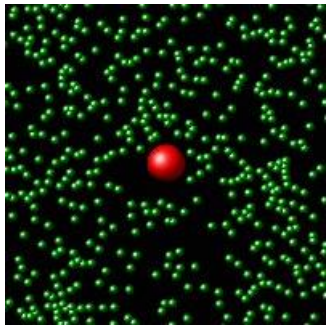
Memory Function Approach and Brownian Motion Theory



Changho Kim

Lawrence Berkeley National Laboratory

Outline

1. Quick review on Brownian motion
2. Generalized Langevin equation
3. Subtle issues on memory function approach
4. Microscopic theory of finite-mass Brownian motion
5. Brownian motion in a confined Rayleigh gas

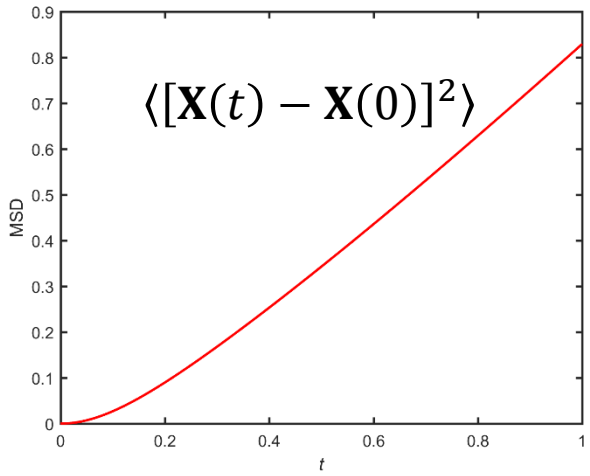
- Appendix A: Algebraic decay of VACF and vortex formation
- Appendix B: Uncertainty quantification for MD (or particle-based) simulations

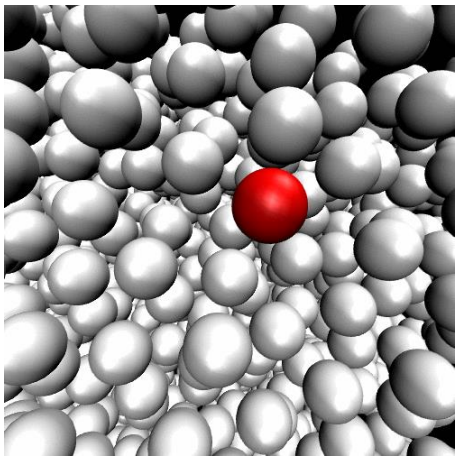
Part 1.
Quick Review on Brownian Motion

- MSD / VACF / FACF
- Basic relations
- Einstein model
- Langevin model

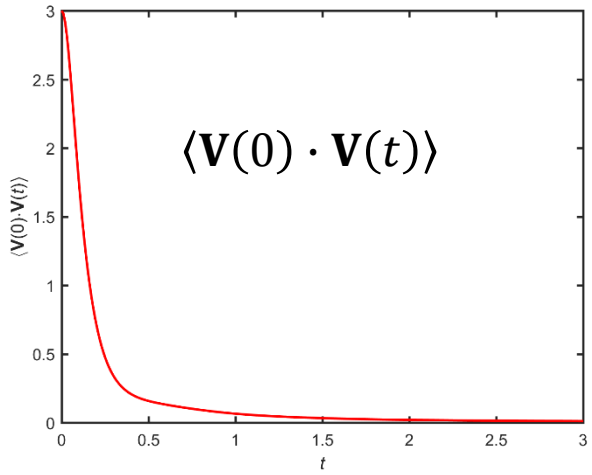
MSD, VACF, FACF

Mean-squared displacement

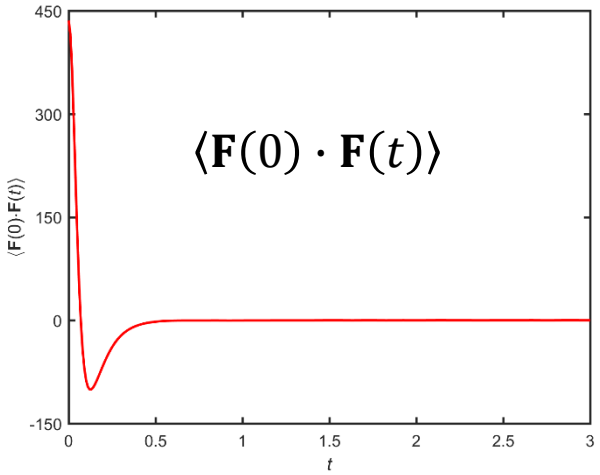




Velocity autocorrelation function



Force autocorrelation function



Basic Relations

Derivatives of VACF

$$C(t) = \langle \mathbf{V}(0) \cdot \mathbf{V}(t) \rangle$$

$$\dot{C}(t) = \frac{1}{M} \langle \mathbf{V}(0) \cdot \mathbf{F}(t) \rangle$$

$$\ddot{C}(t) = -\frac{1}{M^2} \langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle$$

$$\langle A(0)B(t) \rangle = \langle A(-t)B(0) \rangle$$

$$\langle A(0)\dot{B}(t) \rangle = -\langle \dot{A}(0)B(t) \rangle$$

MSD and VACF

$$\frac{d}{dt} \langle [\mathbf{X}(t) - \mathbf{X}(0)]^2 \rangle = 2 \int_0^t C(t')\, dt'$$

$$D = \frac{1}{d} \int_0^\infty C(t')\, dt'$$

Equipartition theorem

$$C(0) = \langle \mathbf{V} \cdot \mathbf{V} \rangle = \frac{dk_B T}{M}$$

❖ $\dot{C}(0) = \frac{1}{M} \langle \mathbf{V} \cdot \mathbf{F} \rangle = 0$

Einstein Model (1905) and MSD

Diffusion equation

$$\frac{d}{dt}\rho(\mathbf{x},t) = D\nabla^2\rho(\mathbf{x},t)$$

$$\rho(\mathbf{x},0) = \delta(\mathbf{x})$$

$$\langle[\mathbf{X}(t) - \mathbf{X}(0)]^2\rangle = 2dDt$$

Diffusion coefficient

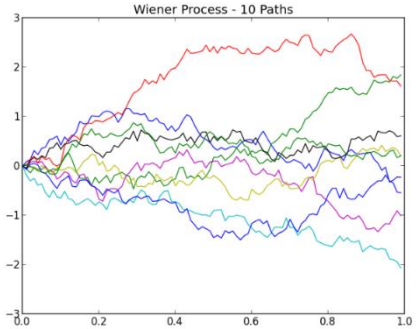
$$D = \lim_{t\to\infty}\frac{\langle[\mathbf{X}(t) - \mathbf{X}(0)]^2\rangle}{2dt}$$

Stokes-Einstein relation

$$D = \frac{k_\mathrm{B}T}{\gamma} = \frac{k_\mathrm{B}T}{6\pi\eta R}$$

$$\mathbf{X}(t) = \sqrt{2D}\mathbf{W}(t)$$

$\mathbf{W}(t)$: Wiener process
(continuous but non-differentiable)
Velocity is not well-defined!



github.com/matthewfieger

Langevin Model (1908) and VACF

$$M\dot{\mathbf{V}}(t) = -\gamma \mathbf{V}(t) + \sqrt{2k_{\mathrm{B}}T\gamma}\,\dot{\mathbf{W}}(t)$$

Exponential decay of VACF

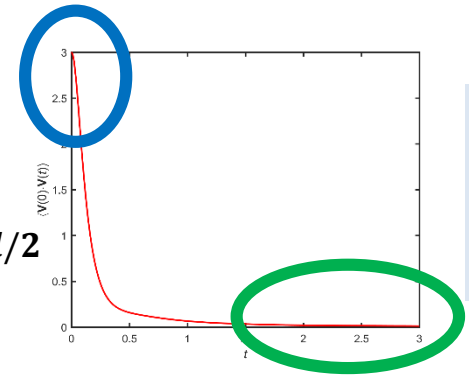
$$C(t) = \frac{dk_{\mathrm{B}}T}{M} e^{-\frac{\gamma}{M}t}$$

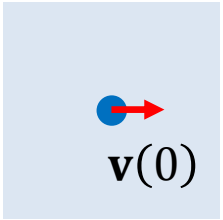
- γ = friction coefficient
- **Fluctuation-dissipation relation**
- $D = \frac{1}{d}\int_0^\infty C(t)dt = \frac{k_{\mathrm{B}}T}{\gamma}$

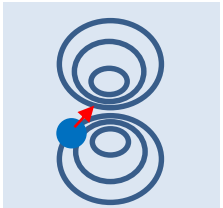
Deviations

- **At short time**: zero slope at $t = 0$
  - ➢ **microscopic** origin
- **At long time**: **algebraic decay** $t^{-d/2}$

  (Alder and Wainwright, 1970)
  - ➢ **hydrodynamic** origin







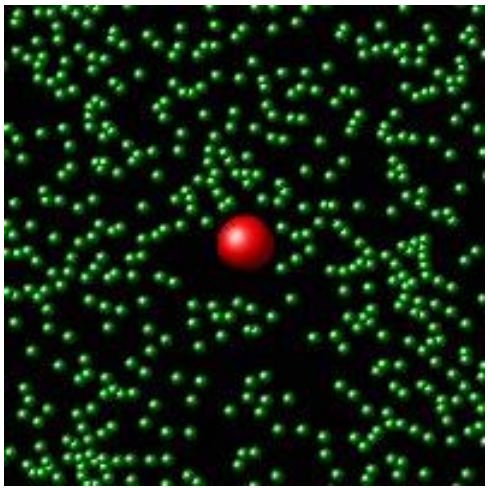
Part 2.
Generalized Langevin Equation

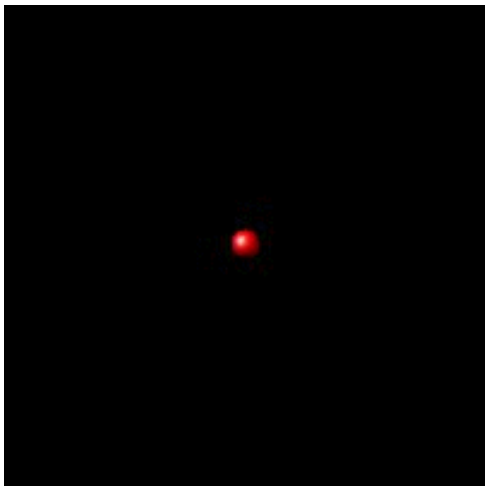
- Heuristic explanation of Langevin equation from GLE
- MZ formalism
- Derivation of FDT
- Volterra equation
- MD observations: MF, VACF, FACF

From Microscopic To Mesoscopic

$$\frac{1}{2}m\langle \mathbf{v}^2 \rangle = \frac{1}{2}M\langle \mathbf{V}^2 \rangle \longrightarrow$$

On the time scale of Brownian particle $t_{\mathrm{Br}} = \sqrt{\frac{M}{m}}t$





$$M\dot{\mathbf{V}}(t) = -\sum_i \nabla U\big(\mathbf{X}(t) - \mathbf{x}_i(t)\big)$$

?

