Mode-coupling theory of single-file diffusion

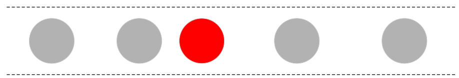
Ooshida Takeshi (大信田 丈志)
in collaboration with
S. Goto, T. Matsumoto, A. Nakahara & M. Otsuki

arXiv:1212.6947 (submitted to PRE)

Physics of glassy and granular materials
YITP (Kyoto), 2013-Jul-17

Outline

- Introduction
  - MCT: theory of F and M
  - SFD is slow: $\langle R^2 \rangle \propto \sqrt{t}$



- Problem:
  improve over standard MCT, as it does not work in 1D

- Lagrangian MCT
  - formulation
  - results

$$\langle R^2 \rangle = c_0 \sqrt{t} + c_1 \qquad \chi_4^{\mathrm{S}} \simeq \frac{\text{const.}}{t^{1/4}} + 0.6454 \times \frac{\rho_0/S}{k_{\mathrm{B}}T}\, a^2$$

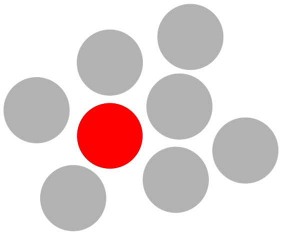
$(c_1 < 0)$

Slow dynamics due to "crowdedness"

shrine on the New Year's day

Gion festival: Parade's Eve

repulsive Brownian particles



cage effect

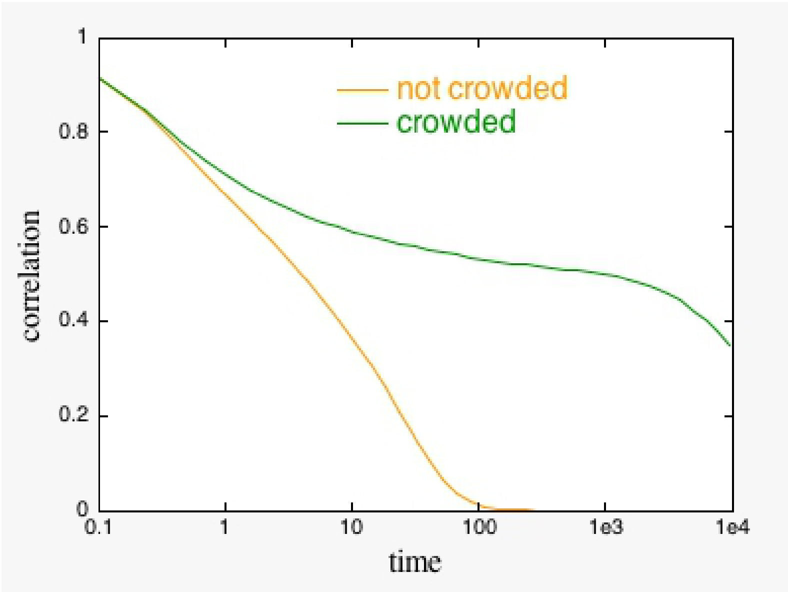
$$m\ddot{\mathbf{r}}_i = -\mu\dot{\mathbf{r}}_i - \frac{\partial}{\partial \mathbf{r}_i}\sum_{j<k} V(r_{jk}) + \mu \mathbf{f}_i(t)$$

$$\left\langle \mathbf{f}_i(t) \otimes \mathbf{f}_j(t') \right\rangle = \frac{2k_{\mathrm{B}}T}{\mu}\delta_{ij}\delta(t-t')\mathbb{1}$$

Mode-Coupling Theory (MCT) for glassy liquids

Equation for the correlation $F(k,t) \propto \langle \widehat{\rho}(k,t)\widehat{\rho}(-k,0)\rangle$

$$\left(\partial_t + D_{\mathsf{C}}k^2\right) F(k,t) = -\int_0^t \mathrm{d}t' M(k,t-t')\partial_{t'} F(k,t')$$
$$M(k,s) \propto \sum V^2 F(p,s)F(q,s)$$



A theory for the two aspects of caged dynamics?

- each particle is confined within a narrow space
- collective motion of numerous particles is produced

$\rho_0,\ \sigma;\ S(k)$ → MCT → $F(k,t) \propto \langle \widehat{\rho}\widehat{\rho} \rangle$

$F_\mathrm{s} = 1 - \frac{1}{2}k^2 \langle R^2 \rangle + \cdots$

$\rho_0,\ \sigma;\ S(k)$ → ?? → $\chi_4(t)$ 4-point corr.

short range

$\lambda(t)$ dyn. corr. length

long range

dynamical

Single-File Diffusion (SFD): eternal cages

1D system of Brownian particles

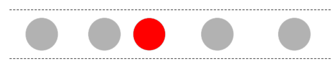
+ "no-passing" repulsive interaction

$$m\ddot{X}_i = -\mu\dot{X}_i - \frac{\partial}{\partial X_i}\sum_{j<k} V(X_k - X_j) + \mu f_i(t)$$

interaction   random force

a problem of 1965-vintage:

Harris (1965), Jepsen (1965), Levitt (1973), ...



model of ideal cages, polymer entanglement etc.

Rallison, JFM **186** (1988)

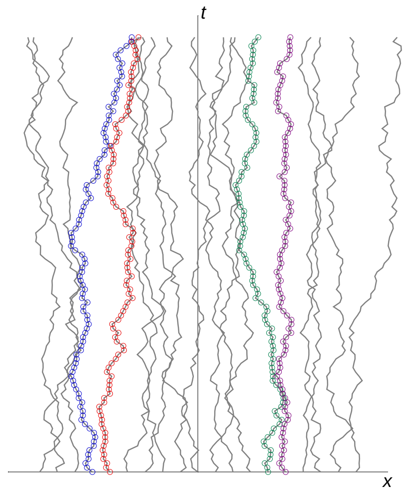
Miyazaki & Yethiraj, JCP **117** (2002)

Lefèvre *et al.*, PRE **72** (2005)

Miyazaki, Bussei Kenkyû **88** (2007)

Abel *et al.*, PNAS **106** (2009)

Ooshida *et al.*, JPSJ **80** (2011)



