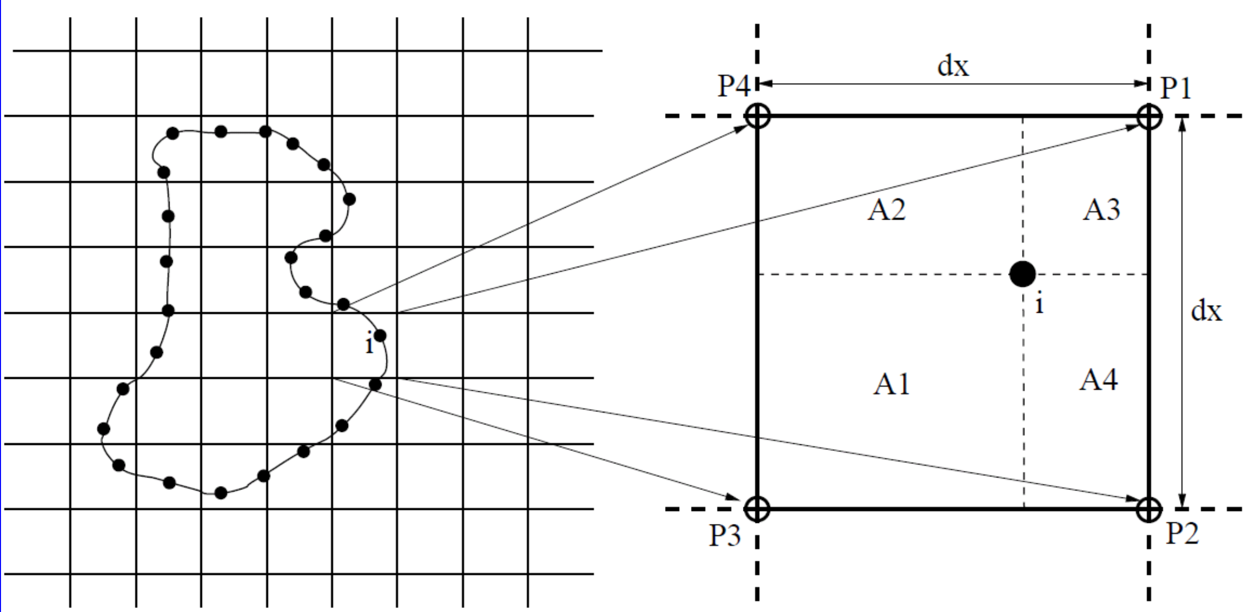
Does T(k=0)=0 matter?

(It is just a consequence of CM V=0)

We “fix” it byvthermostating the CM velocity using a Langevin thermostat

so that $\frac{1}{2}M_T\langle V_\alpha^2\rangle = \frac{1}{2}k_B T$ for CM.

- Each node represents a fixed area ΔA_i
- Nodes are distributed onto the lattice



- weights proportional to the opposite enclosed area within the cell.

Eg. ξ_{i1}=A1/dx^2

- Easily generalized to 3-D (use volume instead of area).
  - Peskin's Immersed boundary method is similar. With compact support spreading 2 lattice sites from nodes lattice effects can be almost eliminated.
    - First done for non-point objects in LB by Duenweg & Lobaskin, NJP (2004).

Modelling:

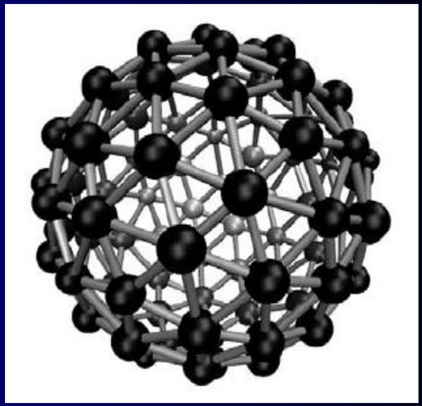
• Particles live off-lattice and evolve using molecular dynamics (written as a package for LAMMPS).
• Particles are mapped to the mesh using NDA algorithm and hydrodynamic forces on each particle computed from:

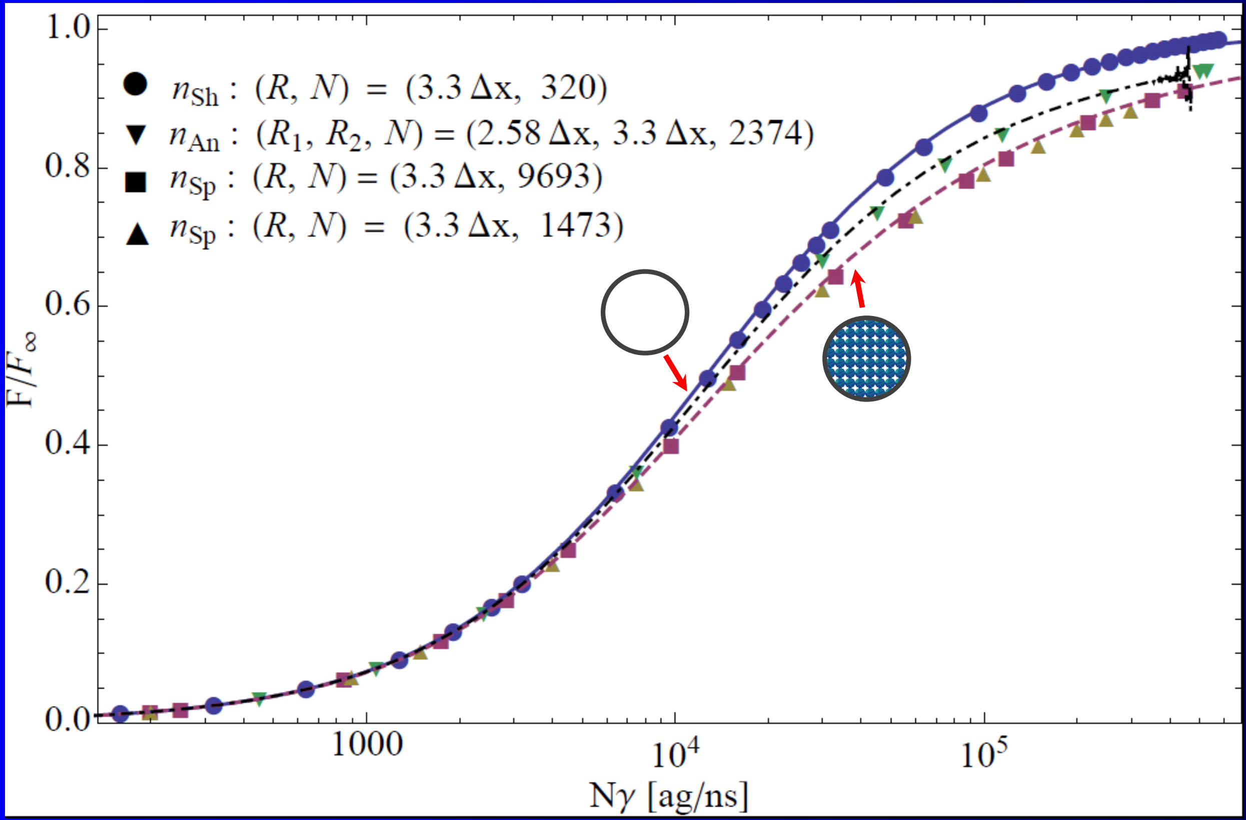
$$\mathbf{F}_{ij} = (\mathbf{v}_i - \hat{\mathbf{u}}_i)\xi_{ij}\gamma$$

$$\mathbf{F}_i = \sum_{j=1}^{n} \mathbf{F}_{ij} = (\mathbf{v}_i - \hat{\mathbf{u}}_i^{(I)})\gamma$$

• γ is "drag" coefficient (to be determined), v_p is the particle velocity, and u_i is the interpolated fluid velocity at node *i*. The resulting torque is also computed for rotational motion.
•The fluid experience an equal and opposite force.