$M \gg m$

$$M\dot{\mathbf{V}}(t) = -\gamma \mathbf{V}(t) + \sqrt{2k_B T\gamma}\,\dot{\mathbf{W}}_t$$

Langevin Equation

MZ formalism

$$M\dot{\mathbf{V}}(t) = -\int_0^t K(t')\mathbf{V}(t-t')dt' + \mathbf{F}^+(t)$$

Generalized Langevin Equation (GLE)

Generalized Langevin Equation (GLE)

$$M\dot{\mathbf{V}}(t) = -\int_0^t K(t')\mathbf{V}(t-t')ds + \mathbf{F}^+(t)$$

Memory function (MF)

Fluctuating force

cf. Langeivn equation

$$M\dot{\mathbf{V}}(t) = -\gamma\mathbf{V}(t) + \sqrt{2k_BT\gamma}\dot{\mathbf{W}}(t)$$

1. Fluctuating force $\mathbf{F}^+(t)$ behaves like a random force.

$$\langle \mathbf{V}(0)\cdot\mathbf{F}^+(t)\rangle = 0$$

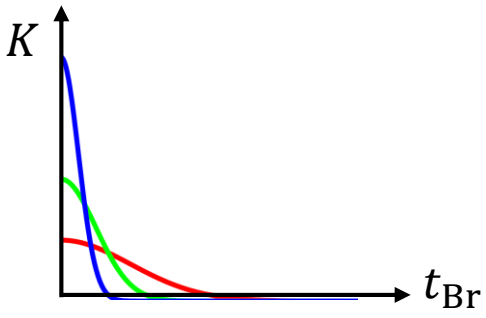
2. It has a non-zero correlation time.

$$\langle \mathbf{F}^+(0)\cdot\mathbf{F}^+(t)\rangle = dk_{\mathrm{B}}T\,K(t)$$

Fluctuation-dissipation relation

3. Langevin equation is obtained if $K(t) = 2\gamma\delta(t)$.

❖ on the Brownian time scale t_{Br} as $M \to \infty$



4. **Markovian approximation**

$$\int_0^t K(t-t')\mathbf{V}(t')dt' \approx \left[\int_0^\infty K(t')dt'\right]\mathbf{V}(t) = \gamma\mathbf{V}(t)$$

Mori-Zwanzig Formalism

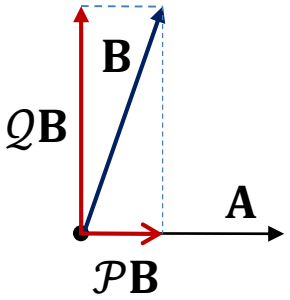
Mori, "Transport, Collective Motion, and Brownian Motion", Progr. Theoret. Phys. **33**, 423 (1965).

For a phase variable $\mathbf{A}$, consider the time evolution equation of $\mathbf{A}(t)$:

$$\frac{d}{dt}\mathbf{A}(t) = i\mathcal{L}\mathbf{A}(t).$$

By using (**Mori's**) projection operators,

$$\mathcal{P}(\star) = \langle \star\, \mathbf{A}^{\mathrm{T}} \rangle \langle \mathbf{A}\mathbf{A}^{\mathrm{T}} \rangle^{-1} \quad \text{and} \quad \mathcal{Q} = I - \mathcal{P},$$



the GLE is obtained as follows:

$$\frac{d}{dt}\mathbf{A}(t) = i\boldsymbol{\Omega}\,\mathbf{A}(t) - \int_0^t \mathbf{K}(t')\mathbf{A}(t-t')dt' + \mathbf{F}^{+}(t)$$

effective force frictional memory random force

$$i\boldsymbol{\Omega} = \langle i\mathcal{L}\mathbf{A}\mathbf{A}^{\mathrm{T}} \rangle \langle \mathbf{A}\mathbf{A}^{\mathrm{T}} \rangle^{-1} \qquad \mathbf{F}^{+}(t) = e^{\mathcal{Q}i\mathcal{L}t}\mathcal{Q}i\mathcal{L}t\mathbf{A} \qquad \mathbf{K}(t) = \langle \mathbf{F}^{+}(\mathrm{t})(\mathbf{F}^{+})^{\mathrm{T}}(0) \rangle \langle \mathbf{A}\mathbf{A}^{\mathrm{T}} \rangle^{-1}$$

Having an appealing form as well as being exact but impossible to directly be estimated

Mori vs. Zwanzig

	Mori	Zwanzig
Projection operator	**Linear projection** (simplest)	**Conditional expectation** (most accurate)
Effective force	Only linear (-)	General form (+)
Memory term	Convolution (+)	General form (-)

$$\langle \mathbf{F}(t)|\mathbf{V}(0)\rangle \approx \frac{\langle \mathbf{V}(0)\cdot\mathbf{F}(t)\rangle}{\langle \mathbf{V}\cdot\mathbf{V}\rangle}\mathbf{V}(0)$$

Conditional expectation → General function of $\mathbf{V}(0)$

Linear projection

$$\frac{d}{dt}\mathbf{y}(t) = \mathbf{f}^{\mathrm{eff}}\big(\mathbf{y}(t)\big) - \int_0^t \mathbf{K}\big(t';\mathbf{y}(t)\big)\mathbf{y}(t-t')dt' + \mathbf{f}^{+}\big(t;\mathbf{y}(t)\big) \qquad (?)$$

Derivation of FDT

Assumption 1.	$M\dot{\mathbf{V}}(t) = -\int_0^t K(t')\mathbf{V}(t-t')dt' + \mathbf{F}^+(t)$
Assumption 2.	$\langle \mathbf{V}(0) \cdot \mathbf{F}^+(t) \rangle = 0$
Conclusion:	$\langle \mathbf{F}^+(0) \cdot \mathbf{F}^+(t) \rangle = M\langle \mathbf{V} \cdot \mathbf{V} \rangle K(t)$

By multiplying $\mathbf{F}(0) = \mathbf{F}^+(0)$ to the GLE and taking average:

$$\langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle = \int_0^t K(t')\langle \mathbf{V}(0) \cdot \mathbf{F}(t-t') \rangle dt' + \langle \mathbf{F}^+(0) \cdot \mathbf{F}^+(t) \rangle$$

By multiplying $\mathbf{V}(0)$ to the GLE and taking average:

$$\langle \mathbf{V}(0) \cdot \mathbf{F}(t) \rangle = -\int_0^t K(t')\langle \mathbf{V}(0) \cdot \mathbf{V}(t-t') \rangle dt'$$

By multiplying $-M$ and differentiating w.r.t. t:

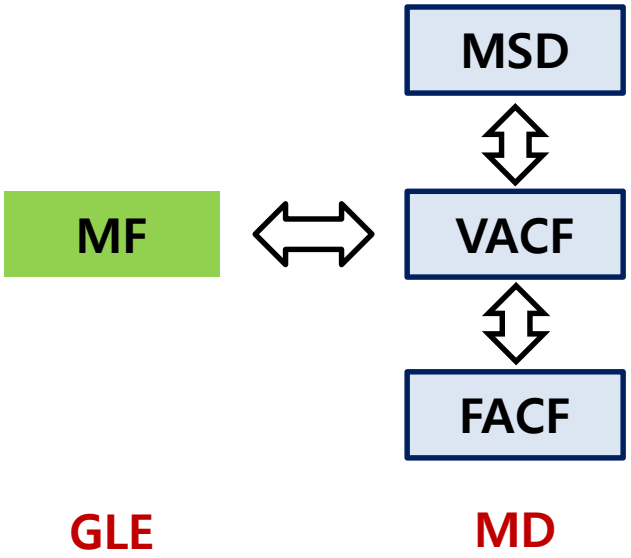
$$\langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle = M\langle \mathbf{V} \cdot \mathbf{V} \rangle K(t) + \int_0^t K(t')\langle \mathbf{V}(0) \cdot \mathbf{F}(t-t') \rangle dt'$$

Volterra Equation

$$M\dot{C}(t) = -\int_0^t K(t')C(t-t')dt'$$

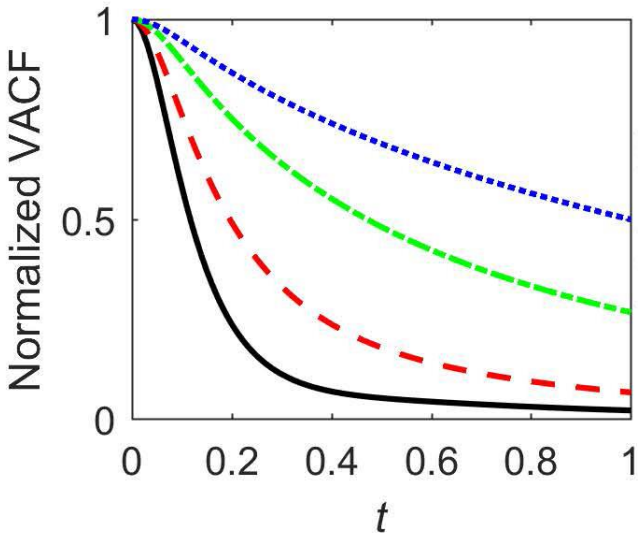
From MD calculation of VACF, MF can be estimated.

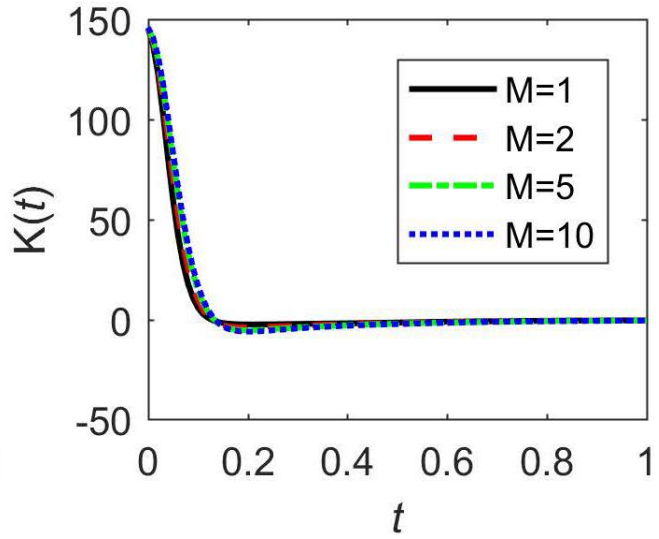
- Shin, Kim, Talkner, and Lee, "Brownian motion from molecular dynamics", *Chem. Phys.* **375**, 316 (2010)

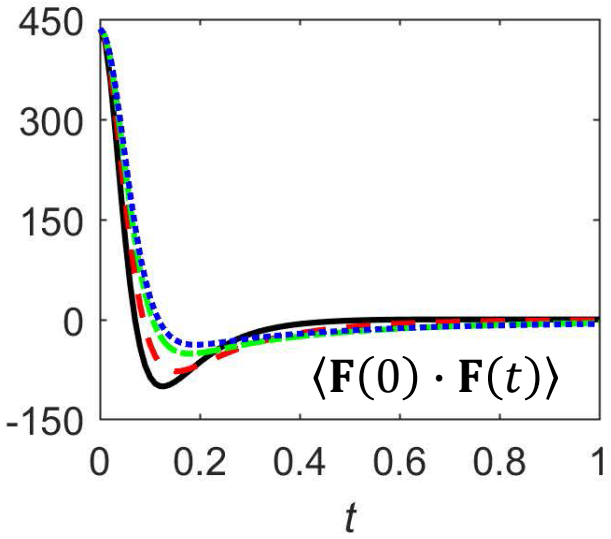


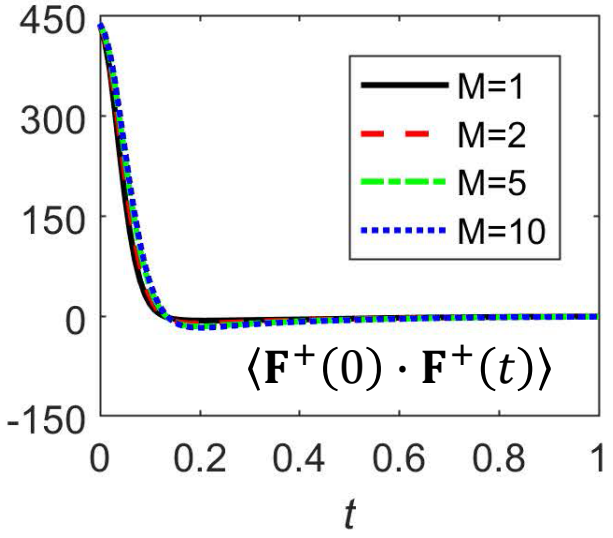
MSD, VACF, FACF, MF contain equivalent information.