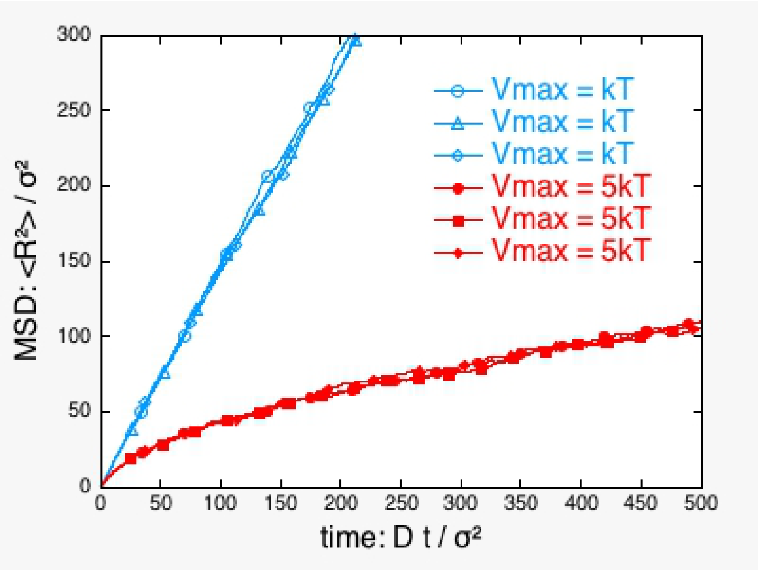
SFD is slow

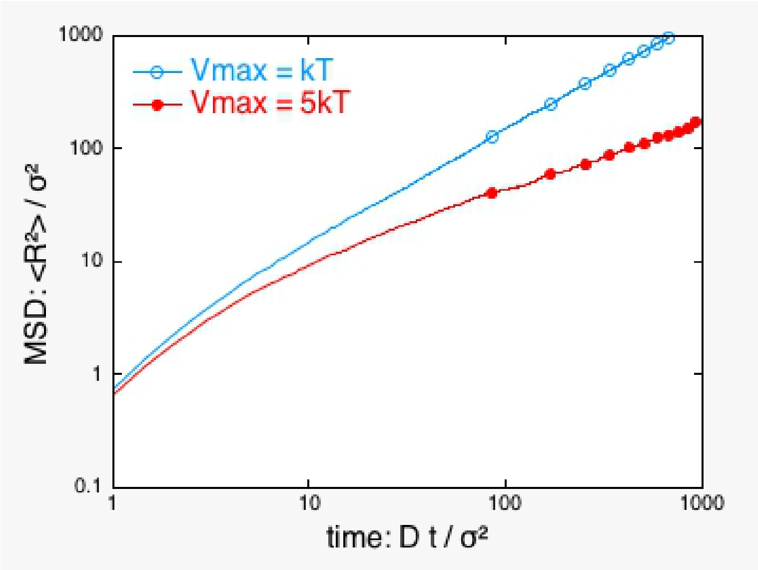
$\rho_0^{-2} \ll Dt \ll L^2 \to \infty$

$R_j \stackrel{\text{def}}{=} X_j(t) - X_j(0)$; study long-time behavior of MSD

- free Brownian particles ($V = 0$): $\langle R^2 \rangle \propto t$
- "no passing" ($V_{\text{max}} = \infty$): $\langle R^2 \rangle = \frac{2S}{\rho_0}\sqrt{\frac{D_c t}{\pi}} \propto t^{1/2}$

  Kollmann, PRL **90** (2003)

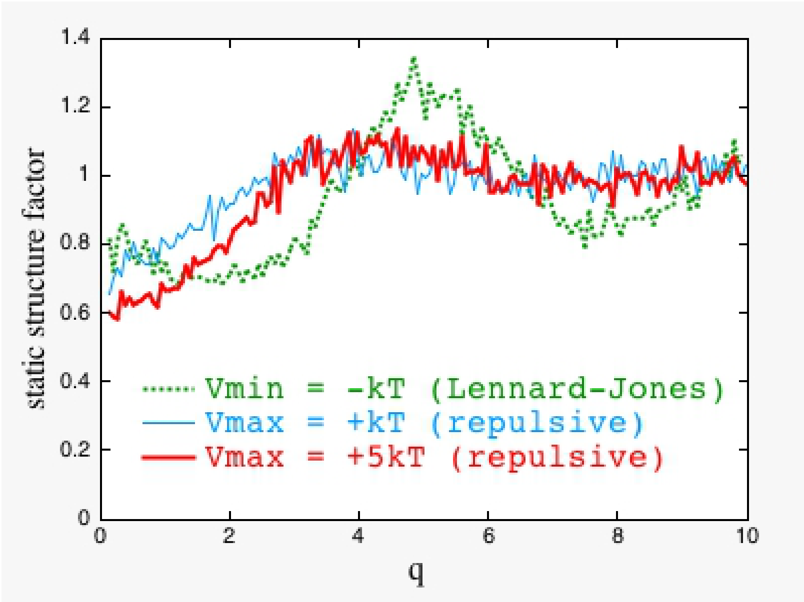




SFD is "glassy": structure behind the slow dynamics

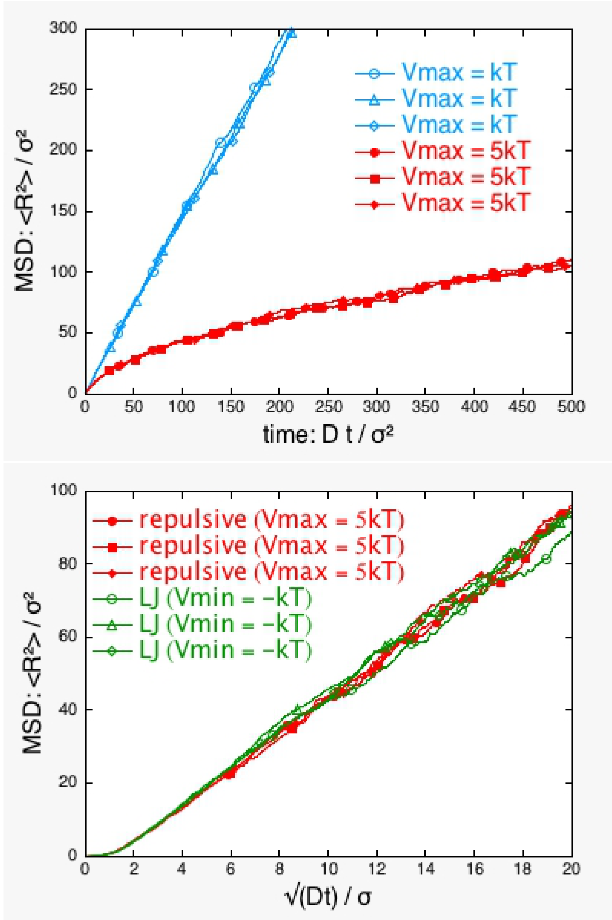
static structure factor

$$S(q) = \frac{1}{N} \sum_{i,j} \left\langle \exp\left[\mathrm{i}q \left(X_j - X_i \right) \right] \right\rangle$$