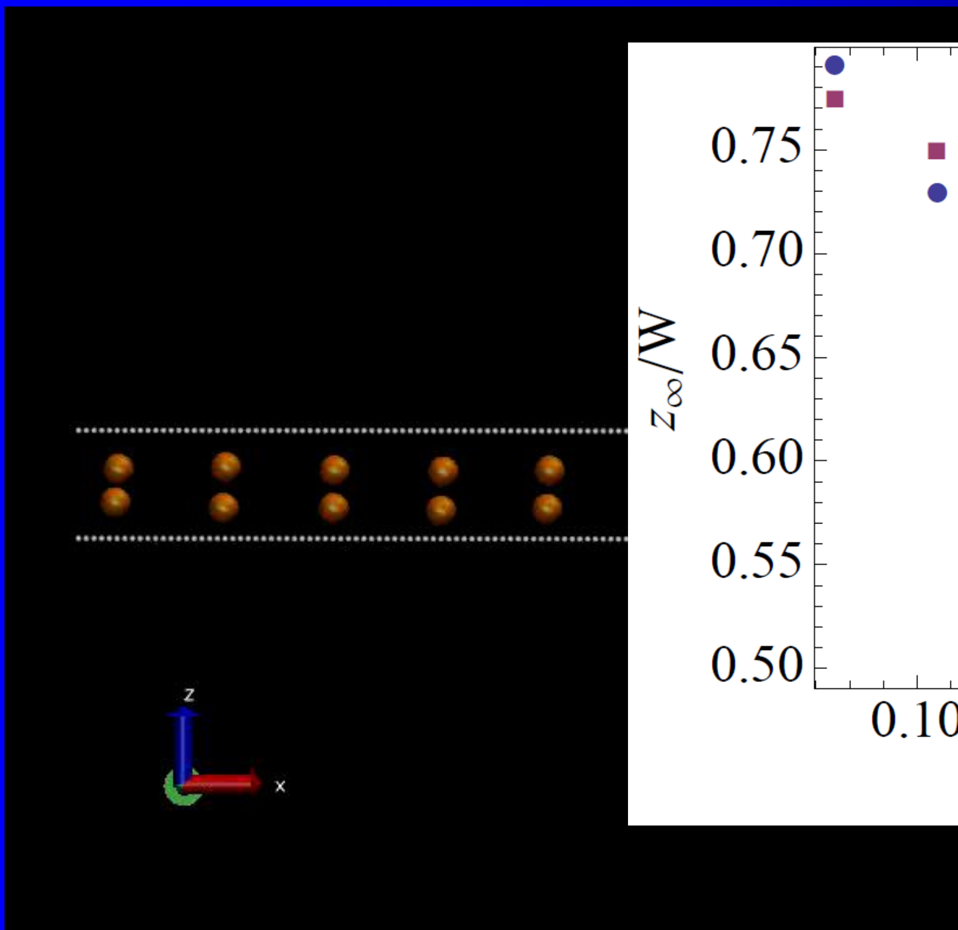
Drag Force

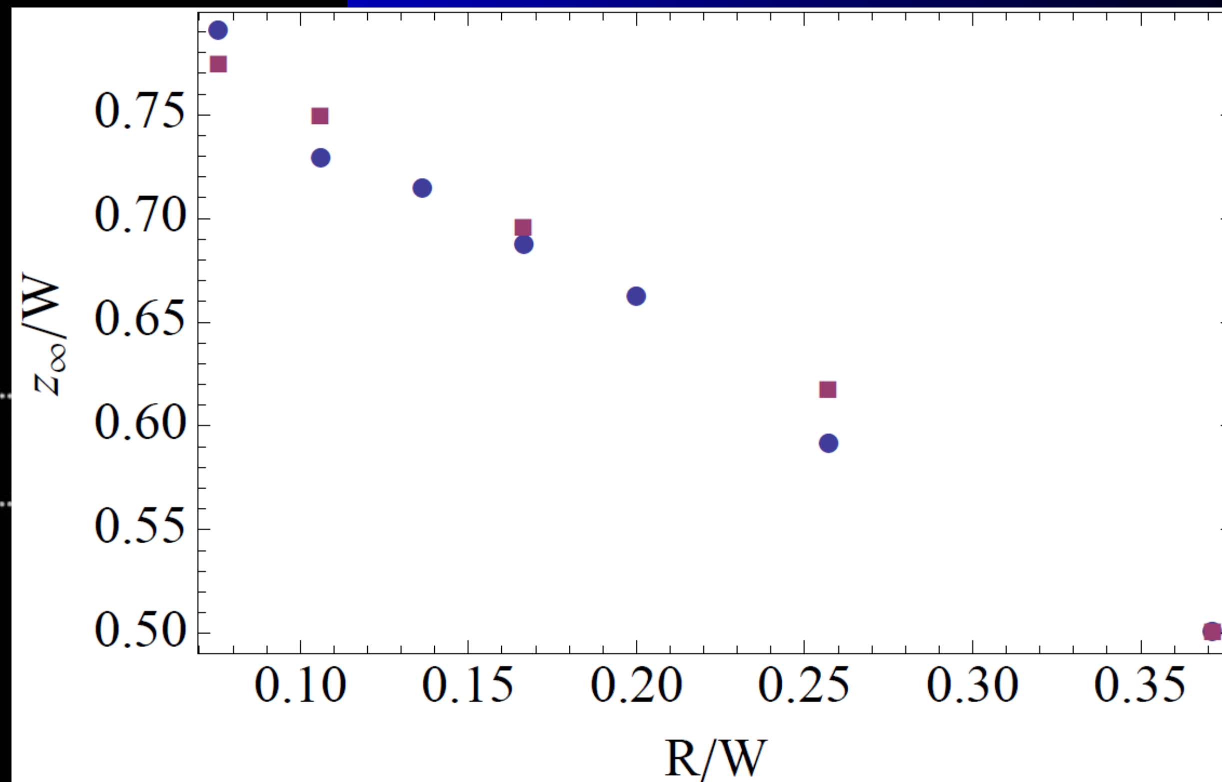




Brinkman Theory: Felderhoff et al., Bhatt & Sacheti

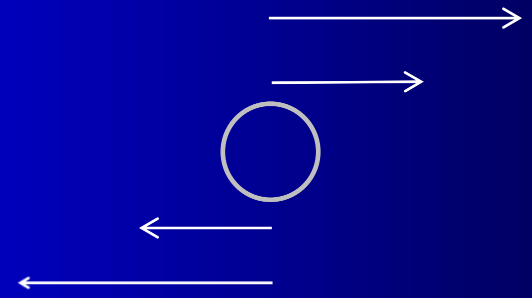
Does inertia matter for small Re?

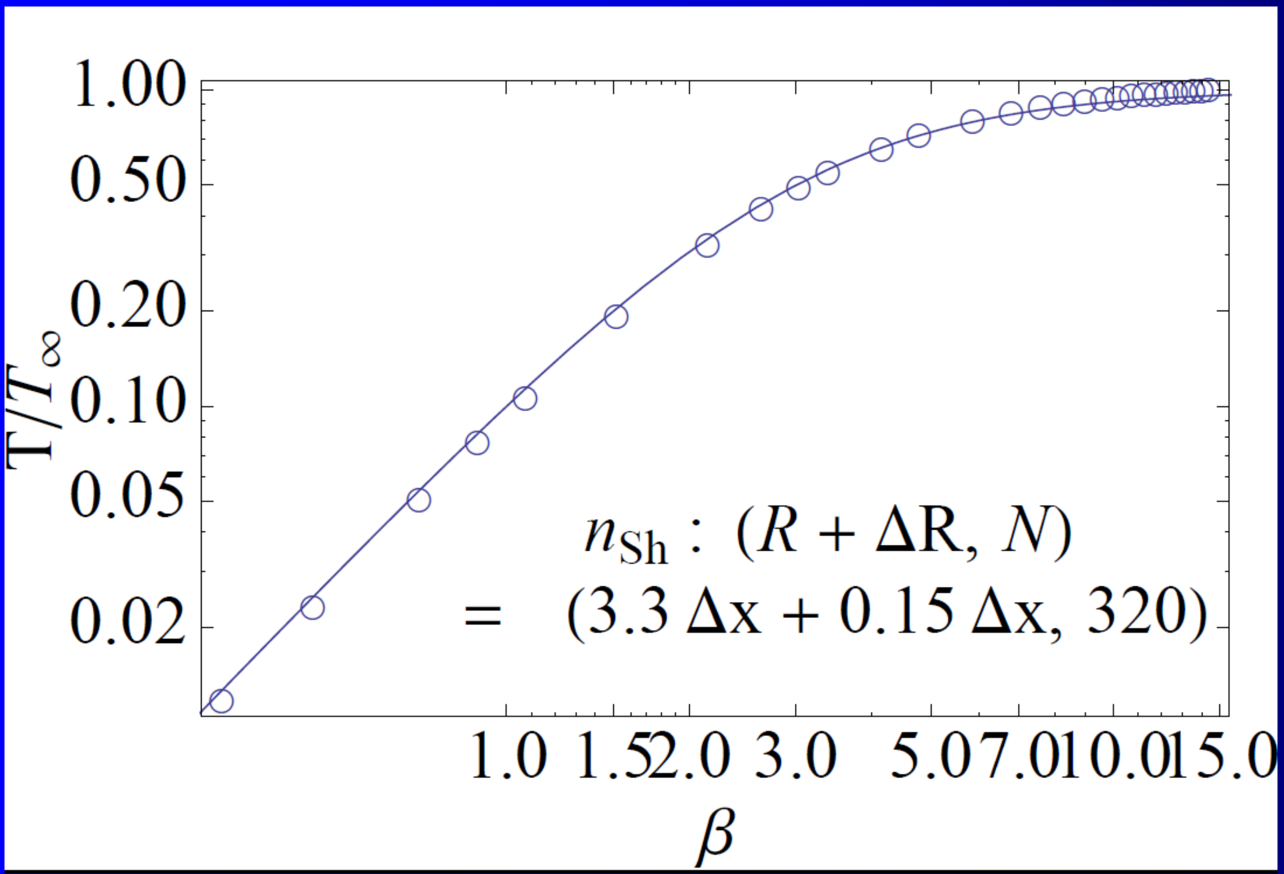




Point particle result:
Segre & Siilberberg (1961),
Ho & Leal (1974)

Drag Torque

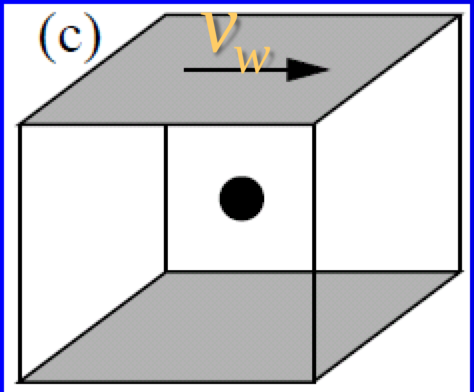




Brinkman Theory: Felderhoff et al.

$\beta = R\sqrt{\gamma n/\eta}$

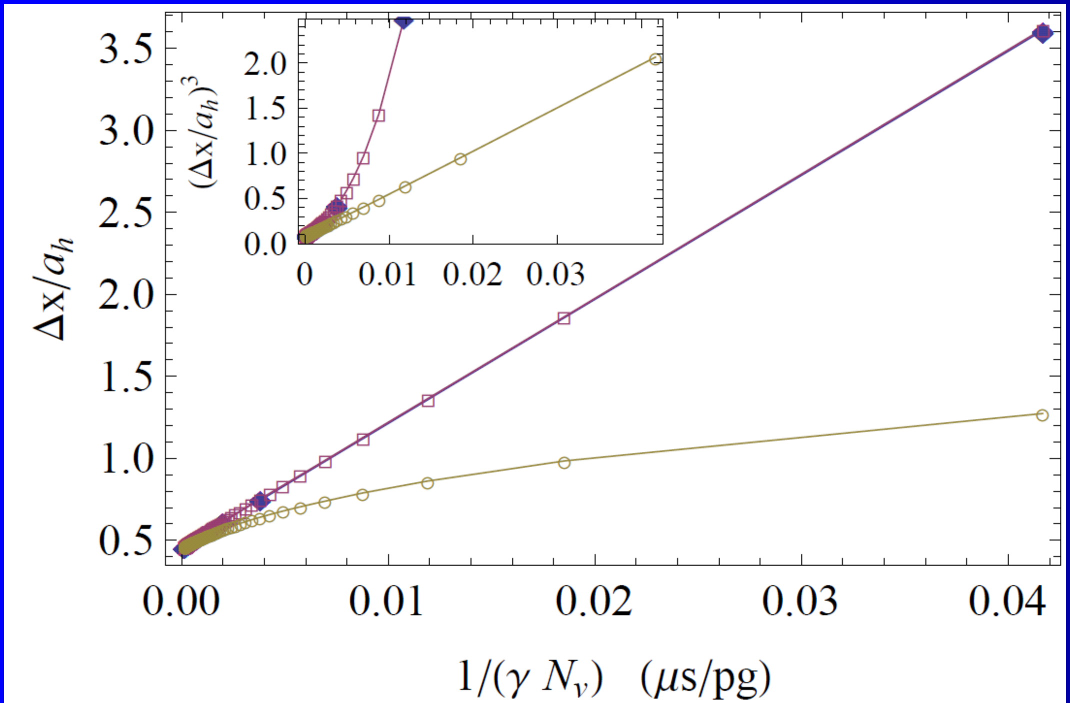
Impenetrable, no-slip limit: Determining drag coefficient γ:



Particle experiences drag force and torque:

$$\mathbf{F} = 6\pi\eta a\mathbf{v} \qquad \mathbf{T} = 4\pi\eta a^3 (v_w/h)\mathbf{n}$$

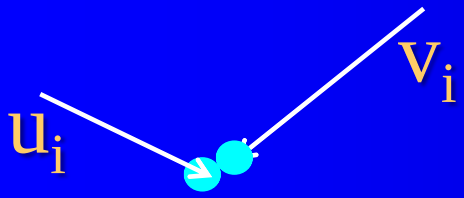
particle radius



The hydrodynamic radius of the porous particle is only consistent with that for an impenetrable particle for both forces and torques if γ is chosen to be quite large.

Can this be turned into a conservative coupling?

Consider the collision of two point particles



If the collision conserves mass and momentum (no potential forces) then:

$$\mathbf{u}_f = \mathbf{u}_i + (\mathbf{v}_i - \mathbf{u}_i)\frac{2m_v}{m_v + m_u}$$

$$\mathbf{v}_f = \mathbf{v}_i + (\mathbf{v}_i - \mathbf{u}_i)\frac{-2m_u}{m_v + m_u}.$$

Reformulate particle-fluid coupling as a collision:

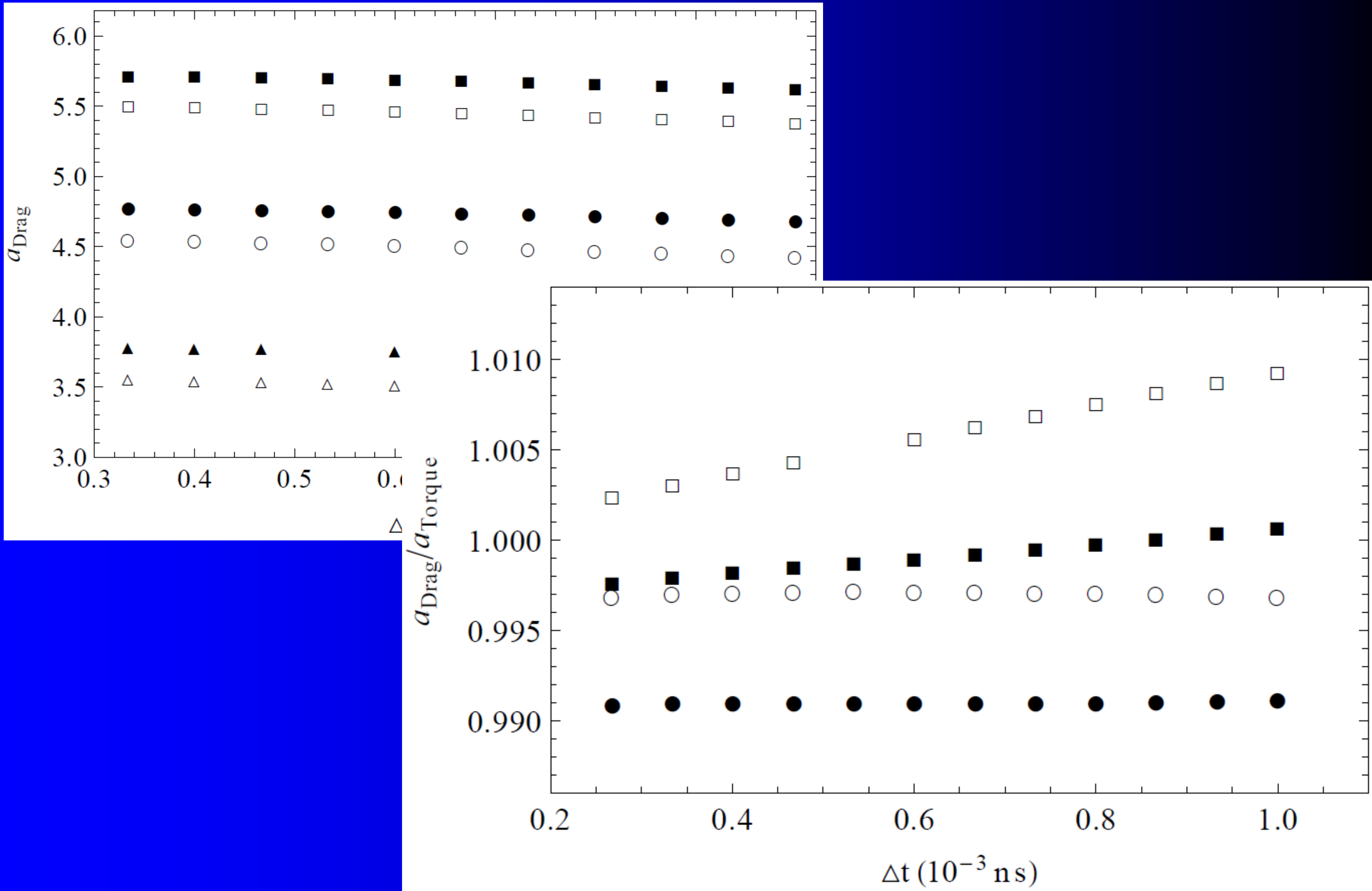
$$\mathbf{F}_{node} = \frac{\Delta p_{node}}{\Delta t_{collision}} = \frac{m_v\left(\mathbf{v}_f - \mathbf{v}_i\right)}{\Delta t_{collision}}$$

$$\mathbf{F}_{fluid} = \frac{\Delta p_{fluid}}{\Delta t_{collision}} = \frac{m_u\left(\mathbf{u}_f - \mathbf{u}_i\right)}{\Delta t_{collision}}.$$

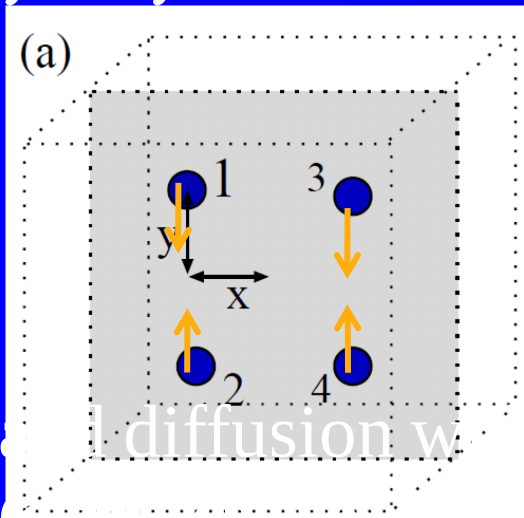
m_v=node mass
m_u=fluid mass interacting with node via interpolation stencil

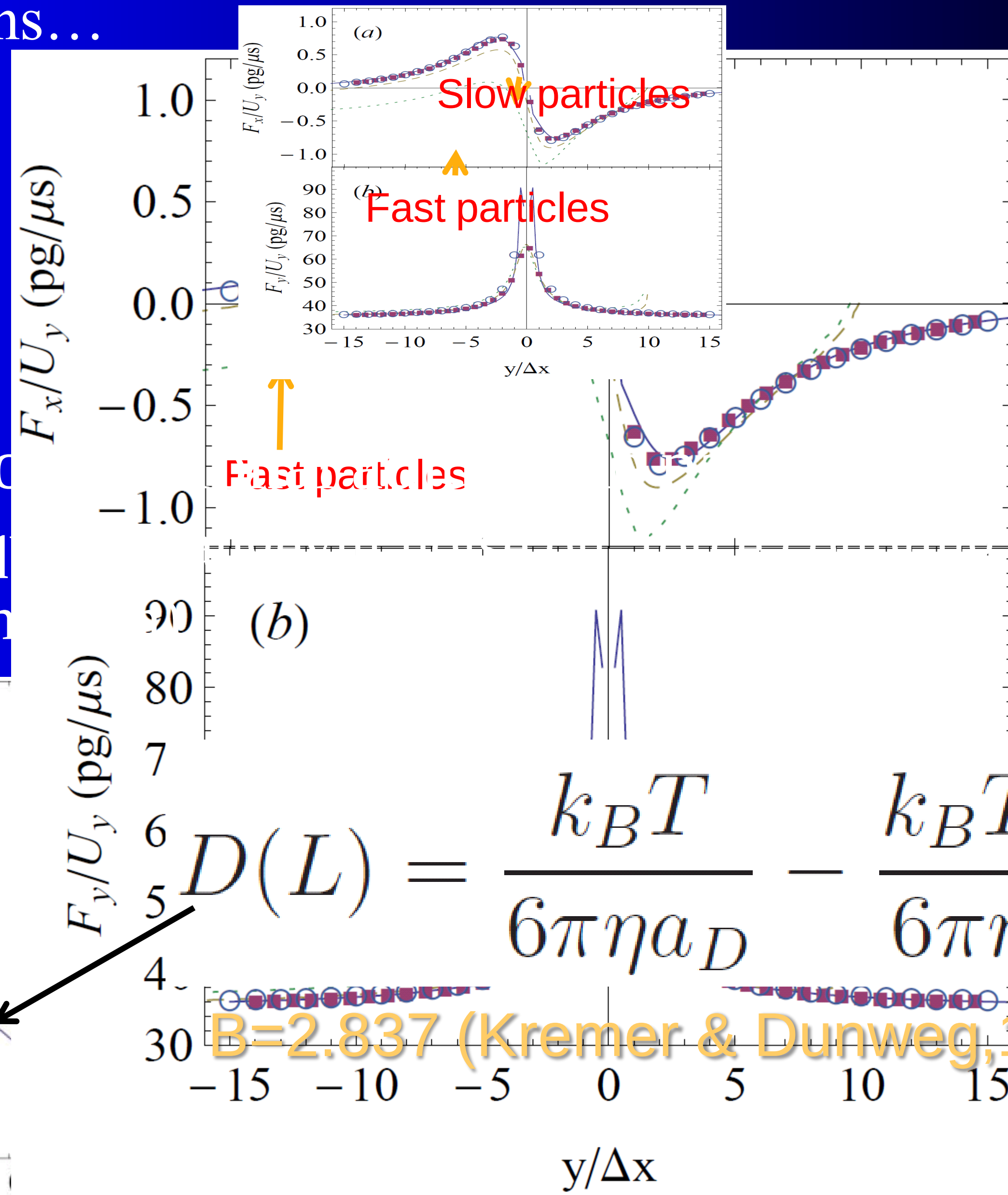
We also take: $\tau/\Delta t_{collision} = 1$