Increasing M





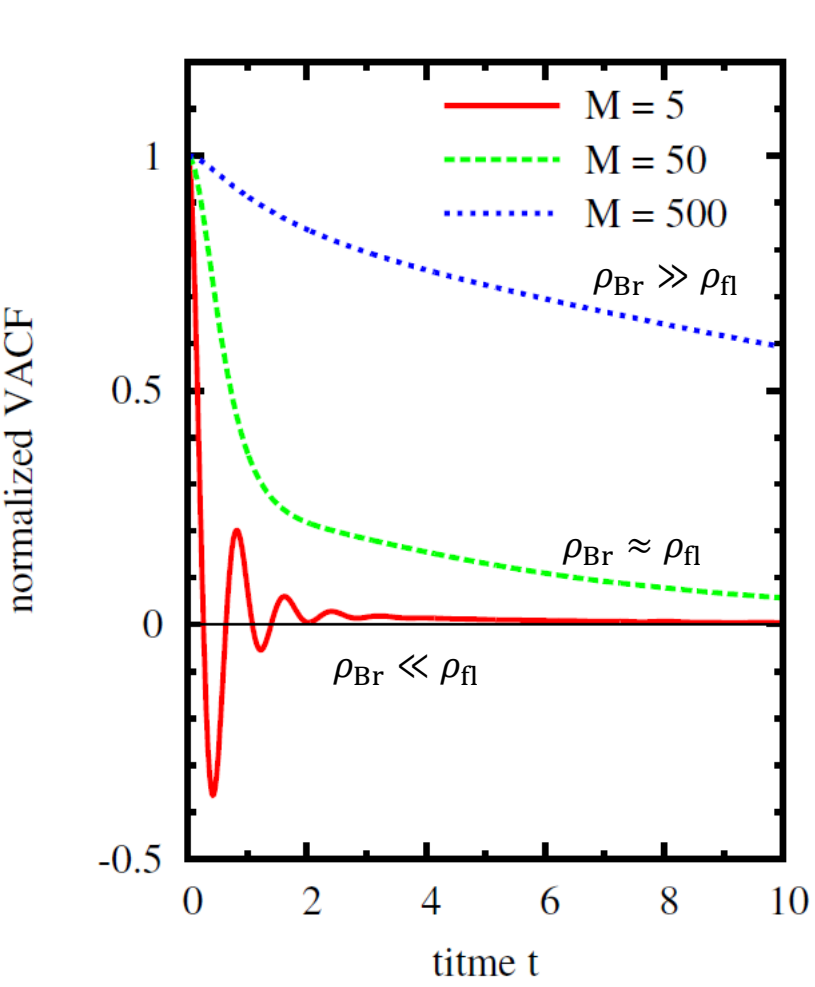


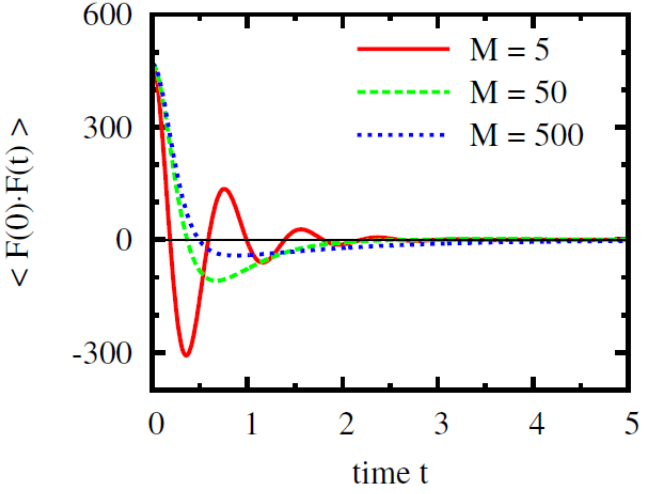


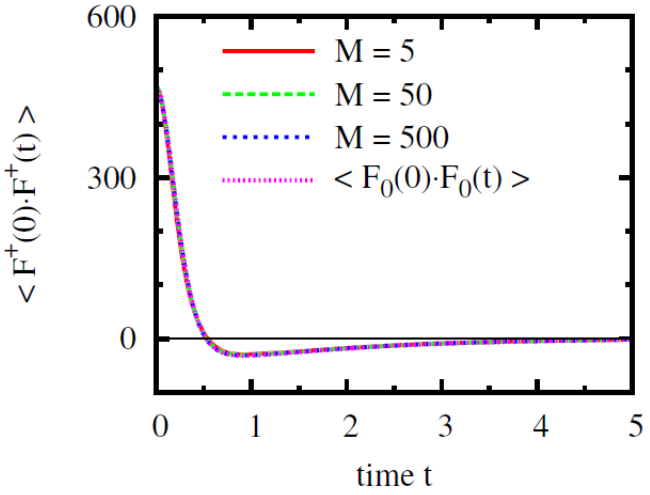
$\langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle \approx \langle \mathbf{F}^{+}(0) \cdot \mathbf{F}^{+}(t) \rangle$ (only) for small t

Large Brownian Particle in a WCA Fluid

$$\frac{\sigma_{\mathrm{Br-fl}}}{\sigma_{\mathrm{fl-fl}}} = 5,\ \frac{\varepsilon_{\mathrm{Br-fl}}}{\varepsilon_{\mathrm{fl}}} = 1,\ \rho_{\mathrm{fl}} = 0.20,\ k_{\mathrm{B}}T = 2.07$$







Part 3.
Subtle Issues in Memory Function Approach

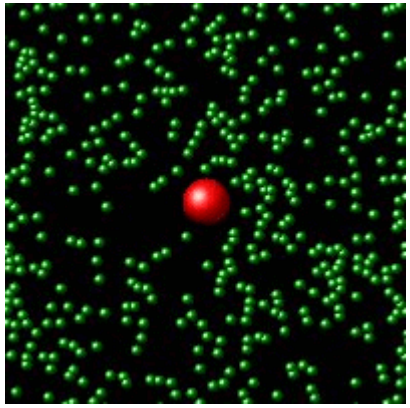
- **Markovian approximation**
  - ➢ **Infinite-mass limit, Limit MF, Kirkwood formula**
- **Long-time tail of MF**
- **Generation of trajectory from GLE**

Limit Memory Function

$$K_0(t) = \lim_{M\to\infty} K(t)$$

$$K_0(t) = \frac{1}{dk_BT}\langle \mathbf{F}_0(0)\cdot\mathbf{F}_0(t)\rangle$$

$$\langle \mathbf{F}_0(0)\cdot\mathbf{F}_0(t)\rangle = \lim_{M\to\infty}\langle \mathbf{F}(0)\cdot\mathbf{F}(t)\rangle = \lim_{M\to\infty}\langle \mathbf{F}^+(0)\cdot\mathbf{F}^+(t')\rangle$$

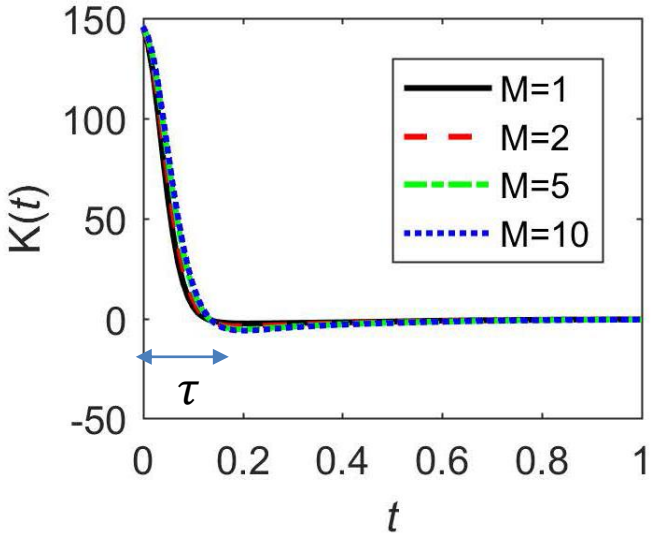


Frozen dynamics

Markovian approximation
(Near the infinite-mass limit)

$$\int_0^t K(t-t')\mathbf{V}(t')dt' \approx \left[\int_0^\infty K_0(t')dt'\right]\mathbf{V}(t) = \gamma\mathbf{V}(t)$$

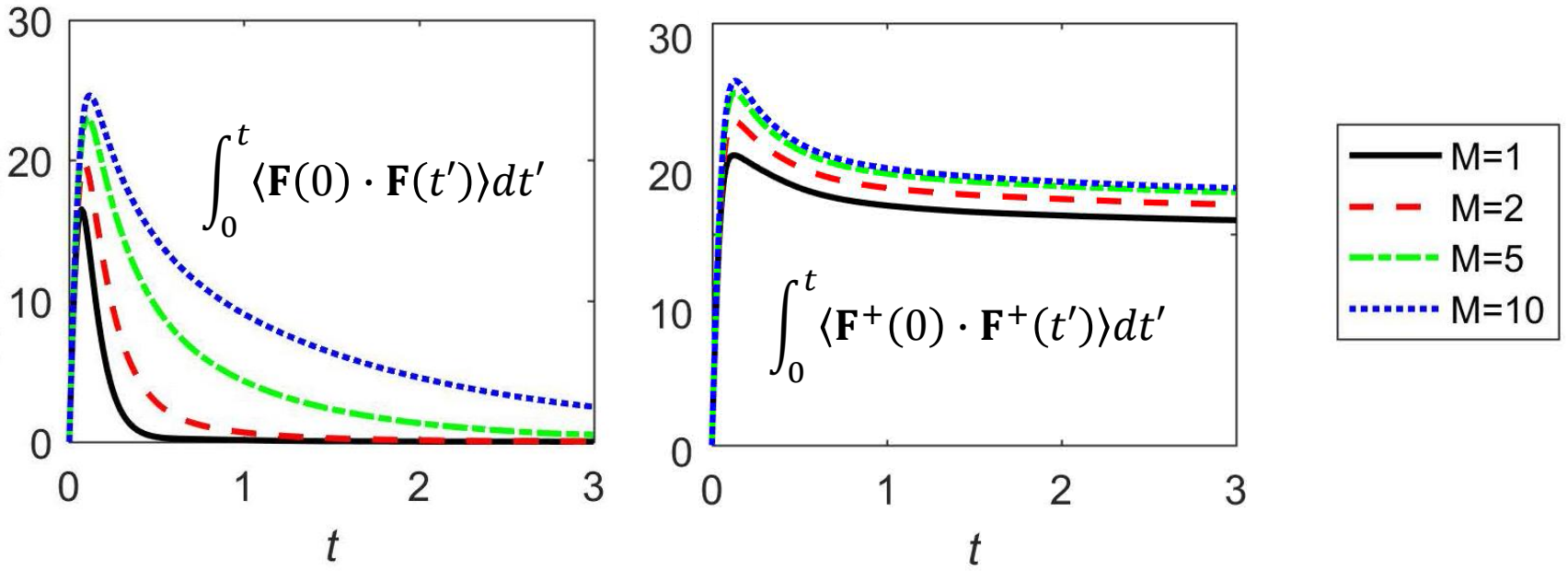
❖ Underresolving $t \lesssim \tau$



Kirkwood Formula (1946)

$$\gamma = \frac{1}{dk_BT}\int_0^\infty \lim_{M\to\infty}\langle \mathbf{F}(0)\cdot\mathbf{F}(t)\rangle\, dt$$

$$\gamma = \int_0^\infty K_0(t)dt = \frac{1}{dk_BT}\int_0^\infty \langle \mathrm{F}_0(0)\cdot \mathrm{F}_0(t)\rangle dt' \quad \text{(in the context of MF approach)}$$



$$\gamma \overset{?}{\approx} \lim_{M\to\infty}\left[\frac{1}{dk_BT}\int_0^\infty \langle \mathbf{F}(0)\cdot\mathbf{F}(t)\rangle dt\right] = -\lim_{M\to\infty}\left[\lim_{t\to\infty}\frac{M}{dk_BT}\langle \mathbf{V}(0)\cdot\mathbf{F}(t)\rangle\right] = 0$$