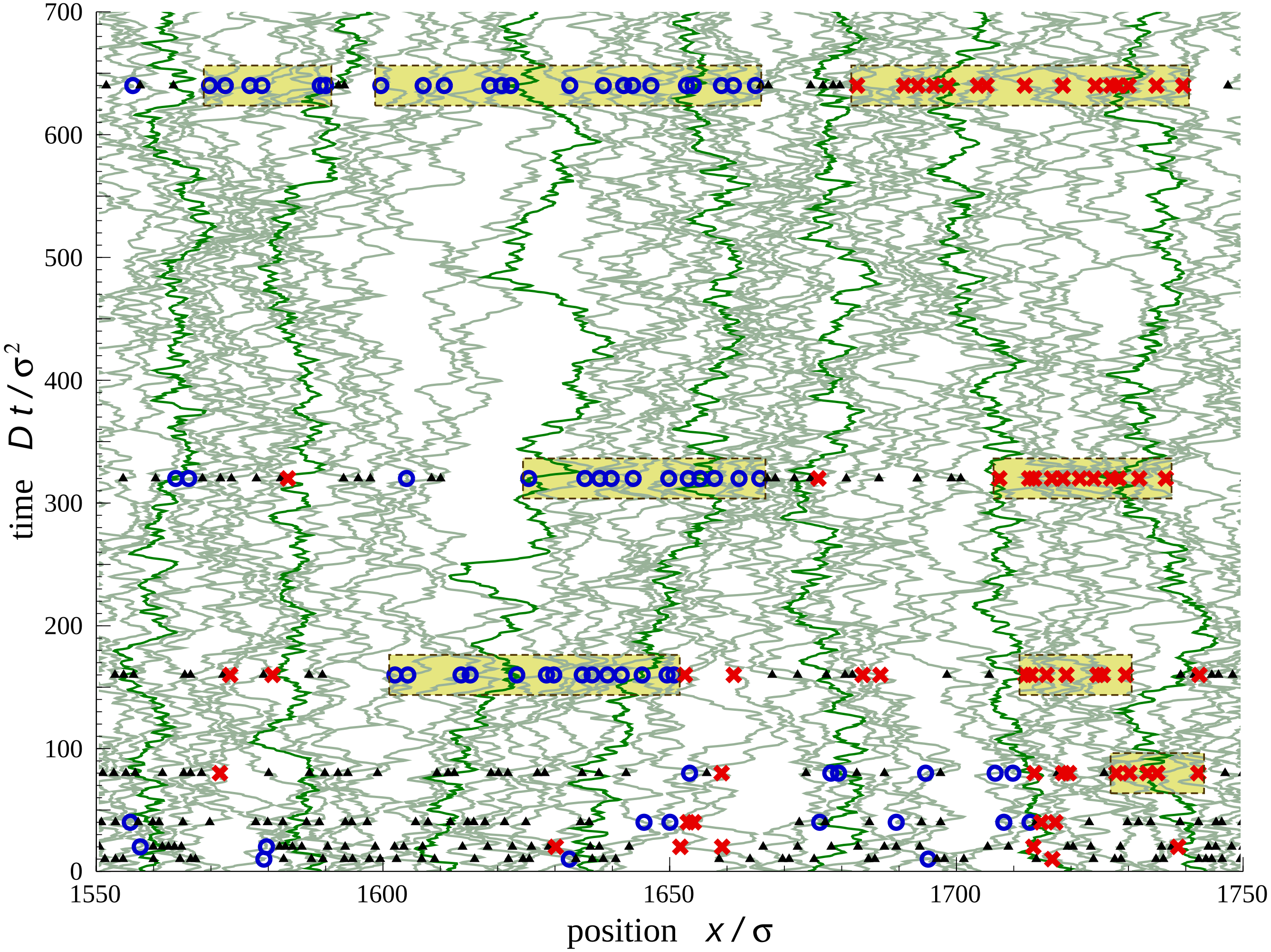
something beyond $S(q)$:
glassy dynamical structure?

$\langle R^2 \rangle$ vs t



Collective motion in space–time diagram

particles moved leftwards (×) and rightwards (○)
relatively to their initial position



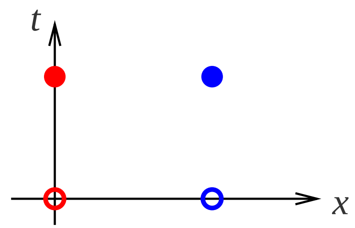
Standard MCT fails in predicting subdiffusion for SFD

2-time correlation of single particle density $\rho_j = \delta(x - X_j(t))$

$$F_\mathrm{s}(k,t) = \left\langle e^{\mathrm{i}k\left(X_j(t)-X_j(0)\right)} \right\rangle = 1 - \frac{1}{2}k^2 \langle R^2 \rangle + \cdots$$

For large t, MCT predicts $\left\langle R^2 \right\rangle \propto t$ wrong!

Miyazaki, Bussei Kenkyû **88** (2007); Abel *et al.*, PNAS **106** (2009)



- "no passing" rule
  $\rightarrow$ space-time 4-point correlation
- Eulerian description with the density field:
  $\langle \rho(\mathbf{r}_1, 0)\rho(\mathbf{r}_1, t)\rho(\mathbf{r}_2, 0)\rho(\mathbf{r}_2, t)\rangle \leftarrow$ 4-body correlation
- MCT approximates $\langle \widehat{\rho}\widehat{\rho}\widehat{\rho}\widehat{\rho} \rangle$ with FF limited accuracy

Construct MCT of SFD ... how?