Hydrodynamics Radius:



Picking γ in this way also give consistent particle-particle hydrodynamic interactions…

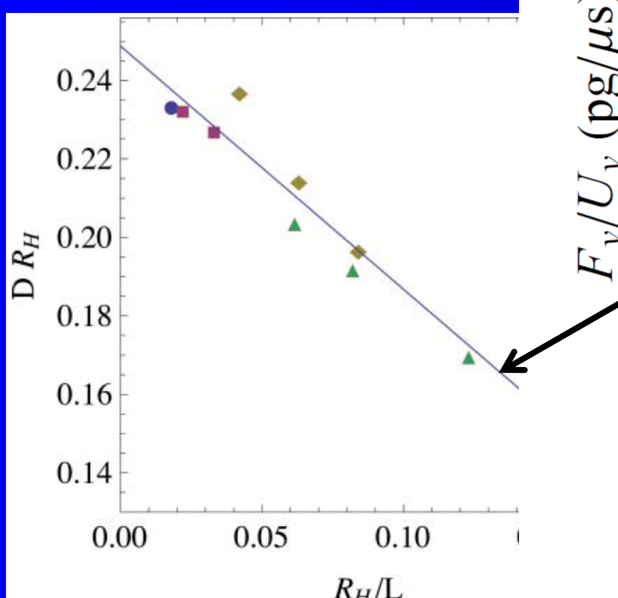




…d diffusion w…h nc…

(… req…

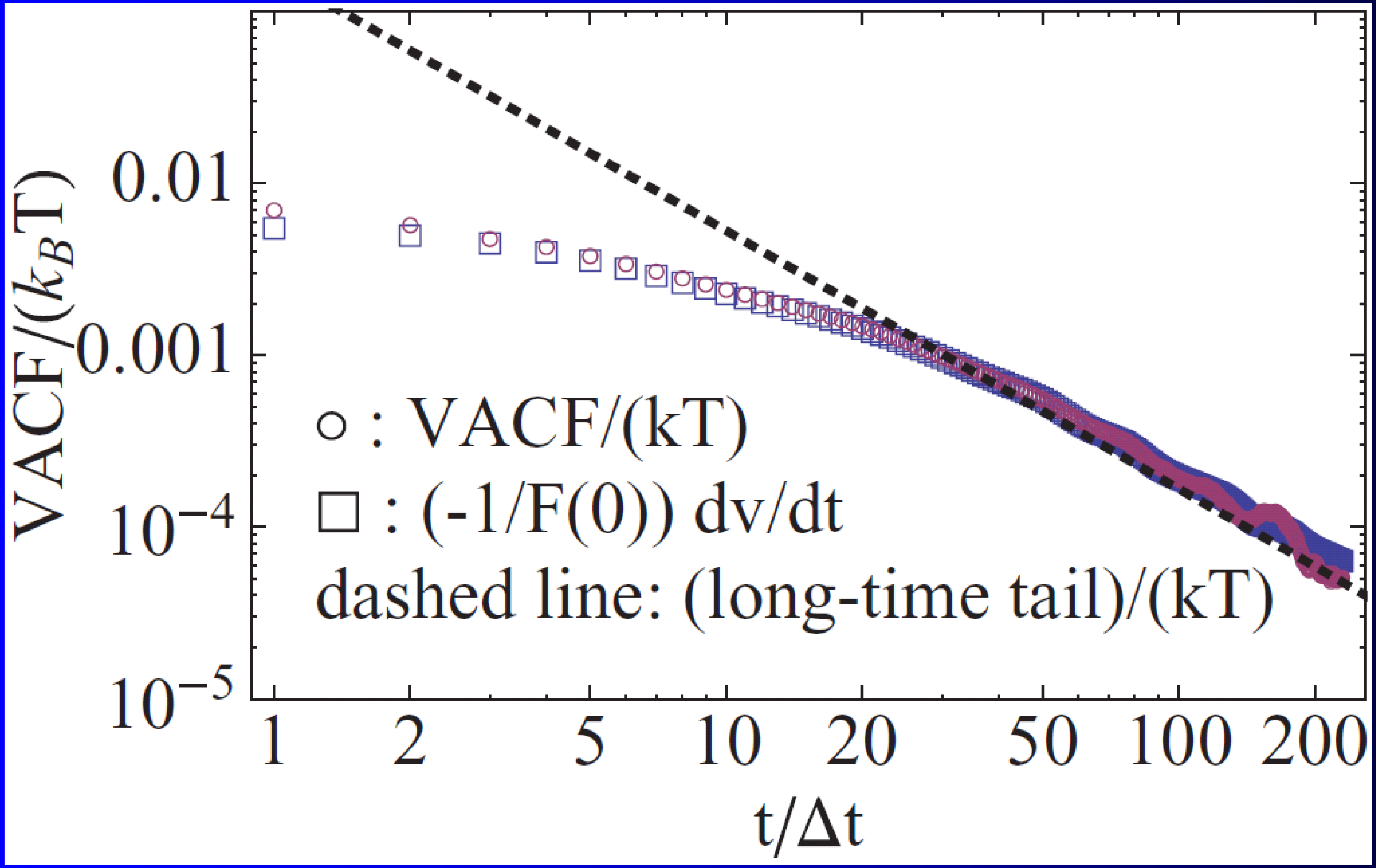
to get correct diffusive n…



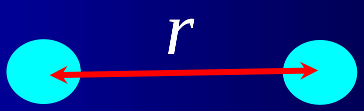
$$D(L) = \frac{k_B T}{6\pi\eta a_D} - \frac{k_B T}{6\pi\eta}\frac{\mathbf{B}}{L}$$

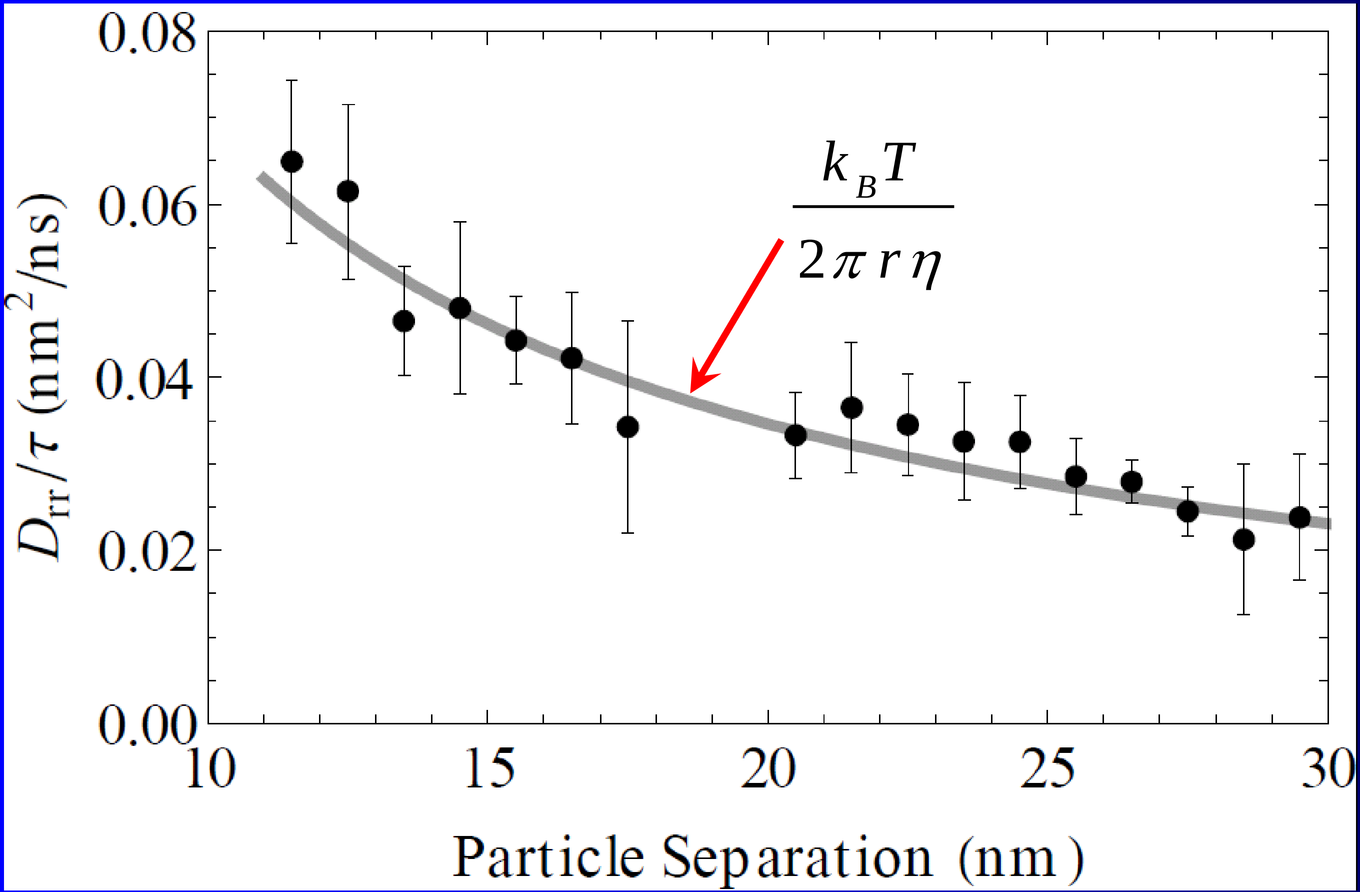
B=2.837 (Kremer & Dunweg,1993)