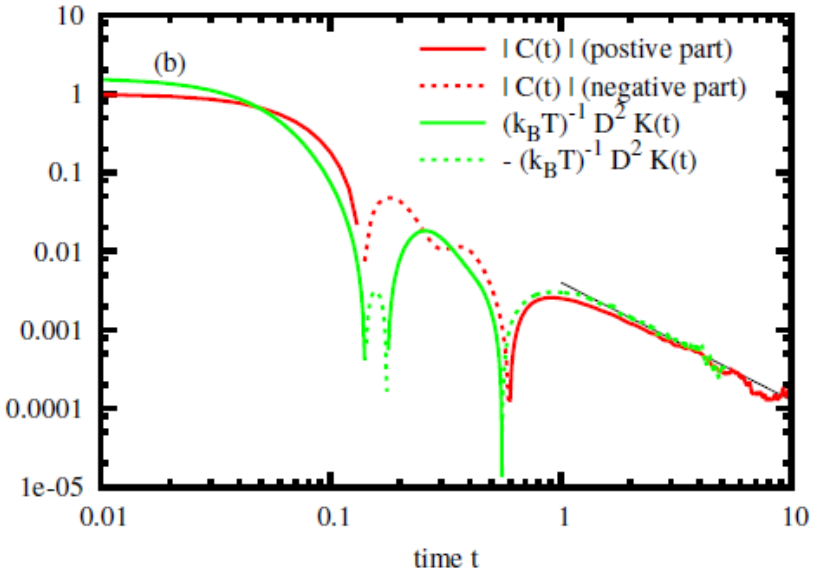
Long-Time Tail

MF does not decay rapidly to zero → Failure of Markovian approximation?

VACF ≈ (positive) $t^{-d/2}$ as $t \to \infty$

Corngold (1972) ⟺

MF ≈ (negative) $t^{-d/2}$ as $t \to \infty$



Boussinesq-Basset force

$$\mathbf{F}_{\mathrm{BB}}(t) = -6\pi\eta R\mathbf{V}(t) - \frac{2}{3}\pi R^3\rho\dot{\mathbf{V}}(t) - 6R^2\sqrt{\pi\eta\rho}\int_0^t \frac{\dot{\mathbf{V}}(t')}{\sqrt{t-t'}}dt'$$

Time scale for the onset of the algebraic decay depends on the density ratio ρ_{Br}/ρ.

Bian, Kim, Karniadakis, "111 Yeas of Brownian Motion" (tutorial review), in revision, Soft Matter.

Approximating fluctuating force by Gaussian noise

In general, $\mathbf{F}^+$ is not a Gaussian process.

GLE approach

1. Generate a Gaussian noise process $\mathbf{F}_{\mathrm{G}}^{+}(t)$ satisfying

$$\langle \mathbf{F}_{\mathrm{G}}^{+}(0) \cdot \mathbf{F}_{\mathrm{G}}^{+}(t) \rangle = d k_{\mathrm{B}} T \, K(t)$$

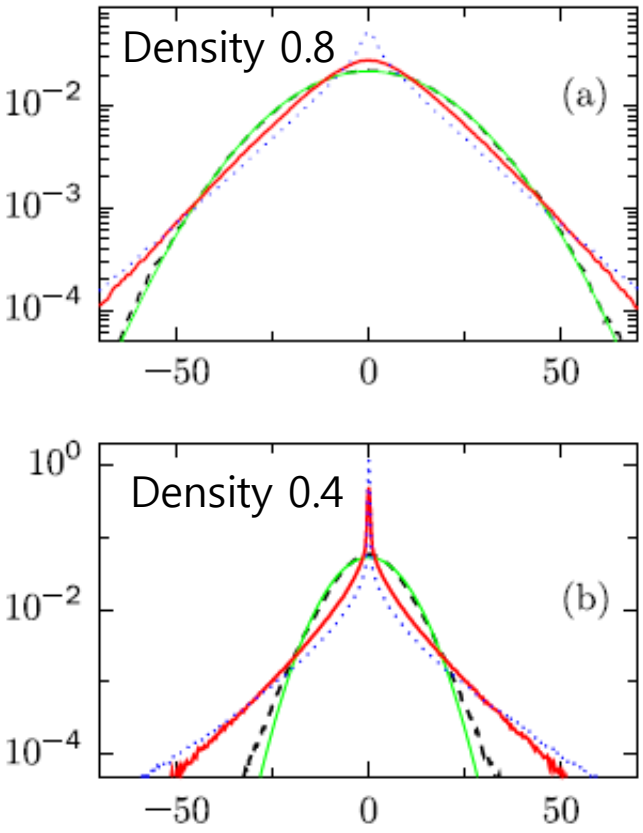
2. Calculate the GLE:

$$M\dot{\mathbf{V}}(t) = -\int_0^t K(t')\mathbf{V}(t-t')dt' + \mathbf{F}_G^+(t)$$

All resulting second moment quantities such as MSD, VACF, FACF will be the same as the original dynamics.

However, **not for higher moments.**

Distribution of F^+



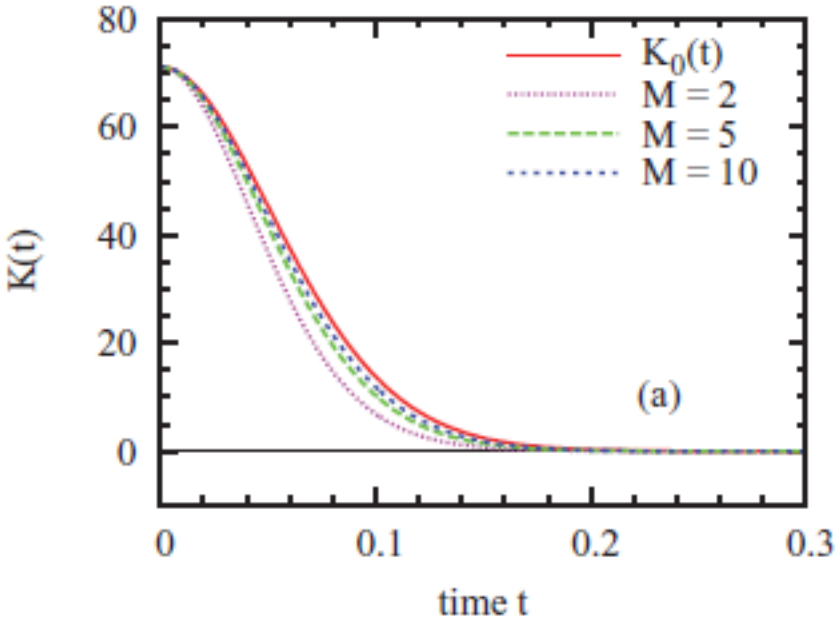
Green: Gaussian distribution
Σ/σ =1 (blue), 5 (red), 10 (black)
$M/m = 100$

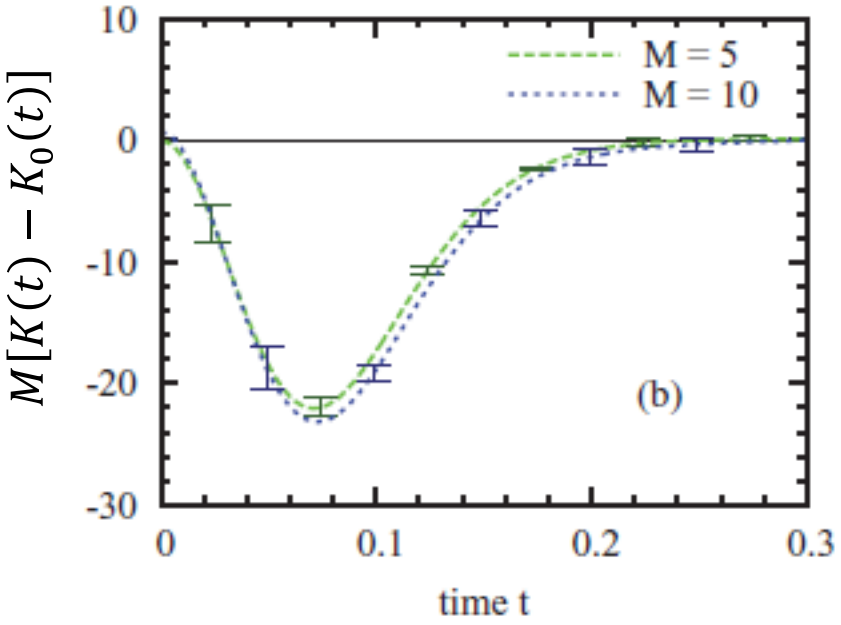
Part 4. Microscopic Theory of Finite-Mass Brownian motion

- MF expansion for finite mass M
- Approximating VACF from MF expansion
- Microscopic origin of MF expansion

MF Expansion for Finite Mass M

$$K(t) \approx K_0(t) + \frac{1}{M} K_1(t)$$



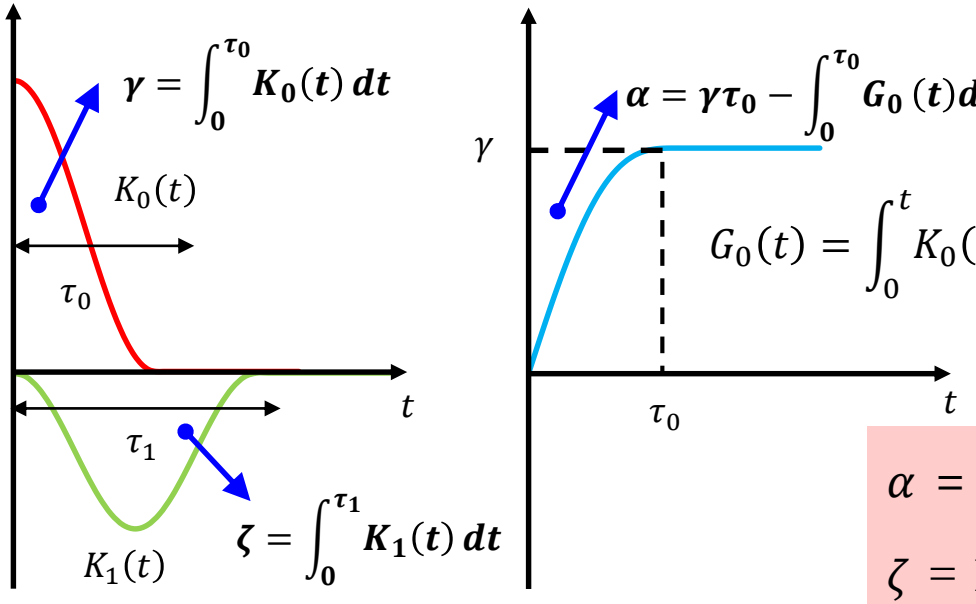


❖ Some of higher-order terms contain scaled time.