$\rho_0,\ \sigma;\ S(k)$ ⇒ **MCT** ⇒ $F(k,t) \propto \langle \hat{\rho}\hat{\rho} \rangle$

$F_\mathsf{s} = 1 - \frac{1}{2}k^2 \langle R^2 \rangle + \cdots$ MSD

$$(\partial_t + \cdots)F = -\int M \partial_{t'} F \mathrm{d}t'$$

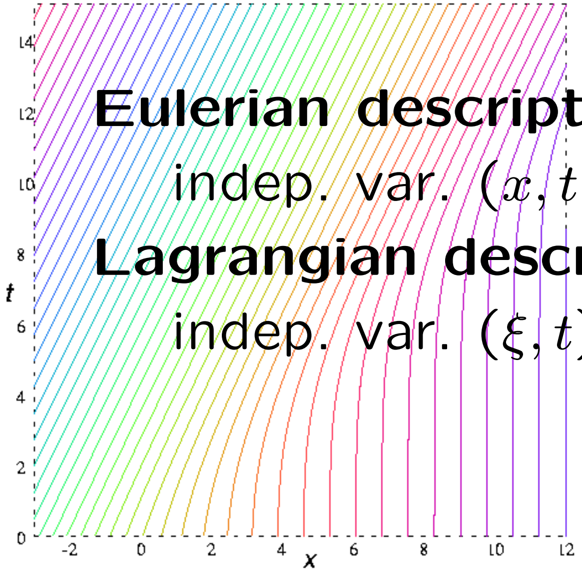
$$(\partial_t + \cdots)F_\mathsf{s} = -\int M_\mathsf{S} \partial_{t'} F_\mathsf{s} \mathrm{d}t'$$

- improve M_S Miyazaki (2007); Abel *et al.* (2009)
- abandon M_S and replace it with something else
  Ooshida *et al.*, arXiv:1212.6947

N.B. M is employed anyway

How to do without M_S: Lagrangian correlation

- introduce label variable ξ : $x = x(\xi, t)$



Lagrangian description

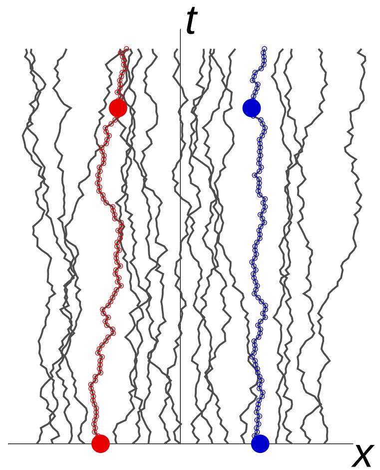
Eulerian description

indep. var. (x, t)

Lagrangian description

indep. var. (ξ, t)

construct $\xi = \xi(x, t)$ as a potential of the cont. eq.:
$\rho = \partial_x \xi$, $Q = -\partial_t \xi$
so that
$\partial_x \rho + \partial_x Q = 0$
$(\partial_t + u\partial_x)\xi = 0$



- space-time 4-point correlation
  → 2-body Lagrangian correlation

Key : 2pDC $\langle R(\xi, t) R(\xi', t) \rangle$

$R(\xi, t) = x(\xi, t) - x(\xi, 0)$

Lagrangian MCT

$\rho_0,\ \sigma;\ S(k)$ ⇒ **L-MCT + m-AP** ⇒

$\check{C}(k,t) = \frac{N}{L^2}\langle\check{\psi}\check{\psi}\rangle$

$\langle R(\xi,t)R(\xi',t)\rangle$

2-pa. disp. corr.

$\Downarrow$

$\langle R^2\rangle = c_0\sqrt{t}+c_1$

$\chi_4^{\mathrm{S}} = \langle \mathcal{Q}_{\mathrm{S}}^2\rangle - \langle\mathcal{Q}_{\mathrm{S}}\rangle^2 = \cdots$

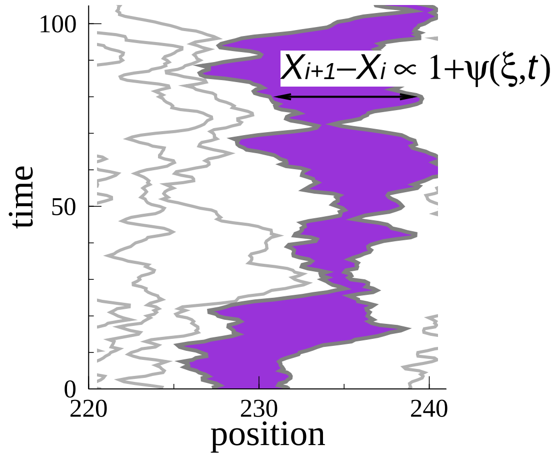
- Rewrite the Langevin eq. with new variables
- Calculate $\check{C}$ with Lagrangian MCT eq.
- Obtain two-particle displacement corr. $\langle RR\rangle$ from $\check{C}$ with modified Alexander–Pincus formula
- 2pDC yields MSD and χ_4^{S}

Rewrite Langevin eq. with label variable

differential operators:

$$\partial_x = \frac{\partial \xi}{\partial x}\partial_\xi = \rho \partial_\xi$$

$$(\partial_t \ \cdot \ )_x = (\partial_t \ \cdot \ )_\xi - Q\partial_\xi$$



kinematic relation for particle interval

$$\partial_t \left[\frac{1}{\rho(\xi,t)}\right] = \partial_\xi \left(\frac{Q}{\rho}\right)$$

particle interval

then we introduce ψ to write $\frac{1}{\rho(\xi,t)} = \frac{1+\psi(\xi,t)}{\rho_0}$

$$\boxed{\partial_t \rho(x,t) + \partial_x Q = 0} \rightarrow \boxed{\partial_t \psi(\xi,t) = -\rho_0 \partial_\xi \left(\frac{Q}{\rho}\right)}$$

Eulerian vs Lagrangian: different nonlinearities

Langevin eq. in the x-space ("Eulerian")

$$\partial_t \rho(x,t) = D\partial_x \left(\underbrace{\partial_x \rho}_{\text{linear}} + \underbrace{\boxed{\frac{\rho}{k_{\mathrm{B}}T}\partial_x U}}_{\text{nonlinear}} \right) + \underbrace{f_\rho(x,t)}_{\text{nonlinear!}}$$

$$\left\langle f_\rho(x,t) f_\rho(x',t') \right\rangle = 2D\partial_x\partial_{x'} \underbrace{\rho(x,t)}_{\text{multiplicative noise}} \delta(x-x')\delta(t-t')$$

Langevin eq. in the ξ-space ("Lagrangian")

$$\partial_t \psi(\xi,t) = -\rho_0^2 D\partial_\xi \left[\underbrace{\partial_\xi \left(\frac{1}{1+\psi} \right)}_{\text{nonlinear}} + \underbrace{\boxed{\frac{\rho}{\rho_0 k_{\mathrm{B}}T}\partial_\xi U}}_{\text{nonlinear}} \right] + \underbrace{f_{\mathrm{L}}}_{\text{harmless}}$$

$$\left\langle f_{\mathrm{L}}(\xi,t) f_{\mathrm{L}}(\xi',t') \right\rangle = 2D\partial_\xi\partial_{\xi'} \sum_i \delta\left(\xi - \Xi_i\right) \delta(\xi-\xi')\delta(t-t')$$

$\rightarrow$ no FDT-violation

Derivation of Lagrangian MCT eq.