Velocity auto-correlation function



Two-particle diffusion:

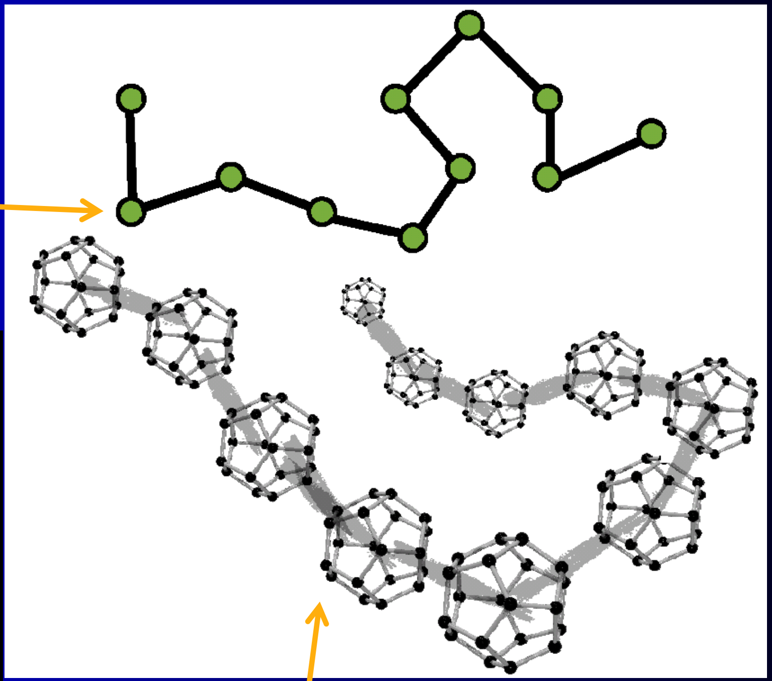


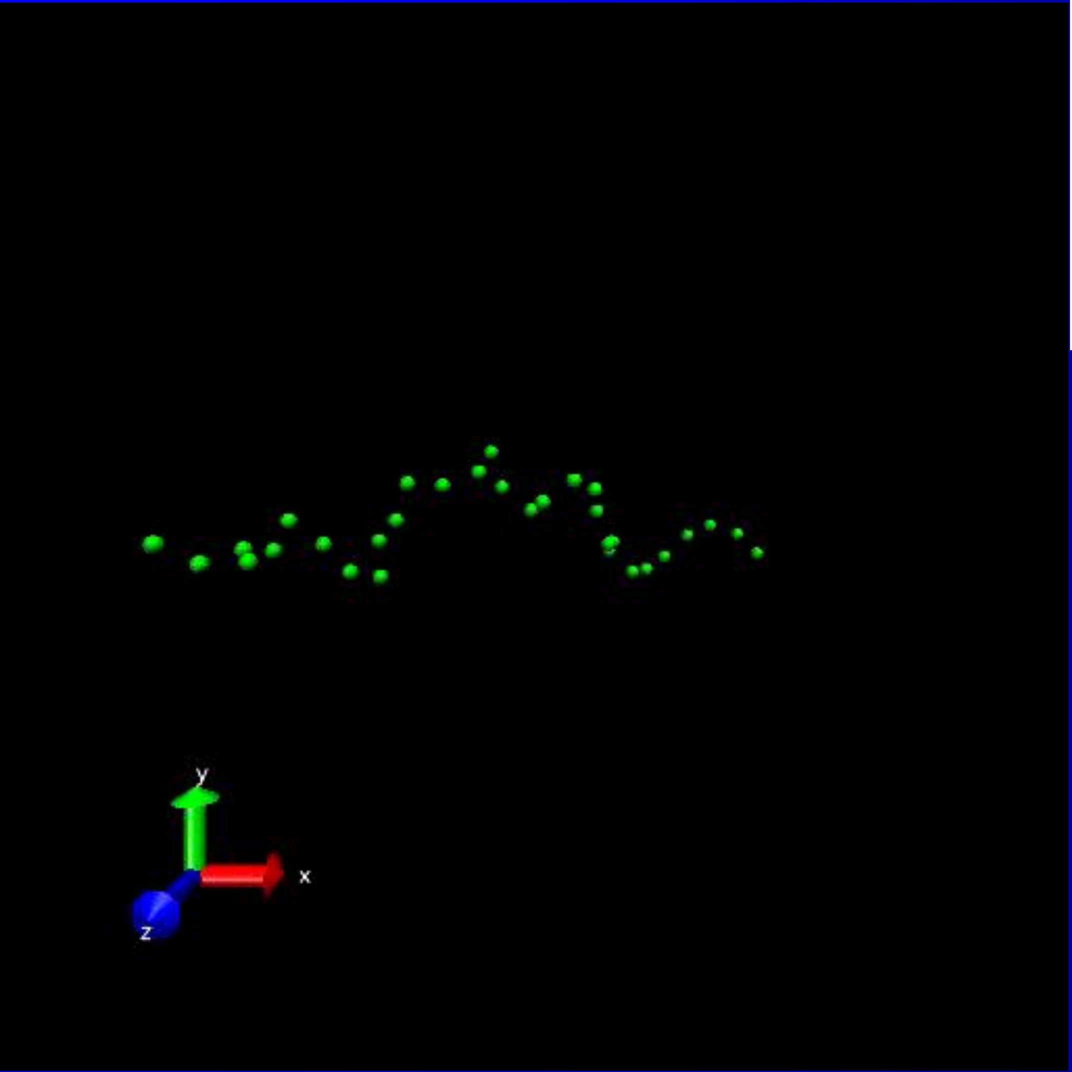


Theory curve: Crocker et al.,PRL **85**, 888 (2000)

Polymer dynamics:

Point particles





Particles with extended size

Polymer Diffusion

Analytic value known = 2.837

Analytic value known = 2.837

Expected:

$$D_{\rm cm} = \frac{k_{\rm B}T}{6\pi\,\eta}\left(\frac{A}{R_g} - \frac{B}{L}\right)$$

$$D_{\rm cm} = \frac{k_{\rm B}T}{6\pi\,\eta}\left(\frac{A}{R_g} - \frac{B}{L}\right)$$

A=1.63±0.01 from bead-spring calculation[1]

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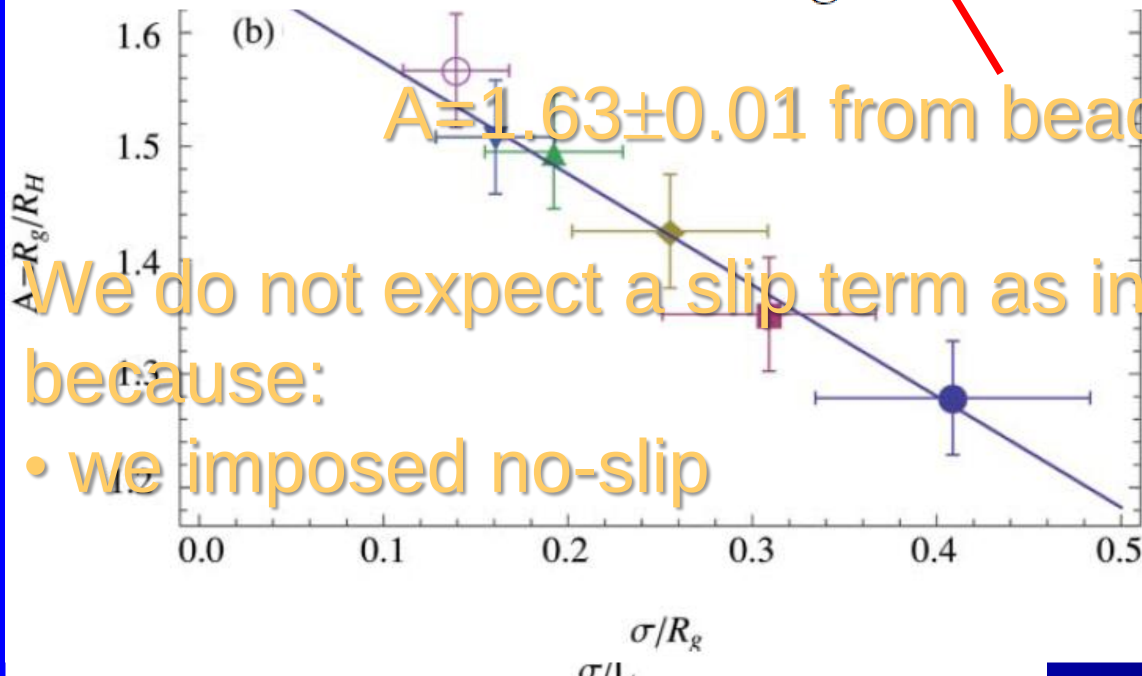


We do not expect a slip term as in Kirkwood model because:

• we imposed no-slip

Asymptotic value
A=1.67 ±0.05

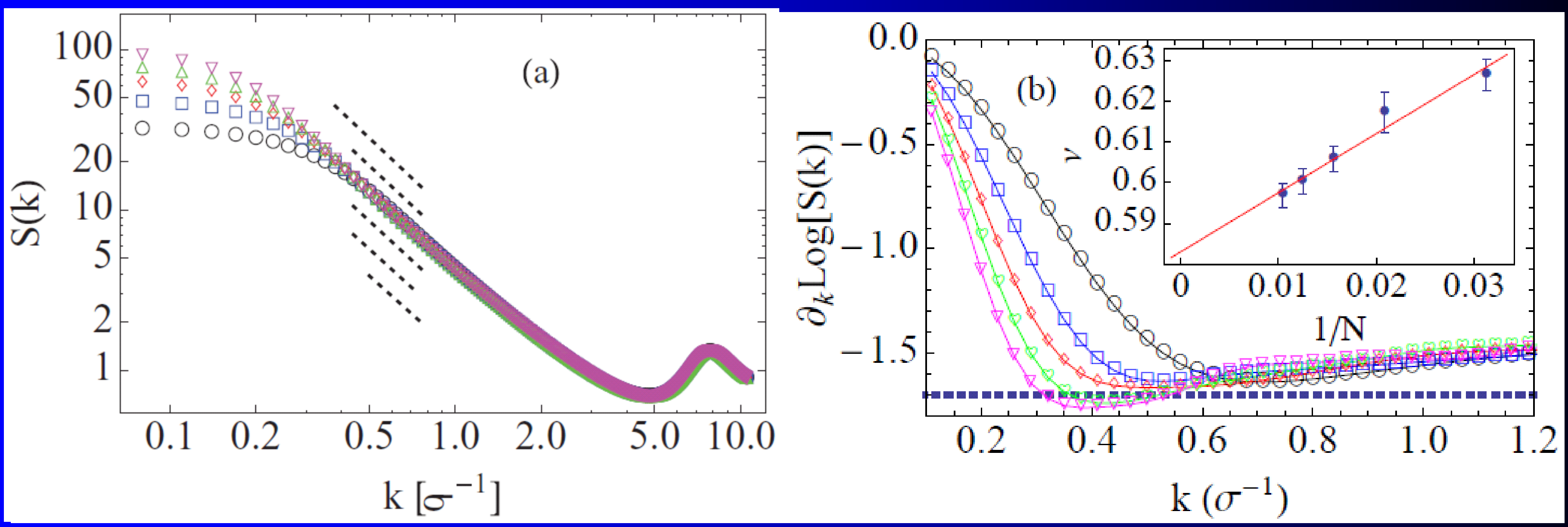
Slope gives
B=2.8±0.05

1. Dünweg et al., JCP **117**, 914 (2002).

Static scaling

$$\langle R_g \rangle \sim N^{\nu}$$ ν=0.5977 for SAW

Direct measurement gives $R_g = (0.49\sigma) N^{0.61}$
using N=48-96



$$S(k) \sim k^{-1/\nu}$$ gives ν=0.586 ± 0.005

Polymer dynamics: Rouse-mode Analysis

For Zimm model one expects

$$\mathbf{X}_p = \frac{1}{N}\sum^{N}$$

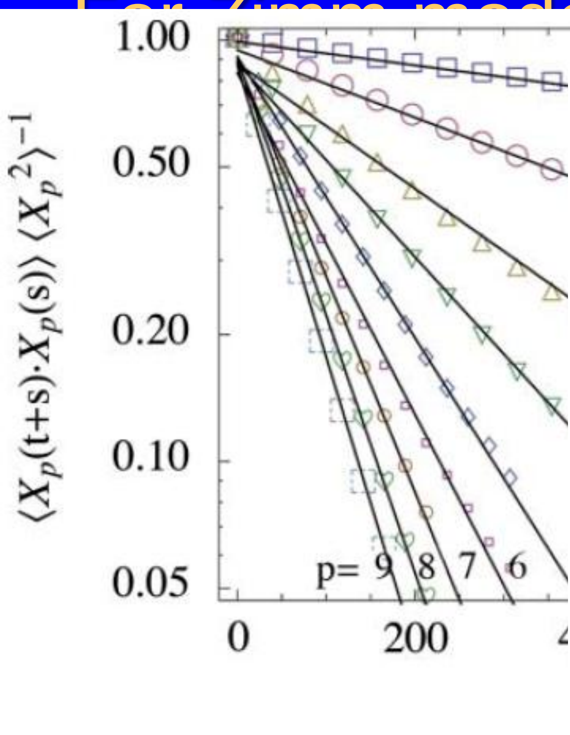
$$\langle \mathbf{X}_p(t+s)\cdot\mathbf{X}_p(s)\rangle_s = \langle \mathbf{X}_p^2\rangle e^{-t/\tau_p}$$

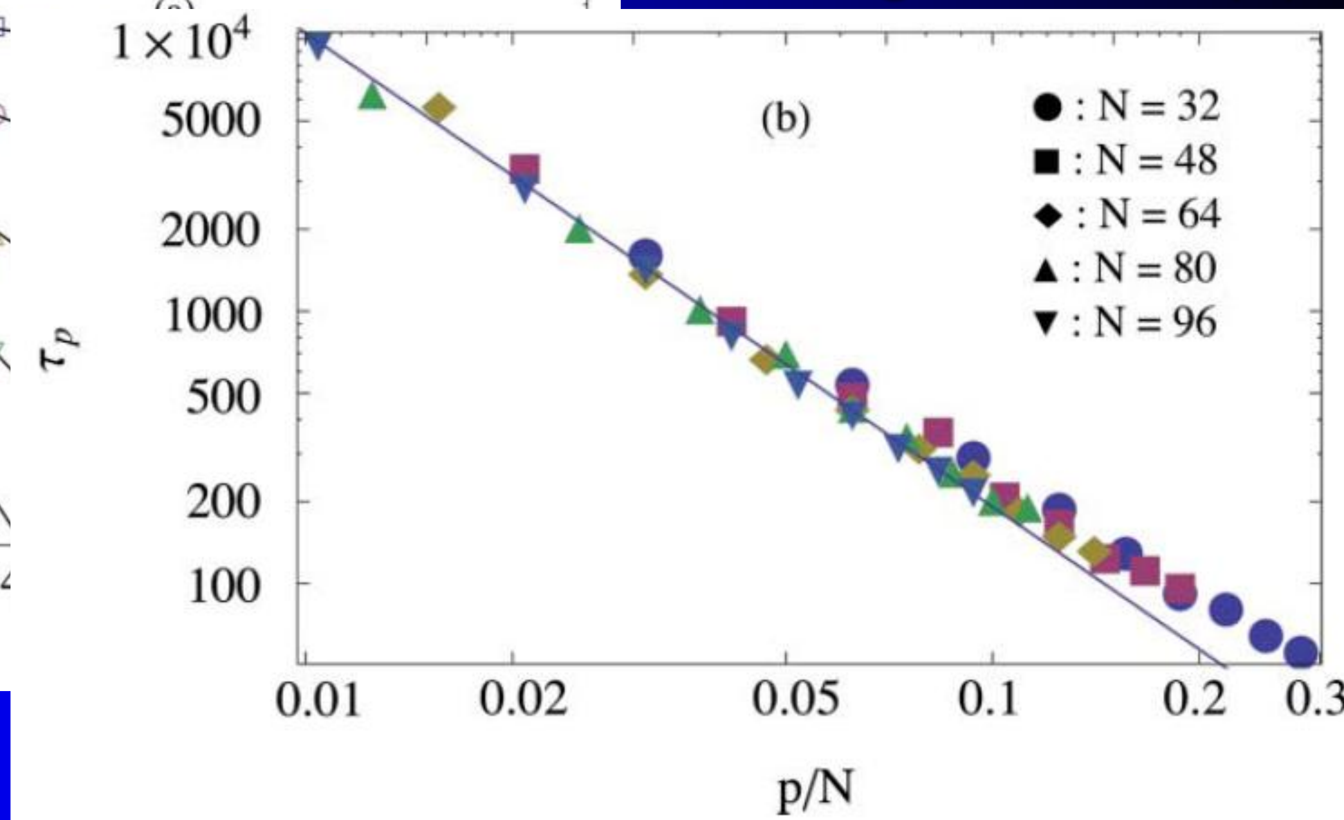
and

$$\tau_p^{-1} \sim \left(\frac{p}{N}\right)^{z\nu} r_\nu(p),$$

Slope gives z=2.97 ± 0.04 using ν from S(k)

For Zimm model one expects





Dynamical Scaling: S(k,t)

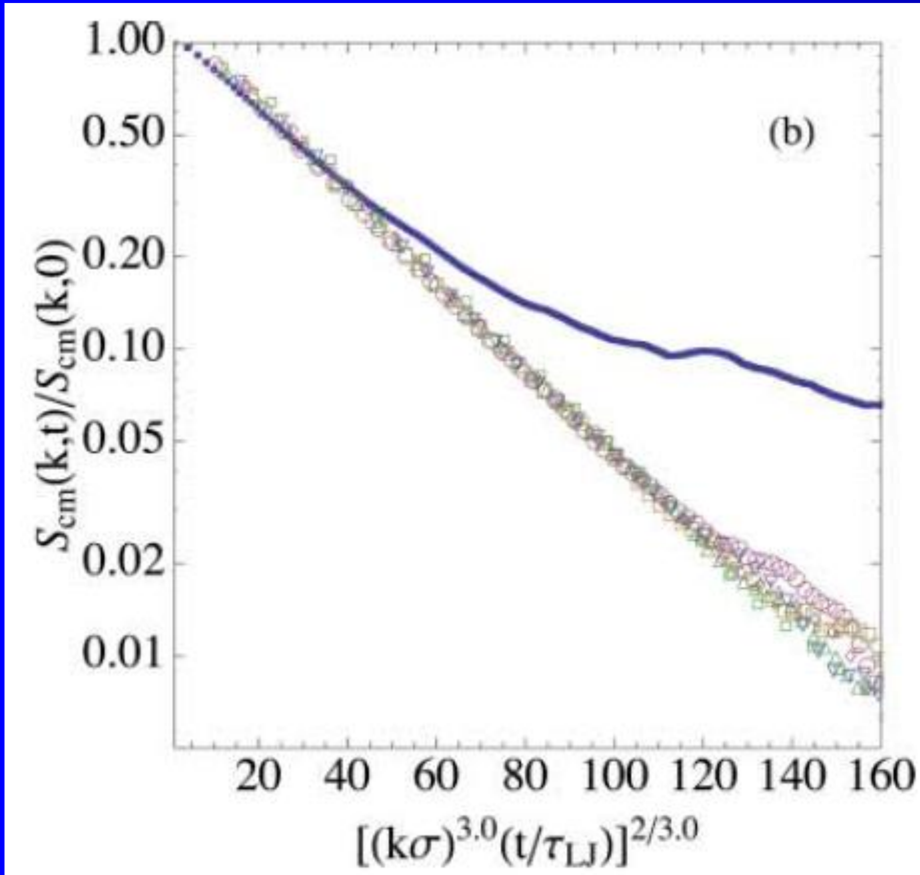
$$S(\mathbf{k}, t) \equiv \frac{1}{N}\langle \hat{\rho}(\mathbf{k}, t+s)\hat{\rho}^*(\mathbf{k}, s)\rangle_s = \frac{1}{N}\sum_{m,n=1}^{N}\langle e^{i\mathbf{k}\cdot(\mathbf{r}_m(t+s)-\mathbf{r}_n(s))}\rangle_s$$