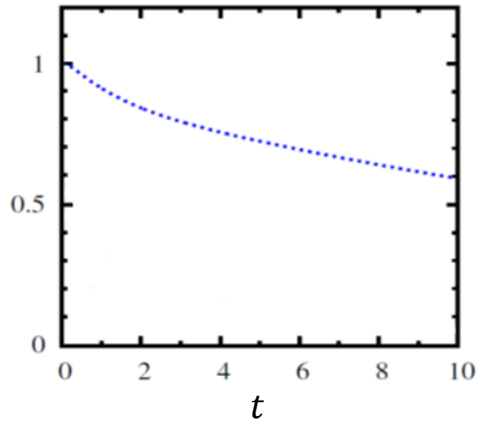
How Different is the VACF from the Langevin Case?

$$K(t) \approx K_0(t) + \frac{1}{M} K_1(t) \longrightarrow M\dot{C}(t) = -\int_0^t K(t')C(t-t')dt'$$

$$K(t) = \gamma\delta(t) \longrightarrow C(t) = \frac{dk_B T}{M} e^{-\frac{\gamma}{M}t}$$



Normalized VACF



α = Effect of microscopic structure of $K_0(t)$

ζ = Effect of finite-mass correction

Approximating VACF from MF

For short time $t \lesssim \tau_0$: $C(t) \approx \frac{dk_BT}{M} \exp\left[-\frac{1}{M}\int_0^t dt' \int_0^{t'} dt'' \, K(t'')\right]$

Derivation: $M\dot{C}(t) \approx -\int_0^t K(t')dt' \; C(t)$

For long time $t \gtrsim \tau_0$: $C(t) \approx \frac{dk_BT}{M}\left(1+\frac{\alpha}{M}\right) \exp\left[-\frac{\gamma}{M}\left(1+\frac{\alpha+\zeta/\gamma}{M}\right)t\right]$

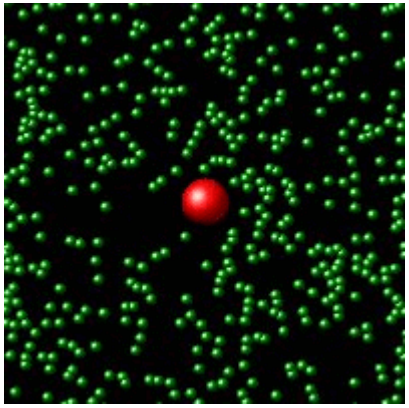
Derivation: use the Laplace transform

$$M\left[s\tilde{C}(s) - C(0)\right] = -\tilde{C}(s)\tilde{K}(s)$$

$$\tilde{C}(s) = \frac{k_BT}{Ms+\tilde{K}(s)} \approx \tilde{C}_0(s)\sum_{n=0}^{\infty}\left(-\frac{\tilde{K}_1(s)\tilde{C}_0(s)}{k_BTM}\right)^n \qquad \text{Reference: } \tilde{C}_0(s) = \frac{k_BT}{Ms+\tilde{K}_0(s)}$$

Kim and Karniadakis, "Time correlation functions of Brownian motion and evaluation of friction coefficient in the near-Brownian-limit regime", *Multiscale Model. Sim.* **12**, 225 (2014)

"Taylor Expansion" in MD

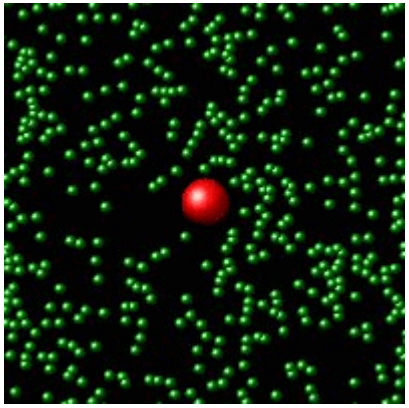


Full dynamics

Finite mass M

$\{\mathbf{X}(t), \mathbf{V}(t)\}$

$\mathbf{F}(t)$

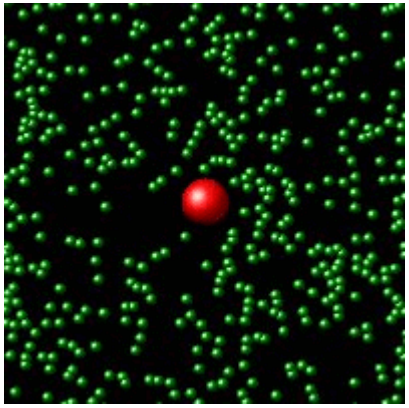


Frozen dynamics

$\mathbf{X}_0(t) = \mathbf{X}(0)$

$\mathbf{V}_0(t) = 0$

$\mathbf{F}_0(t)$



Constant-velocity dynamics

$\mathbf{X}_1(t) = \mathbf{X}(0) + t\mathbf{V}(0)$

$\mathbf{V}_1(t) = \mathbf{V}(0)$

$\mathbf{F}_1(t)$

Thermal noise

Friction force

$$\mathbf{F}(t) = \mathbf{F}_0(t) + [\mathbf{F}_1(t) - \mathbf{F}_0(t)] + [\mathbf{F}(t) - \mathbf{F}_1(t)]$$

$$= O(1) + O\left(\frac{1}{\sqrt{M}}\right) + O\left(\frac{1}{M}\right)$$

$$O(V(0)) = \frac{1}{\sqrt{M}}$$

Microscopic Origin of MF Expansion

❖ $\mathbf{X}_1(t) - \mathbf{X}_0(t) = t\mathbf{V}(0)$

$$\mathbf{F}_1(t) - \mathbf{F}_0(t) \approx \mathbf{A}_1(t)\mathbf{V}(0) + \mathbf{A}_2(t)\mathbf{V}^2(0) + \mathbf{A}_3(t)\mathbf{V}^3(0)$$

❖ $\mathbf{X}(t) - \mathbf{X}_1(t) = \frac{1}{M}\int_0^t dt' \int_0^{t'} dt'' \, \mathbf{F}(t'')$

$$\mathbf{F}(t) - \mathbf{F}_1(t) \approx \frac{1}{M}[\mathbf{B}_1(t) + \mathbf{B}_2(t)\mathbf{V}(0)]$$

$$K(t) \approx K_0(t) + \frac{1}{M}K_1(t)$$

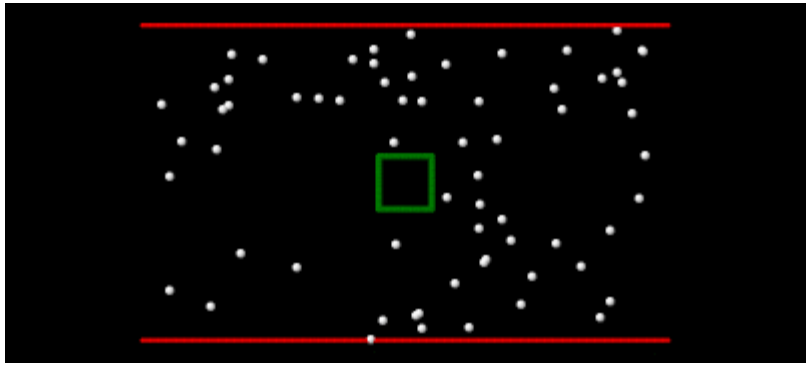
$$K_1(t) = \dot{a}_1 * a_1 + \bar{a}_2 + \frac{\beta}{d}\bar{b}_1$$

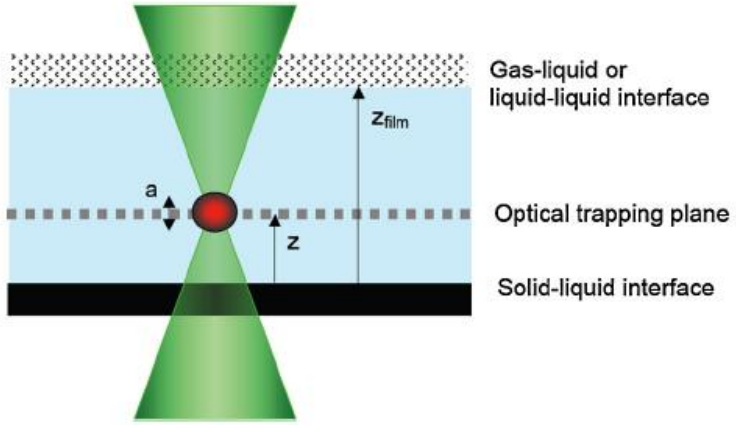
$$\langle \mathbf{A}_1(t) \rangle_\Theta = a_1(t)\mathbf{I} \qquad \langle \mathbf{F}(0)\mathbf{A}_2(t) \rangle_\Theta = \bar{a}_2(t)\mathbf{I}$$

$$\langle \mathbf{F}(0) \cdot \mathbf{B}_1(t) \rangle_\Theta = \bar{b}_1(t)$$

❖ $\langle \quad \rangle_\Theta$ denotes the conditional average given $\mathbf{V}(0)$.

Part 5. Brownian motion in a confined Rayleigh gas model



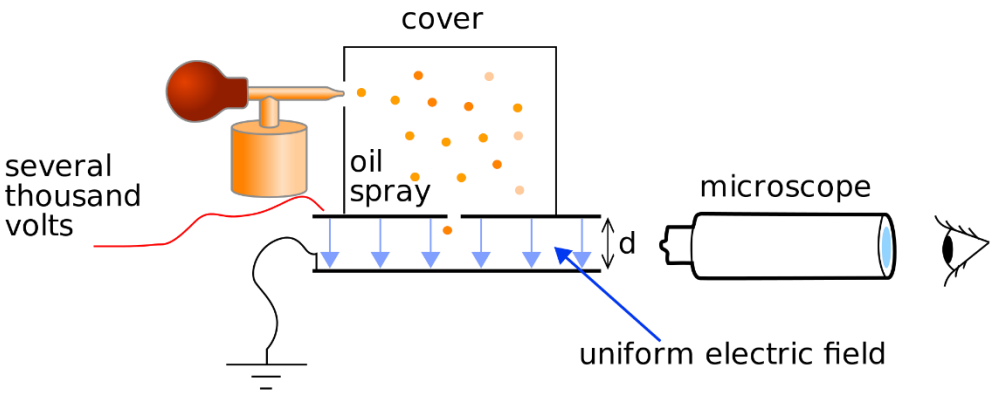


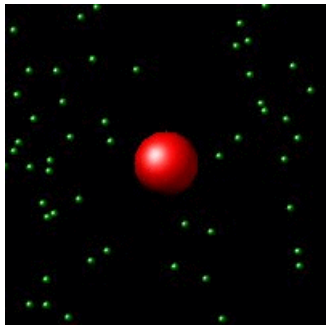
Phys. Rev. Lett. **103**, 248303 (2009)

Rayleigh Gas Model

Brownian motion in an ideal gas

- No hydrodynamic interaction from the surrounding fluid
- Friction is proportional to R^{d-1}