Langevin eq. for ψ

$\to$ Fourier representation $\qquad \check{\psi}(k,t) = \frac{1}{N}\int \mathrm{d}\xi\, e^{\mathrm{i}k\xi}\psi(\xi,t)$

$\to$ equation for $\check{C} \overset{\text{def}}{=} \frac{N}{L^2}\langle\check{\psi}(k,t)\check{\psi}(-k,0)\rangle$:

$$\left[\partial_t + \frac{D_*}{S(k)}k^2\right]\check{C}(k,t)$$

$$= \frac{N}{L^2}\sum \mathcal{V}_k^{pq}\langle\check{\psi}(-p,t)\check{\psi}(-q,t)\check{\psi}(-k,0)\rangle + \rho_0\langle\check{f}_\mathrm{L}\check{\psi}(-k,0)\rangle$$

vanishes!

where

$$D_* = \rho_0^2 D, \qquad S = \left(1 + \frac{2\sin\rho_0\sigma k}{k}\right)^{-1}$$

$$\mathcal{V}_k^{pq} = D_* k^2 W_{pqk} = D_* k^2 \underline{\left(1 + \frac{k}{pq}\sin\rho_0\sigma k + \frac{p}{kq}\sin\rho_0\sigma p + \frac{q}{kp}\sin\rho_0\sigma q\right)}$$

symmetrical

$\left\langle \check{f}_{\mathsf{L}} \widehat{\psi} \right\rangle$ vanishes
symmetry of W_{pqk} $\Big\}$

$\rightarrow$ field-theoretical closure consistent with FDT

Lagrangian MCT eq.

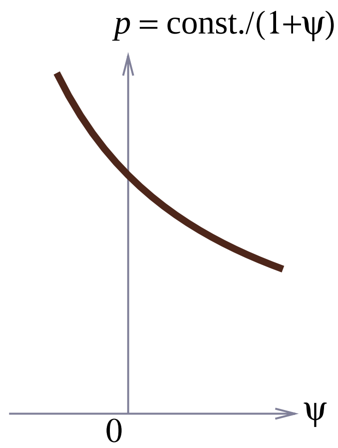
$$\left(\partial_t + \frac{D_*}{S}k^2\right)\check{C}(k,t) = -\int_0^t \mathrm{d}t' M(k,t-t')\partial_{t'}\check{C}(k,t')$$

$$M(k,s) = \frac{2L^4}{N}D_* k^2 \sum_{p+q=k} W_{pqk}^2 \check{C}(p,s)\check{C}(q,s)$$

$$W_{pqk} = 1 + \frac{k}{pq}\sin\rho_0\sigma k + \frac{p}{kq}\sin\rho_0\sigma p + \frac{q}{kp}\sin\rho_0\sigma q$$

N.B. long-wave limit of W is regular (as $p+q+k=0$): $W_{pqk} \simeq 1+3\rho_0\sigma$

Solution to L-MCT eq.



Focus on "ideal" entropic nonlinearity:

for $\rho_0 \sigma \to +0$,

U vanishes but $D\partial_\xi \left(\dfrac{\rho_0}{1+\psi} \right)$ remains nonlinear

$$\check{C} \simeq \frac{e^{-\rho_0^2 D k^2 t}}{L^2} \left[1 + \frac{2}{3}\sqrt{\frac{2}{\pi}} \rho_0^3 k^4 (Dt)^{3/2} + \cdots \right]$$

linear solution — correction due to M

$\rho_0,\ \sigma;\ S(k)$ ⇒ L-MCT + m-AP ⇒ $\check{C}(k,t)$, $\langle R(\xi_1) R(\xi_2) \rangle$

Calculate 2pDC: modified Alexander–Pincus formula

$$R = \int_0^t \frac{\partial x(\xi,\tilde{t})}{\partial \tilde{t}} \mathrm{d}\tilde{t} = \partial_\xi^{-1} \left(\frac{1+\psi}{\rho_0} \right) \Big|_0^t \qquad \frac{\partial x}{\partial \xi} = \frac{1}{\rho} = \frac{1+\psi}{\rho_0}$$

Two-particle displ. corr. (**2pDC**) calculated from $\langle \psi\psi \rangle$:

$$\left\langle R(\xi,t)R(\xi',t) \right\rangle = \frac{L^4}{\pi N^2} \int_{-\infty}^{\infty} \mathrm{d}k\, e^{-\mathrm{i}k(\xi-\xi')} \frac{\check{C}(k,0)-\check{C}(k,t)}{k^2} \quad (\diamondsuit)$$

where $\check{C}(k,t) \overset{\text{def}}{=} \frac{N}{L^2} \langle \check{\psi}(k,t)\check{\psi}(-k,0) \rangle$ $\qquad \check{\psi}(k,t) = \frac{1}{N} \int \mathrm{d}\xi\, e^{\mathrm{i}k\xi} \psi(\xi,t)$

Lagrangian corr.