Zimm model predicts $S(k, t) = S(k, 0)F(k^z t)$ assuming one is looking at internal motions of the chain. But there is no clear separation of time scales of CM motion and internal monomer motion. As a result one should expect[1,2] $S(q,t) = S(q,0)g(q^{8/3}t)$

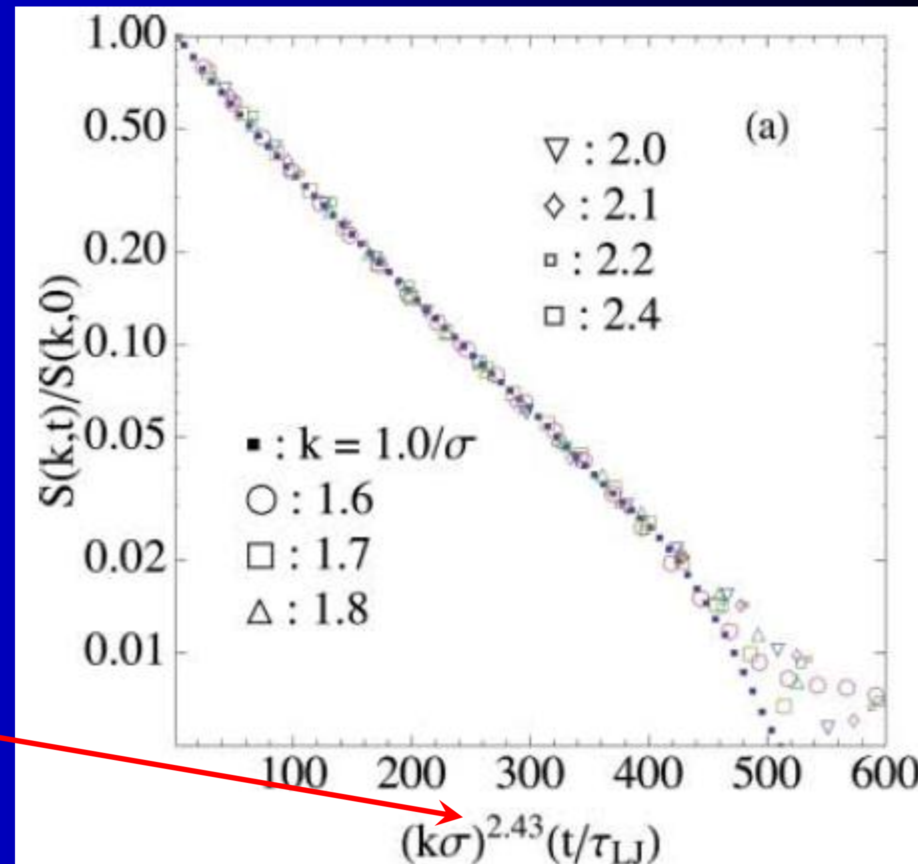
To get Zimm prediction should measure:

$$S_{\mathrm{cm}}(\mathbf{k}, t) \equiv \frac{1}{N}\sum_{m,n=1}^{N}\langle e^{i\mathbf{k}\cdot(\tilde{\mathbf{r}}_m(t+s)-\tilde{\mathbf{r}}_n(s))}\rangle_s \qquad \tilde{\mathbf{r}}_m(t) = \mathbf{r}_m(t) - \mathbf{r}_{\mathrm{cm}}(t)$$

1. Mussawisade et al., JCP **123**, 144905 (2005).
2. Winkler et al., Macromol. Theory Sim. **6**, 1007 (1997).



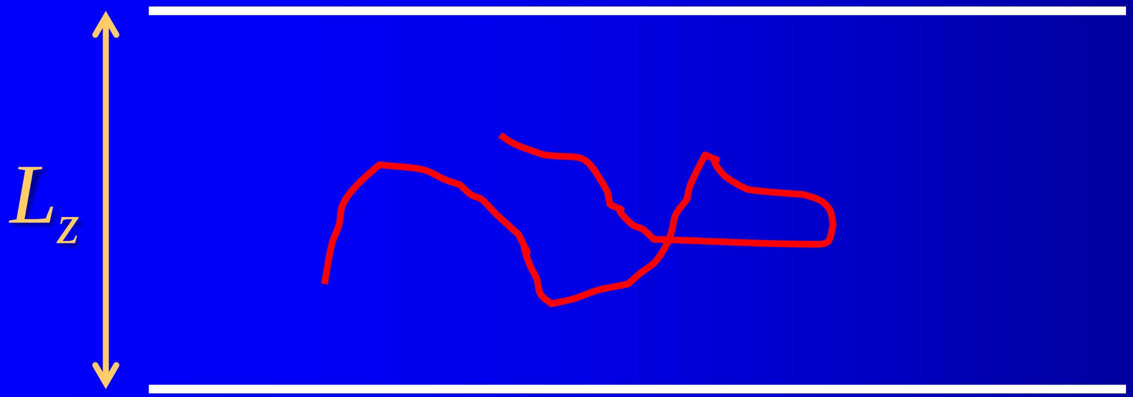
32-mer



64-mer gives 2.54, closer to 8/3~2.67

Ollila, CD, et al., JCP **134**, 064902 (2011)

Polymer in a channel



$$C = \frac{R_{G,\infty}}{L_z}$$

Periodic in x and y

2D to 3D crossover

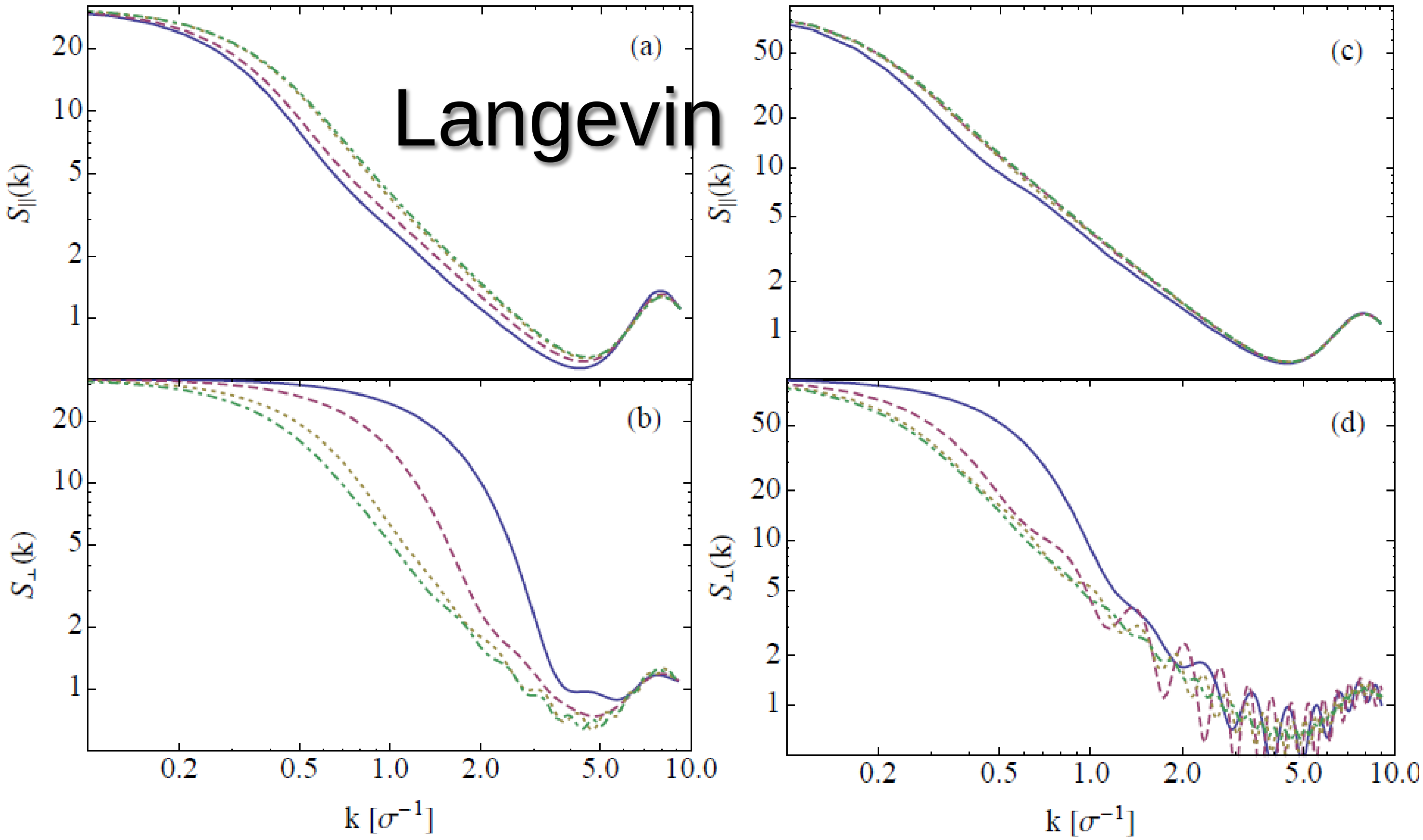


FIG. 2. Static structure factor from Langevin simulations probed (a) for $N = 32$ and (c) $N = 96$ in the plane of the walls ($\mathbf{k}_{\|} = k(\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y)/\sqrt{2}$) and (b) for $N = 32$ and (d) for $N = 96$ normal to the walls ($\mathbf{k}_{\perp} = k\hat{\mathbf{e}}_z$) at different levels of confinement: panels (a) and (b) $C = 1.8$ (solid line), 0.9 (dashed), 0.5 (dotted) and 0.3 (dot-dashed); panels (c) and (d) $C = 1.0$ (solid line), 0.5 (dashed), 0.3 (dotted) and 0.25 (dot-dashed).