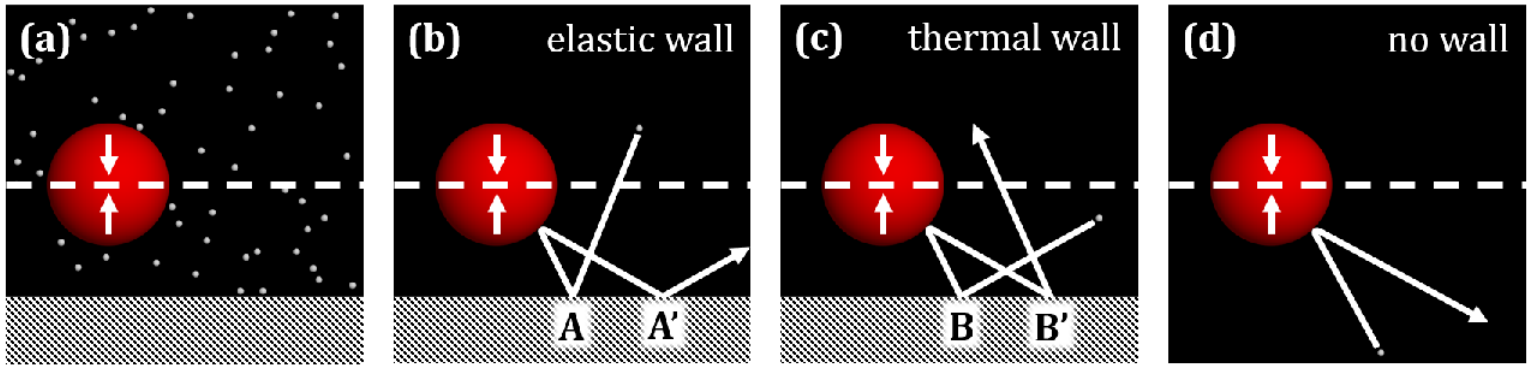


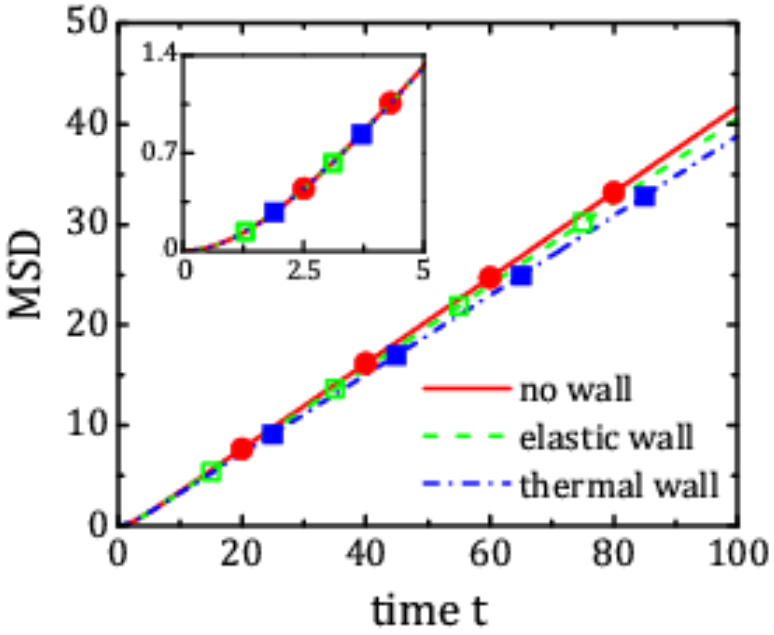
Oil drop experiment (en.wikipedia.org)

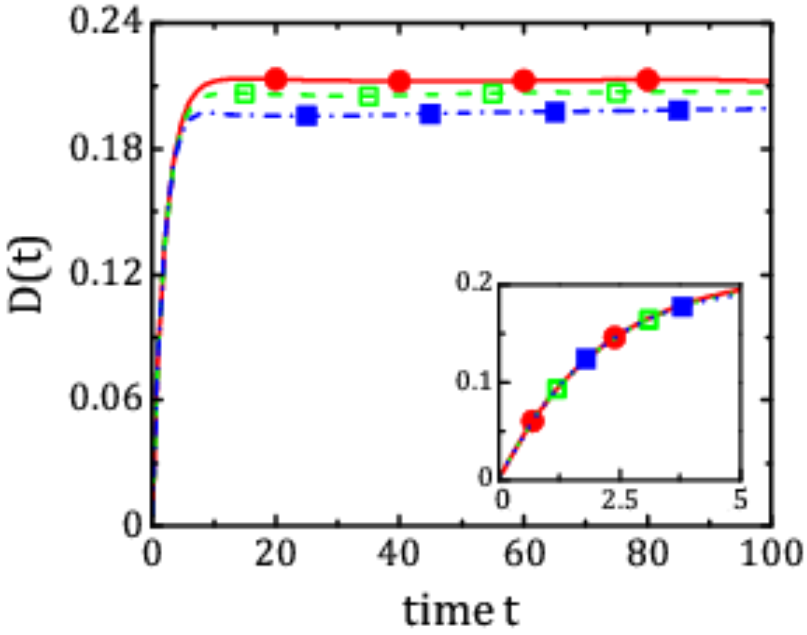
- In the frozen dynamics, the dynamics of each gas particle becomes decoupled.
- Analytic results are available.

C. Kim and G. Karniadakis, "Microscopic theory of Brownian motion revisited: The Rayleigh model", *Phys. Rev. E* **87**, 032129 (2013)

Reduced Diffusivity







Let's investigate $\gamma(t) = \int_0^t K_x(t')dt'$.

Brownian particle under a harmonic potential

GLE: Apply the Mori projection technique to $(X_d, V_1, \cdots, V_d)$

$$\dot{X}_i(t) = V_i(t),$$

$$M\dot{V}_i(t) = -\int_0^t K_i(t-s)V_i(s)ds + F_i^+(t), \quad i = 1, 2, \ldots, d-1,$$

$$\dot{X}_d(t) = V_d(t),$$

$$M\dot{V}_d(t) = \boxed{-kX_d(t)} - \int_0^t K_d(t-s)V_d(s)ds + F_d^+(t),$$

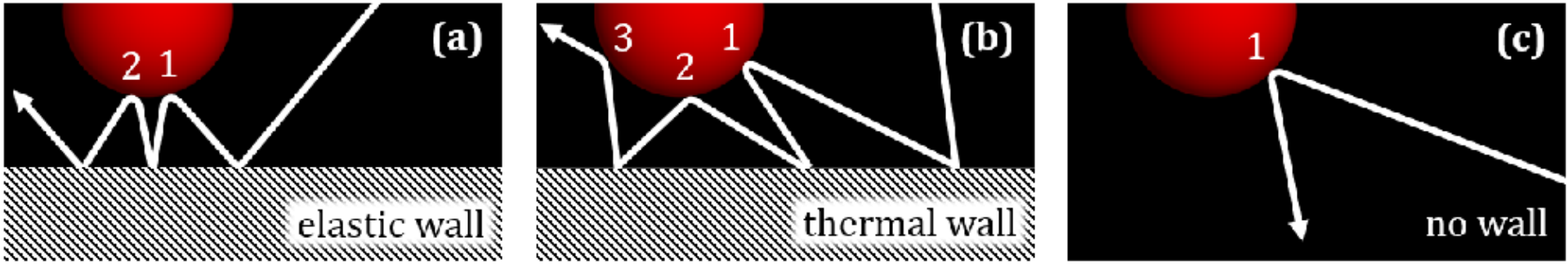
FDT: the same as the unbounded case

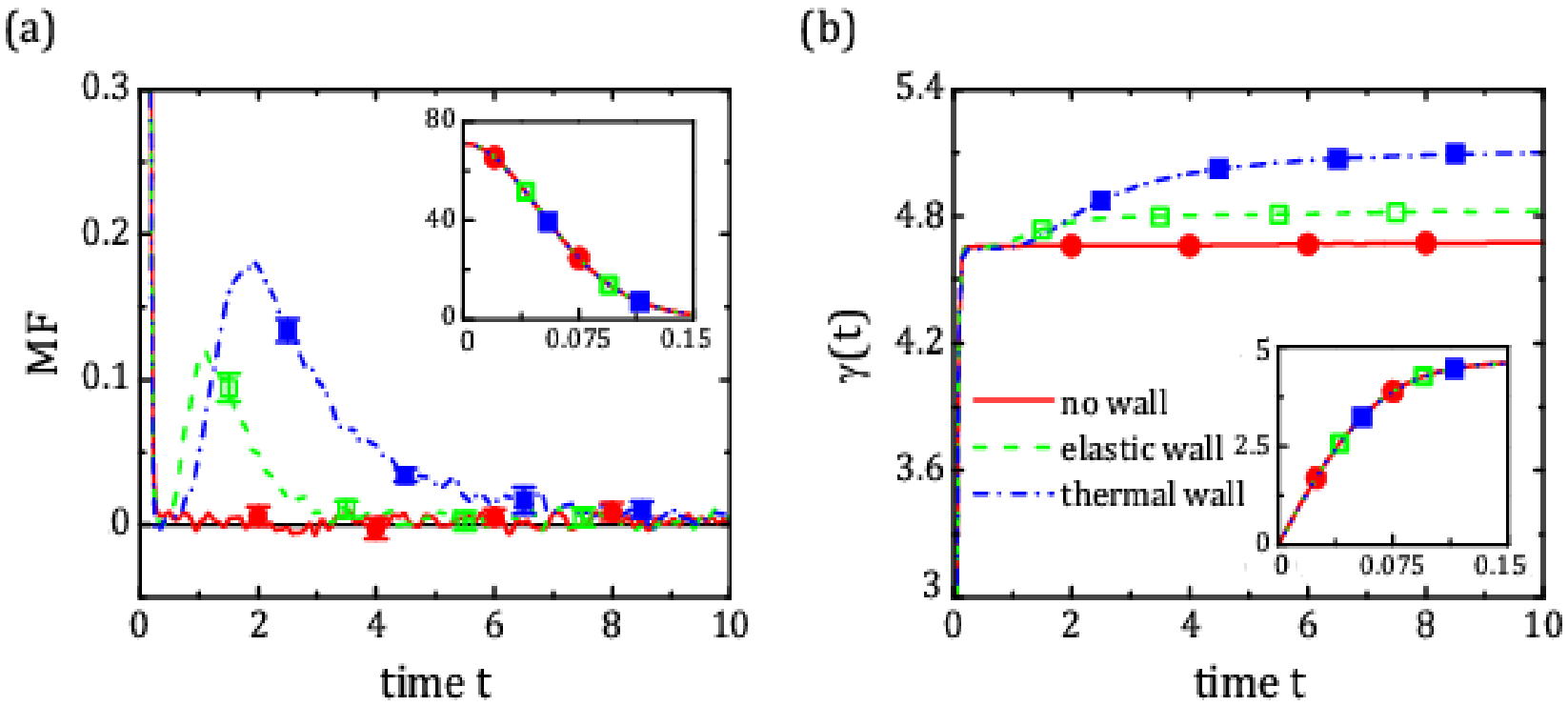
$$K_i(t) = \beta\left\langle F_i^+(0)F_i^+(t)\right\rangle, \quad i = 1, 2, \ldots, d,$$

$$\left\langle F_i^+(0)F_j^+(t)\right\rangle = 0, \quad \text{for } i \neq j.$$

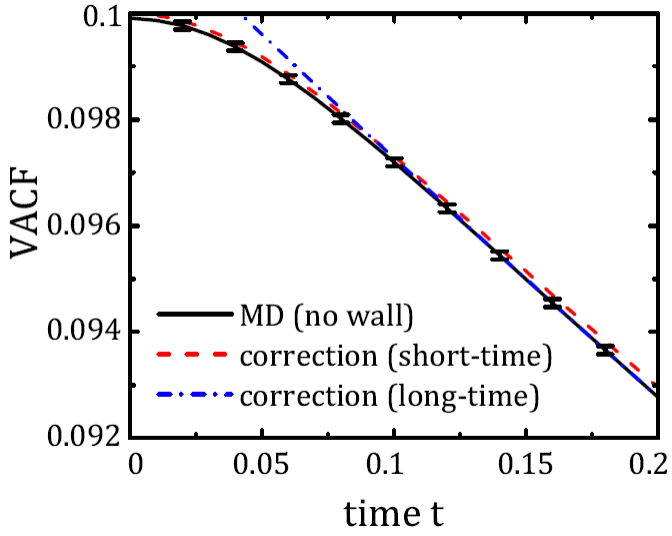
Kim and Karniadakis, "Brownian Motion of a Rayleigh Particle Confined in a Channel: A Generalized Langevin Equation Approach", *J .Stat. Phys.* **158**, 1100 (2015)