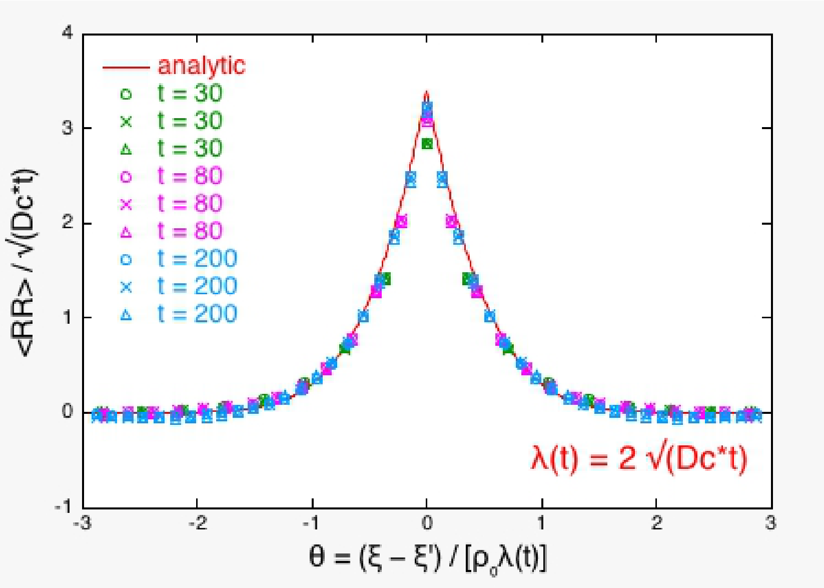
cf. Alexander & Pincus, PRB **18** (1978):

$$\left\langle R(t)^2 \right\rangle \simeq \text{const.} \times \int_{-\infty}^{\infty} \mathrm{d}q\, \frac{F(q,0)-F(q,t)}{q^2} \leftarrow \text{Eulerian corr.}$$

2pDC calculated via L-MCT + m-AP

$$\left\langle R(\xi,t)R(\xi',t)\right\rangle = \frac{2S}{\rho_0}\sqrt{\frac{D_c t}{\pi}}\,\mathrm{exp}\left[-\frac{(\xi-\xi')^2}{4\rho_0^2 D_c t}\right] - \frac{S}{\rho_0^2}|\xi-\xi'|\,\mathrm{erfc}\,\frac{|\xi-\xi'|}{2\rho_0\sqrt{D_c t}} + [\mathrm{correction}]$$

dynamical corr. length: $\lambda(t) = 2\sqrt{D_c t}$, grows in time diffusively)



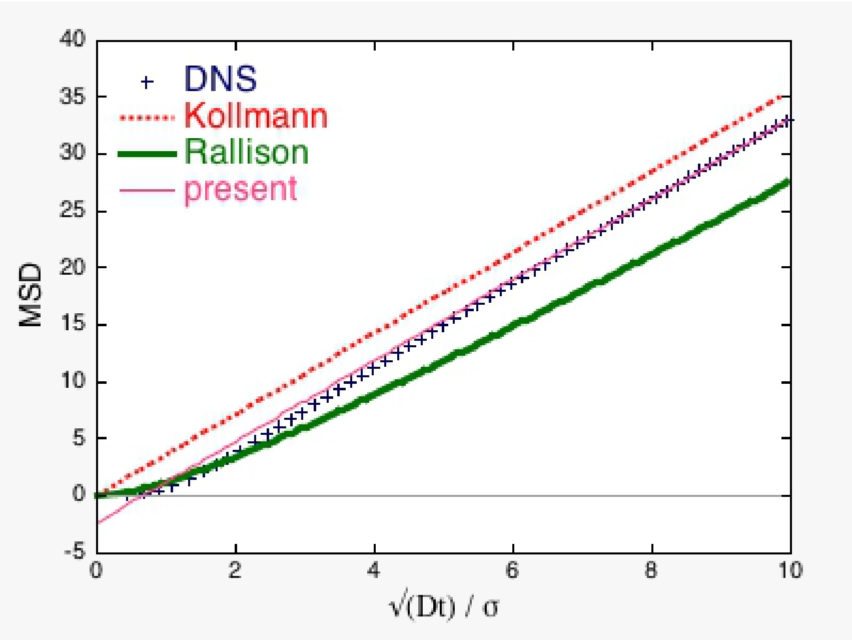
$$\theta \overset{\mathrm{def}}{=} \frac{\xi-\xi'}{\rho_0\lambda(t)} = \frac{\xi-\xi'}{2\rho_0\sqrt{D_c t}}$$

$$\frac{\langle R(\xi,t)R(\xi',t)\rangle}{\sigma\sqrt{D_c t}} \simeq \varphi(\theta)$$

$$= \frac{2S}{\rho_0\sigma}\left(\frac{e^{-\theta^2}}{\sqrt{\pi}} - |\theta|\,\mathrm{erfc}\,|\theta|\right)$$

← direct numerical simulation
(Langevin eq. for particles)
$N = 3000$, $\rho_0 = N/L = 0.2\,\sigma^{-1}$
no ensemble averaging

Behavior of MSD



$\rho_0 \sigma = 0.25, \; S = 0.624$

Hahn & Kärger (1995);
Kollmann (2003)

$$\langle R^2 \rangle \simeq \frac{2S}{\rho_0} \sqrt{\frac{D_c t}{\pi}}$$

Rallison, JFM **186** (1988)

$$\langle R^2 \rangle = \frac{2S}{\rho_0} \sqrt{\frac{D_c t}{\pi}} - \frac{S}{\pi \rho_0^2} \log \left(1 + \rho_0 \sqrt{4\pi D_c t} \right)$$

present

$$\langle R^2 \rangle = \frac{2S}{\rho_0} \sqrt{\frac{D_c t}{\pi}} - \frac{\sqrt{2}}{3\pi} \rho_0^{-2}$$

A more popular form of 4-point correlation

$\mathcal{Q}$-based χ_4: Glotzer *et al.* (2000); Lačević *et al.* (2003)

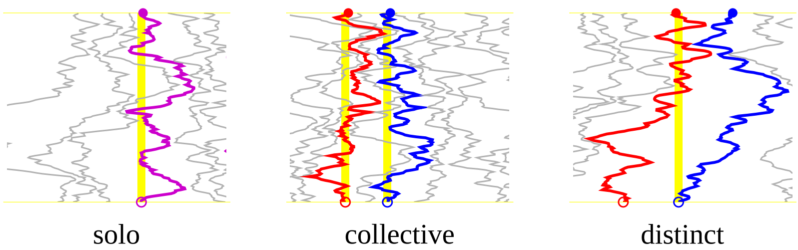
$$\mathcal{Q} = \sum_i \sum_j \bar{\delta}_a(X_j(t) - X_i(0)), \qquad \bar{\delta}_a(r) = \begin{cases} 1 & (0 \le r < a) \\ 0 & (r > a) \end{cases}$$

$$\chi_4(t) = \frac{L}{k_{\mathrm{B}}T} \frac{\left\langle \mathcal{Q}^2 \right\rangle - \langle \mathcal{Q} \rangle^2}{N^2}$$

involves $\sum_i \sum_j \sum_k \sum_l \left\langle \bar{\delta}_a(X_j(t) - X_i(0)) \bar{\delta}_a(X_l(t) - X_k(0)) \right\rangle$

three types of terms

solo $i = j = k = l$
collective $i = j \neq k = l$
distinct $i \neq j$ etc.