Dynamic Scaling

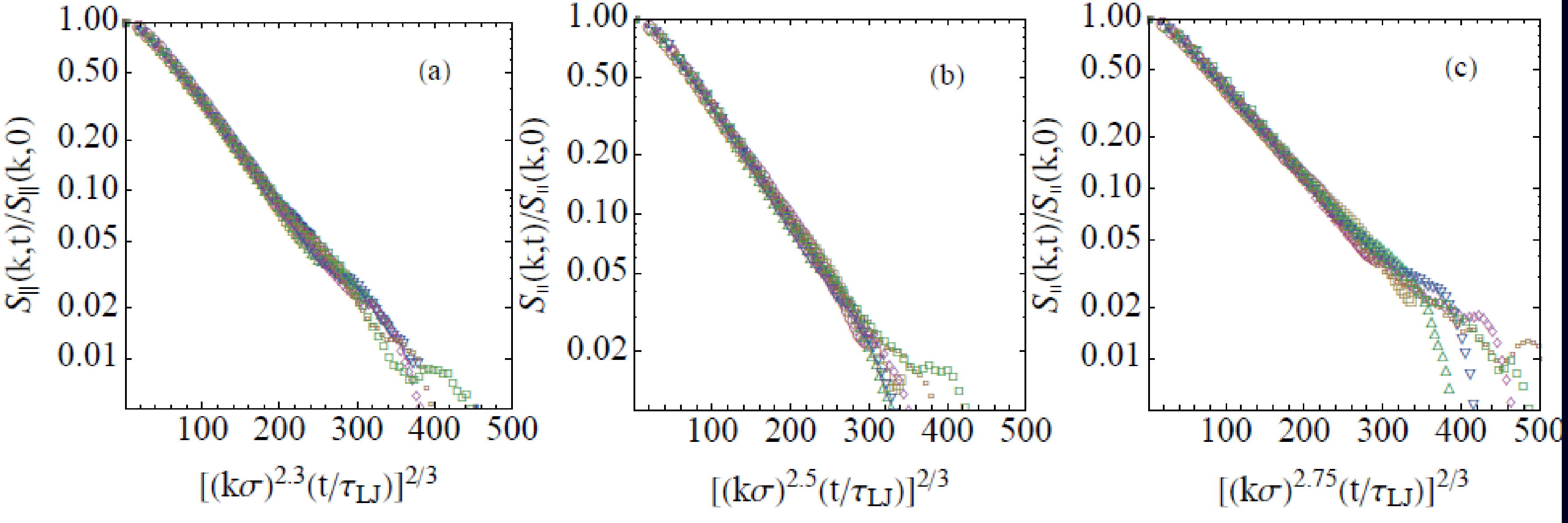


FIG. 5. Dynamic scaling for $N = 32$ in LB fluid along a vector $\mathbf{k} = \mathbf{k}_{\parallel}$ confined to a plane parallel to the confining walls. As the spacing between the walls in increased from (a) $C = 0.9$ to (b) $C = 0.5$ and (c) $C = 0.3$, the scaling exponent increases from $z = 2.3 \pm 0.05$ to $z = 2.75 \pm 0.05$

Continuous change of z-exponent from 2D (2) to 3D value (3) as confinement is reduced.

Diffusion

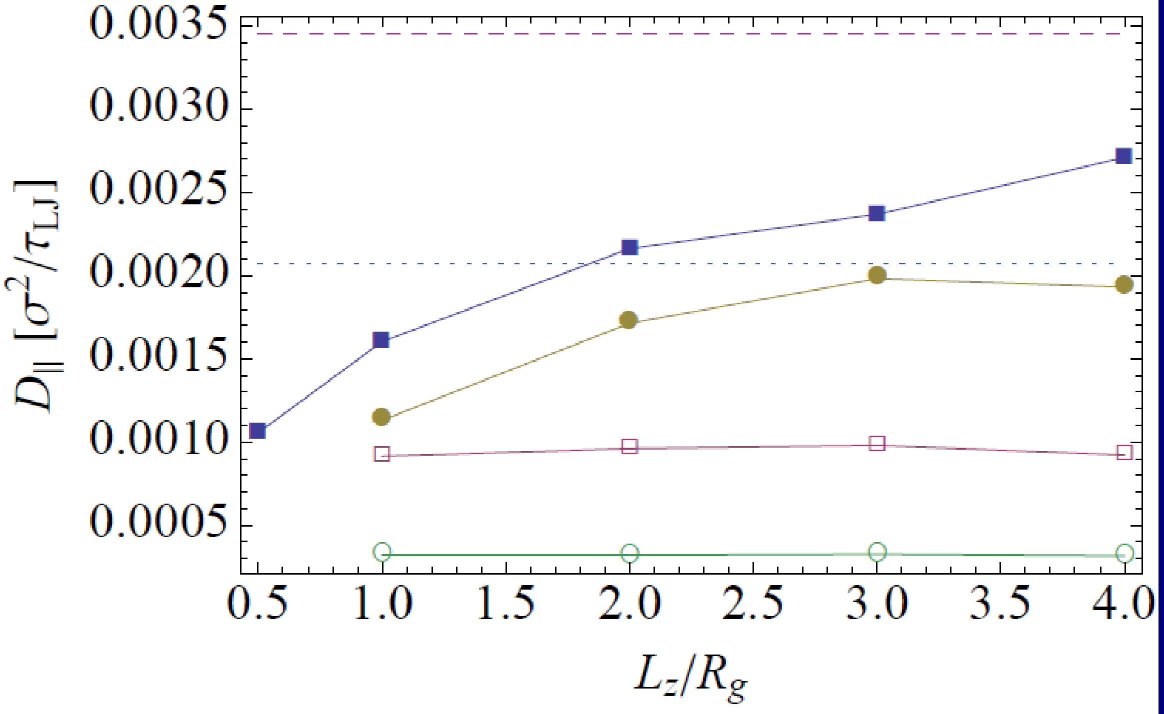
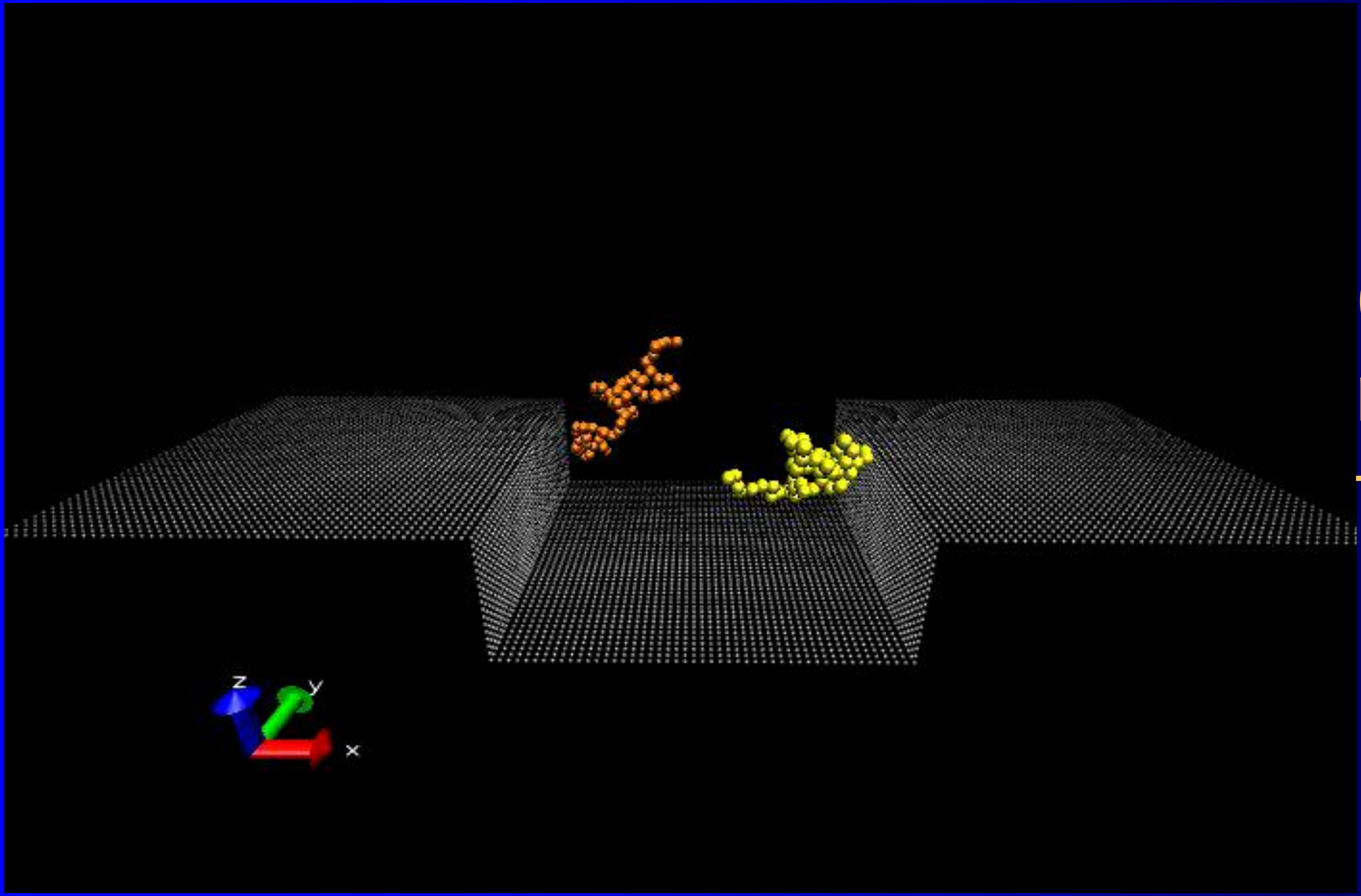


FIG. 9. The planar center-of-mass diffusion coefficient as a function of decreasing degree of confinement in LB (solid symbols) and Langevin simulations (hollow symbols). The shape of the symbol indicates the degree of polymerization: N=32 (square) and N=96 (circles). The finite-size corrected value of the diffusion coefficient is also shown as horizontal lines for N=32 (dashed) and N=96 (dotted).

Polymer in pressure driven flow with trough:



(flat top wall removed for viewing)

Conclusions

- Fluctuations and particles were included in a lattice-Boltzmann model with a conservative coupling between MD and LB
- Intertia can matter at small Re for particles in flow
- Particles included in a way that guaranteed conservative coupling and gave consistency of hydrodynamic size independent of the way it is measured (drag force, torque, diffusion…)
- Polymer structure and dynamics match very well with theory and gives results for S(k,t) in lab frame and CM frame consistent with results from MPC (Winkler et al.)
- Confinement gives smooth crossover from 2D to 3D dynamic exponent