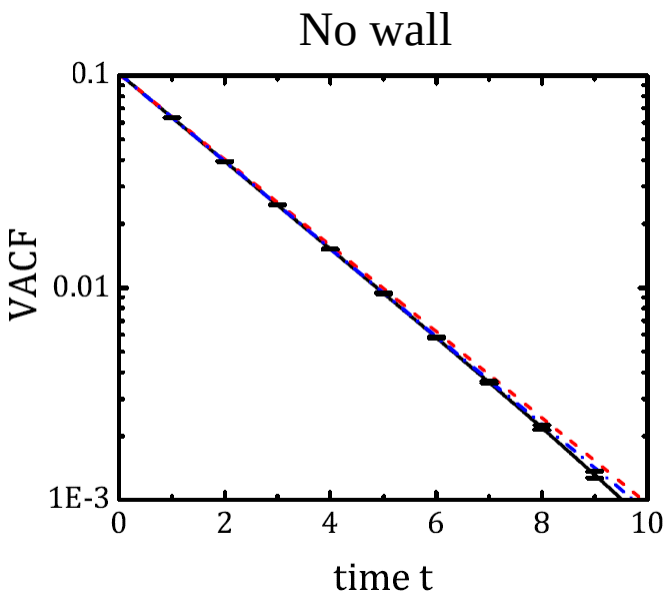
Second Peak in MF

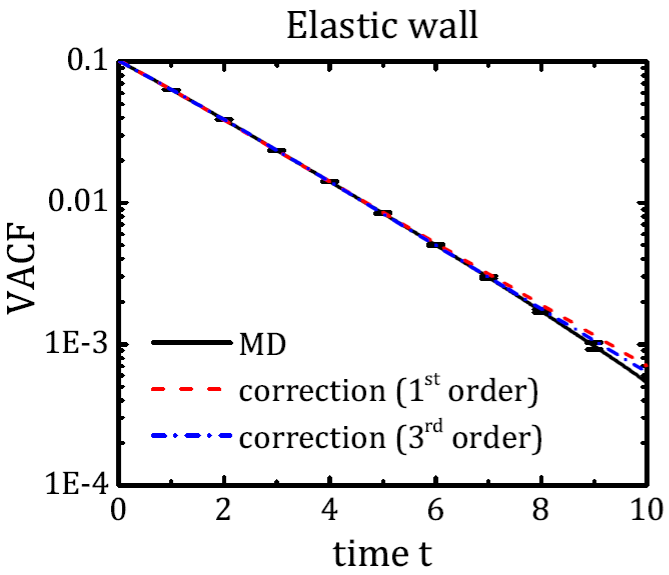


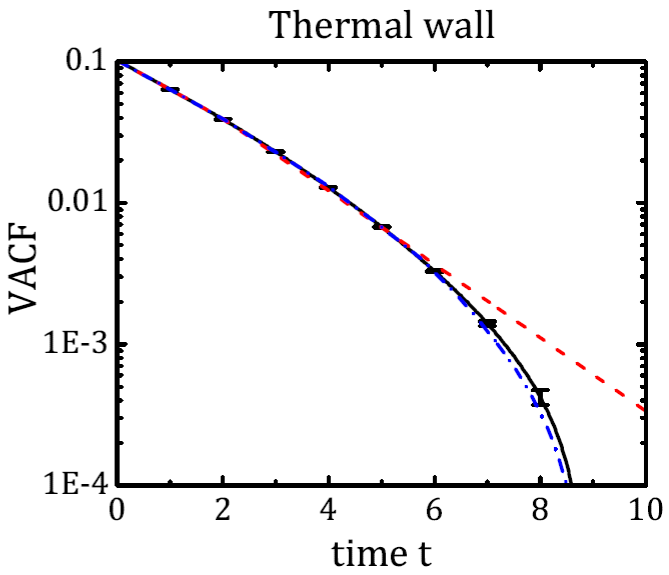


VACF


0.1
0.098
0.096
0.094
0.092
VACF
0
0.05
0.1
0.15
0.2
time t
MD (no wall)
correction (short-time)
correction (long-time)


No wall
0.1
0.01
1E-3
VACF
0
2
4
6
8
10
time t


Elastic wall
0.1
0.01
1E-3
1E-4
VACF
0
2
4
6
8
10
time t
MD
correction (1st order)
correction (3rd order)


Thermal wall
0.1
0.01
1E-3
1E-4
VACF
0
2
4
6
8
10
time t

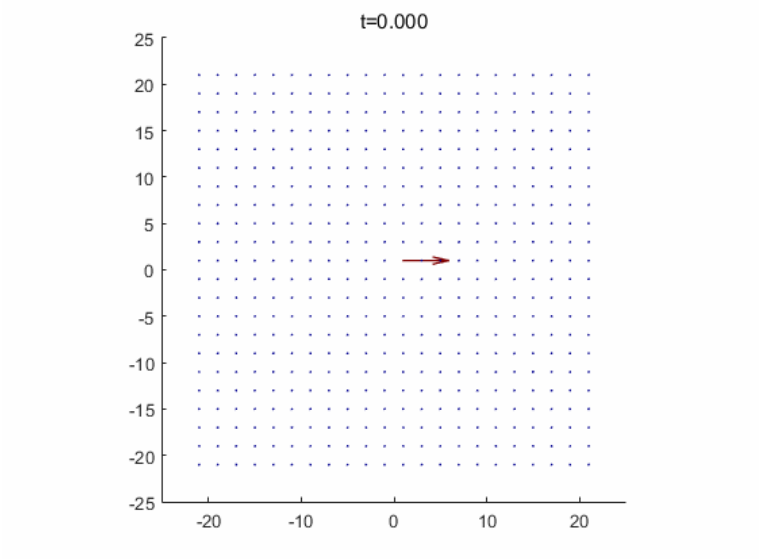
Summary

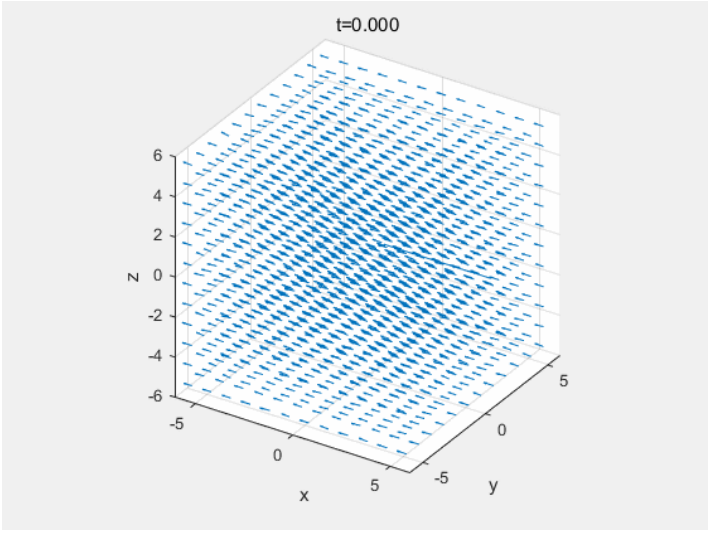
- MF (or $\langle \mathbf{F}^+(0) \cdot \mathbf{F}^+(t) \rangle$) contains equivalent information to MSD, VACF and FACF.
- MF can be calculated from VACF through the Volterra equation, and vice versa.
- Compared to VACF, MF does not drastically change as M changes.

$$K(t) \approx K_0(t) + \frac{1}{M} K_1(t)$$

- At short time, $\langle \mathbf{F}^+(0) \cdot \mathbf{F}^+(t') \rangle \approx \langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle \approx \langle \mathbf{F}_0(0) \cdot \mathbf{F}_0(t) \rangle$
- Compared to FACF, $\langle \mathbf{F}^+(0) \cdot \mathbf{F}^+(t') \rangle$ has a convergent non-zero integral.
- Markovian approximation: $\gamma \approx \int_0^\infty K(t) dt = \frac{1}{dk_B T} \int_0^\infty \langle \mathbf{F}^+(0) \cdot \mathbf{F}^+(t) \rangle dt'$
- Despite the small value, the tail of MF is important; its time integral matters.
- For both microscopic and hydrodynamic reasons, the short- and long-time behaviors of VACF is different from the algebraic decay.

Observation of Vortex Formation from Equilibrium/Non-Equilibrium MD Simulations and the Algebraic Decay of VACF





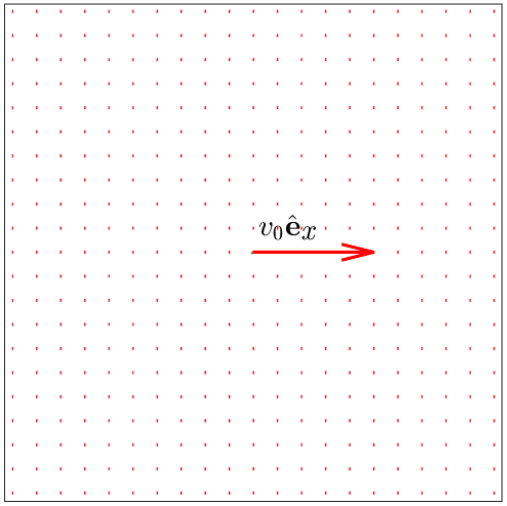
Collaboration with

Kyeonghwan Han, Prof. Eok Kyun Lee (Chemistry, KAIST)

Prof. George Karniadakis (Applied Mathematics, Brown University)

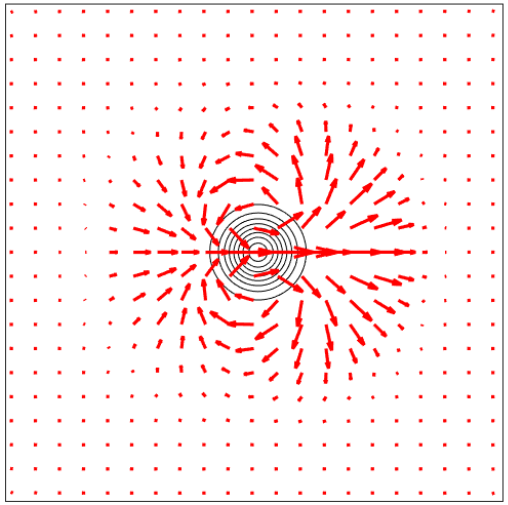
Vortex Formation

$\mathbf{u}(\mathbf{r}, 0|v_0) = v_0\hat{\boldsymbol{e}}_x\delta(\mathbf{r})$



time t

$\mathbf{u}(\mathbf{r}, t|v_0)$



From equilibrium and non-equilibrium MD simulations, we calculate

$$\mathbf{u}(\mathbf{r}, t) = \int \mathbf{u}(\mathbf{r}, t|v_0) f_0(v_0) dv_0$$

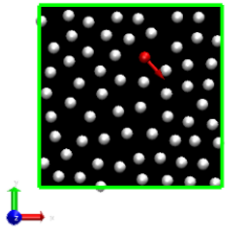
We also calculate

$\mathbf{u}_{\mathrm{tr}}(\mathbf{r}, t)$: velocity field of the tracer particle

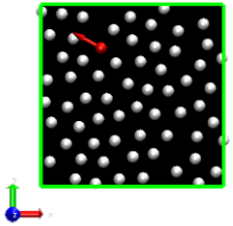
$\rho(\mathbf{r}, t)$: number density of the fluid