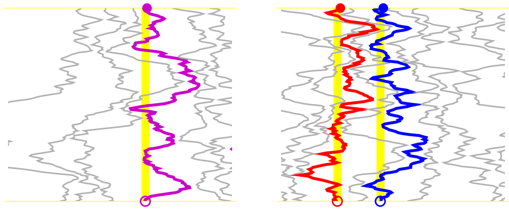


$\chi_4 = \chi_4^{\mathrm{S}} + \chi_4^{\mathrm{D}}, \qquad \chi_4^{\mathrm{S}} = (\chi_4^{\mathrm{S}})_{\mathrm{solo}} + (\chi_4^{\mathrm{S}})_{\mathrm{coll}}$

self

χ_4^{S} can be calculated from 2pDC

focus on the self part ($i = j$) of $\mathcal{Q}$



$$\mathcal{Q}_{\mathsf{S}} = \sum_i \bar{\delta}_a(R_i(t)), \quad \bar{\delta}_a(r) = e^{-r^2/a^2}$$

$$\chi_4^{\mathsf{S}}(t) = \frac{L}{k_{\mathsf{B}}T} \frac{\left\langle \mathcal{Q}_{\mathsf{S}}^2 \right\rangle - \langle \mathcal{Q}_{\mathsf{S}} \rangle^2}{N^2}$$

knowledge of 2pDC allow us to calculate

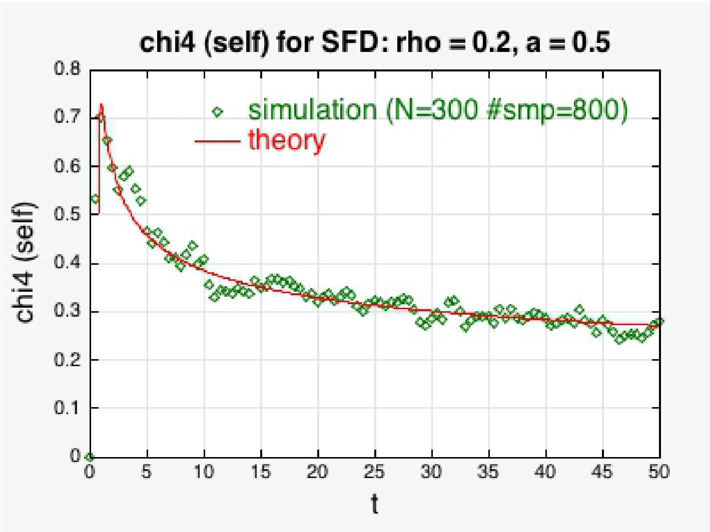
$$\chi_4^{\mathsf{S}} = \frac{L}{N k_{\mathsf{B}} T} \sum_m (\cdots)$$

$\leftarrow$ expressible with $\left\langle R_i R_{i+m} \right\rangle$

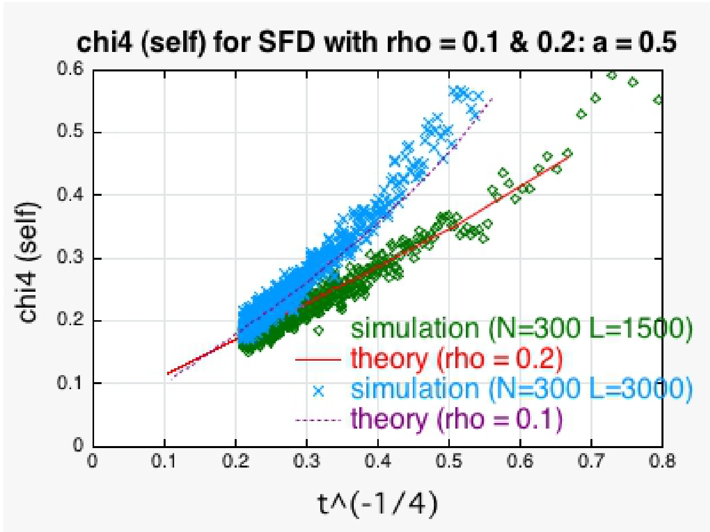
$$\left.\begin{array}{lcl} m = 0 & \rightarrow & (\chi_4^{\mathsf{S}})_{\mathsf{solo}} \\ m \neq 0 & \rightarrow & (\chi_4^{\mathsf{S}})_{\mathsf{coll}} \end{array}\right\} \chi_4^{\mathsf{S}} = (\chi_4^{\mathsf{S}})_{\mathsf{solo}} + (\chi_4^{\mathsf{S}})_{\mathsf{coll}}$$

χ_4^{S} for SFD: analytical & numerical calculations

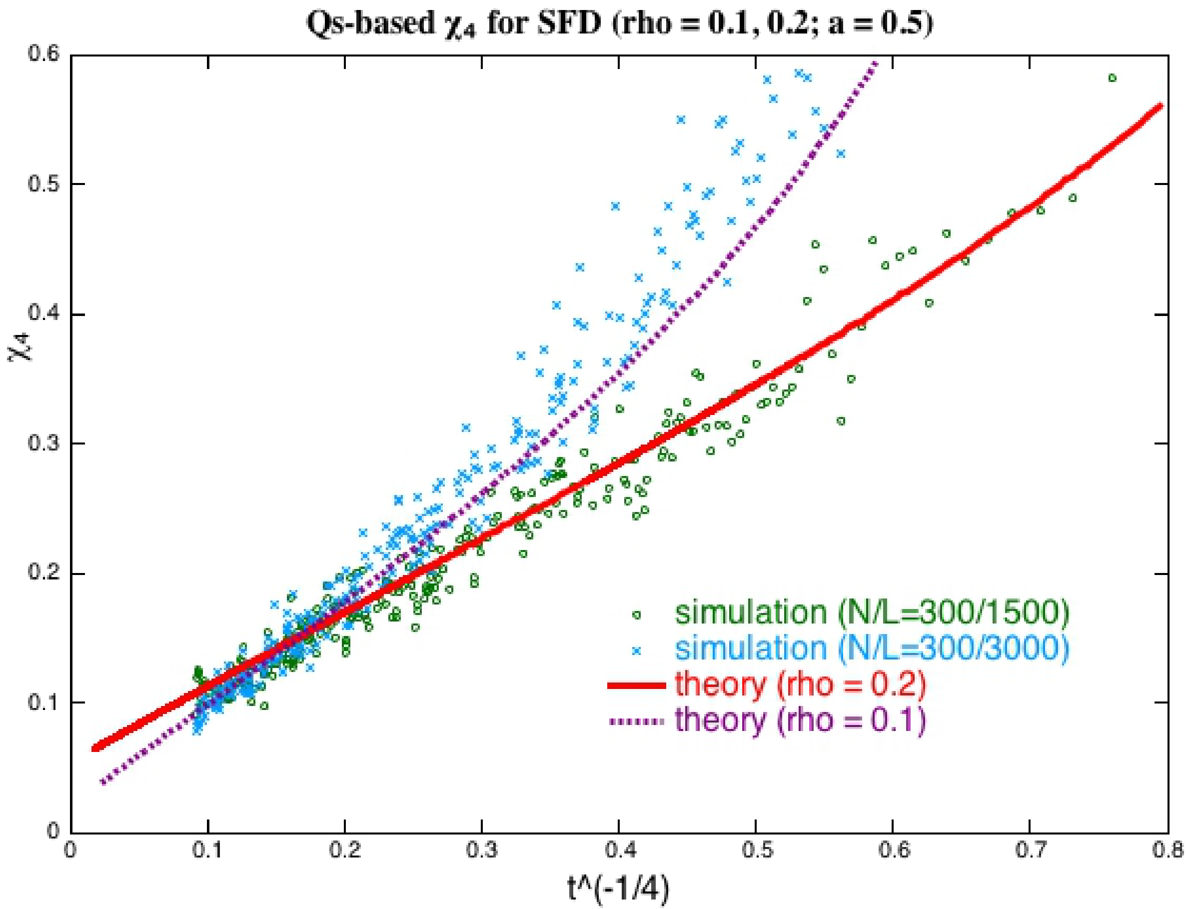
$$\chi_4^{\mathsf{S}} = (\chi_4^{\mathsf{S}})_{\mathsf{solo}} + (\chi_4^{\mathsf{S}})_{\mathsf{coll}} \simeq \frac{\text{const.}}{t^{1/4}} + 0.6454 \times \frac{\rho_0/S}{k_{\mathsf{B}}T}\, a^2$$



short-time "solo" peak



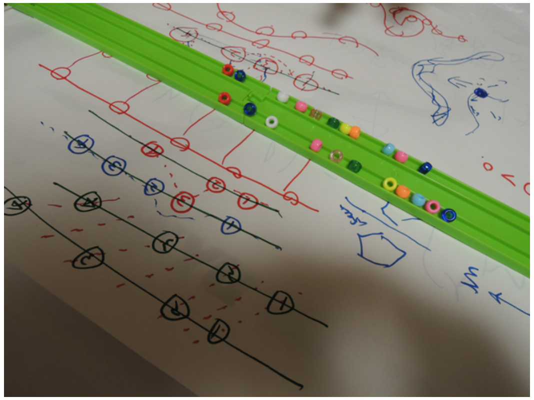
finite for $t \to +\infty$



$$0 < \chi_4^{\mathrm{S}}(\rho_0\sigma = 0.1, t \to +\infty) < \chi_4^{\mathrm{S}}(\rho_0\sigma = 0.2, t \to +\infty)$$

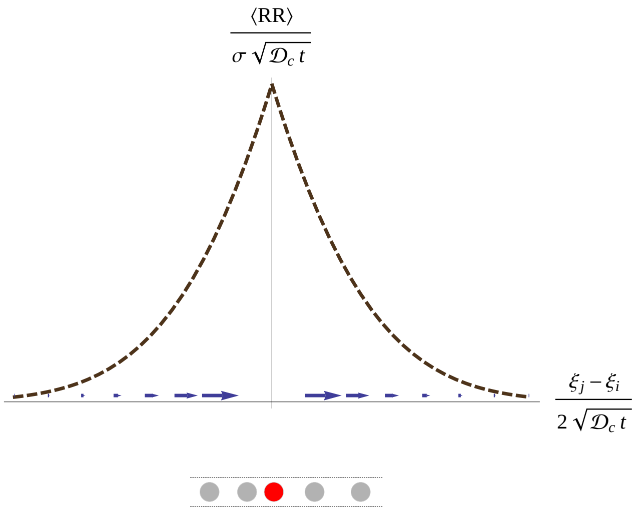
Possible extensions

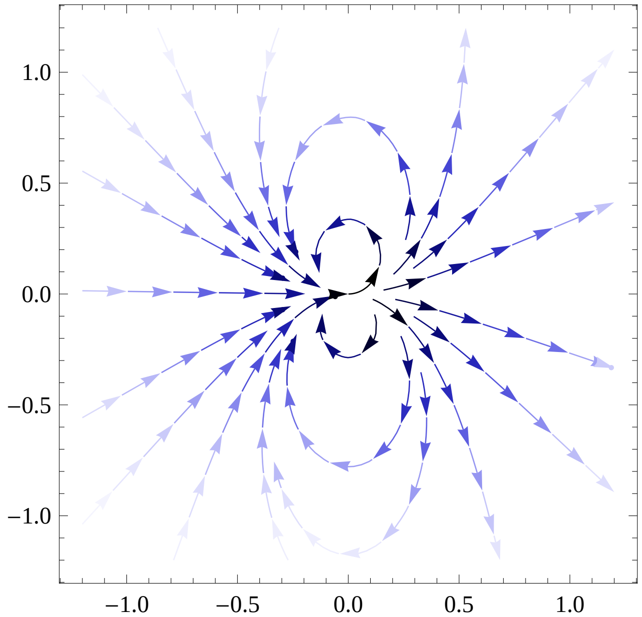
- different potentials
- double-file diffusion



- driven systems

Extension to 2D (in progress)





Summary

ρ_0, σ; $S(k)$ ⇒ **L-MCT + m-AP** ⇒ $\check{C}(k,t) = \frac{N}{L^2}\langle\check{\psi}\check{\psi}\rangle$

$\langle R(\xi,t)R(\xi',t)\rangle$

- no FDT-violation
- 4-point correlations: $\langle RR\rangle$, χ_4^S
- MSD:

$$\left\langle R^2 \right\rangle = \frac{2S}{\rho_0}\sqrt{\frac{D_C t}{\pi}} - \frac{\sqrt{2}}{3\pi}\rho_0^{-2}$$

- extension to 2D (in progress)