$\rho_{\mathrm{tr}}(\mathbf{r}, t)$: number density of the tracer particle

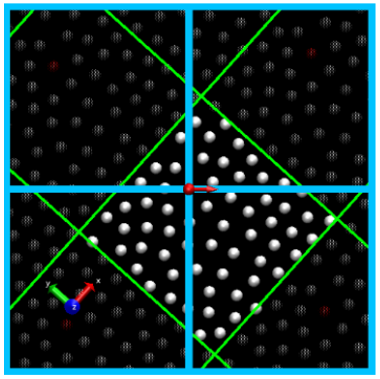
From Equilibrium MD Simulation



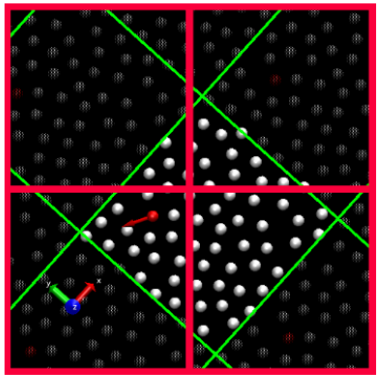
After time t

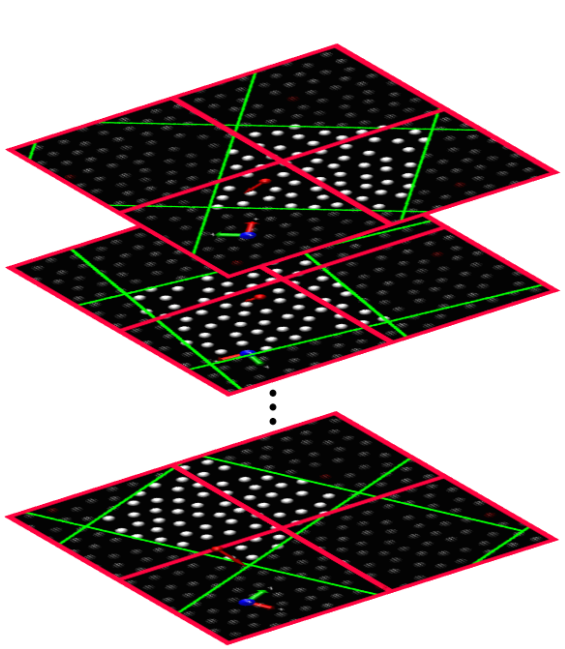


Transform **T**
(translation and rotation)



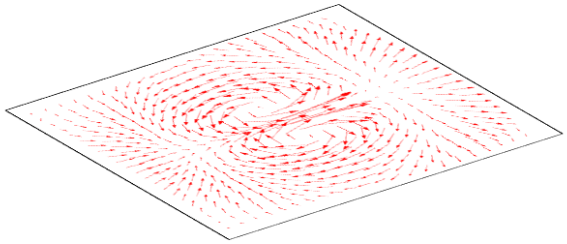
T



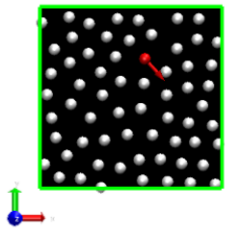


Obtained from
different samples

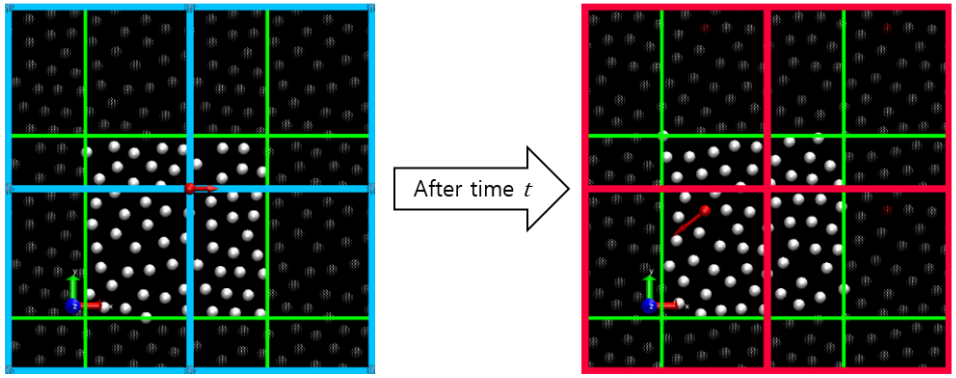
Average

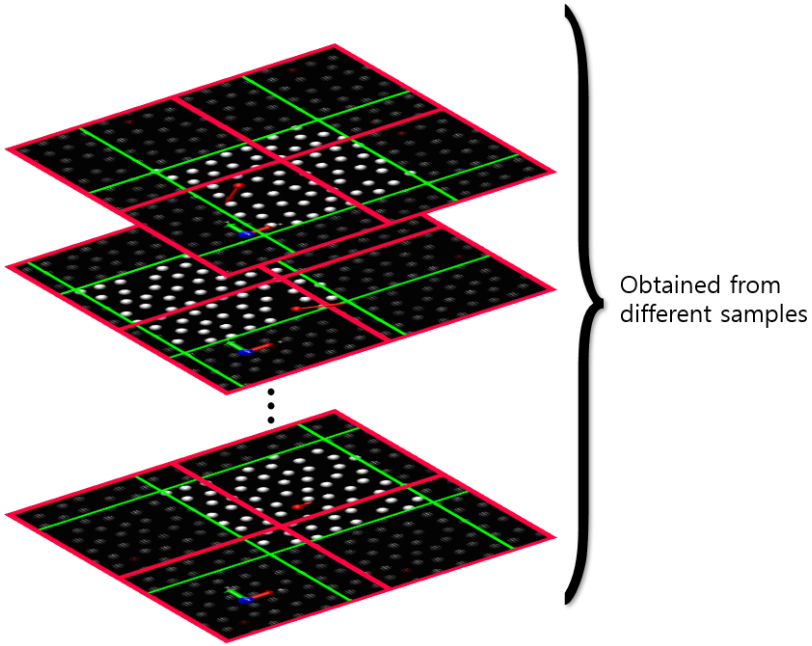


From Non-Equilibrium MD Simulation

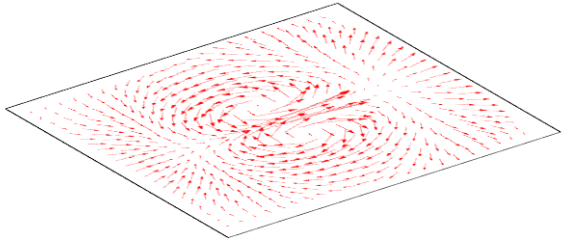


Transform **T**′ (translation) and perturb (tracer rotation)



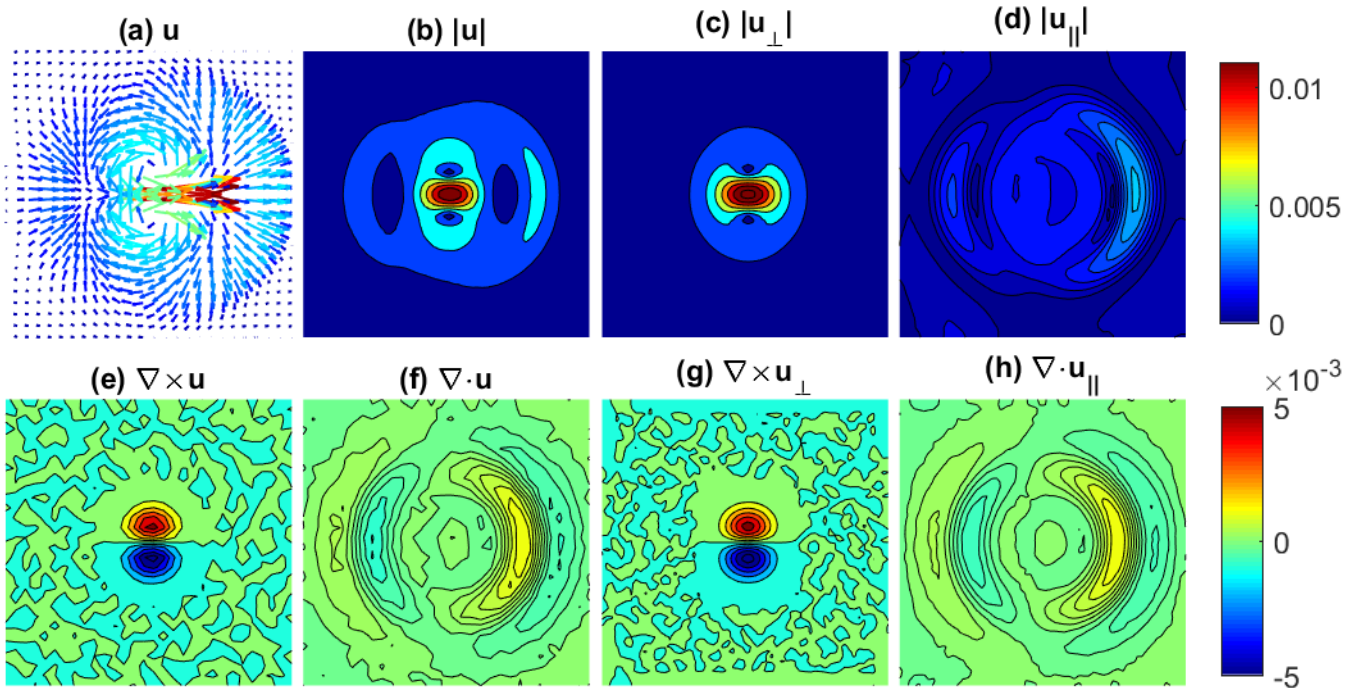


Average



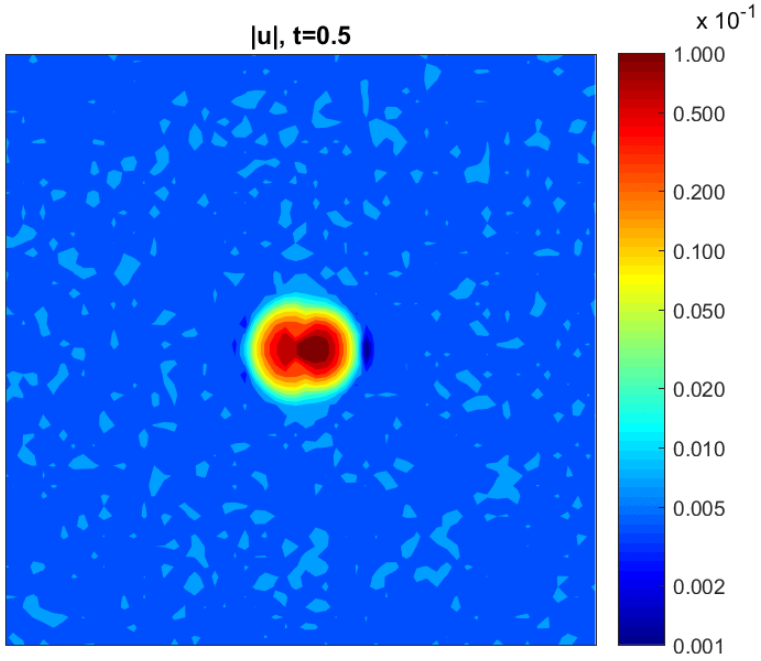
Helmholtz decomposition

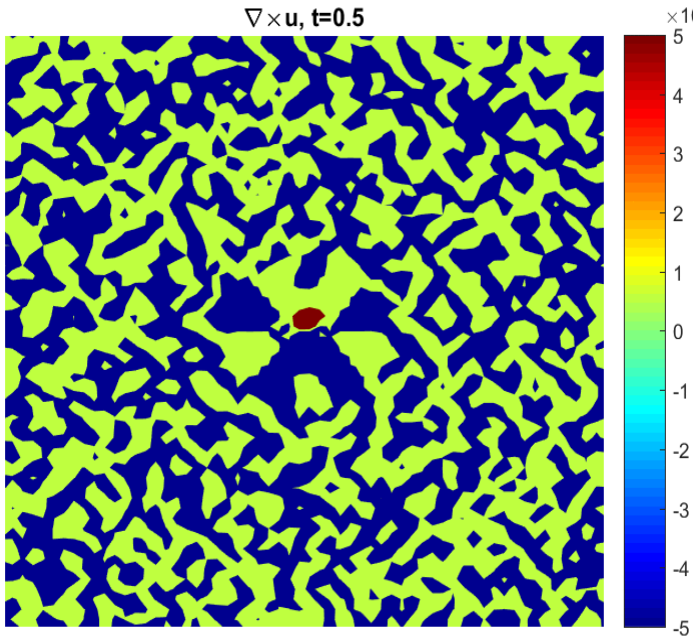
$\mathbf{u} = \mathbf{u}_{\perp}$ (vortex) + $\mathbf{u}_{\parallel}$ (acoustic wave)

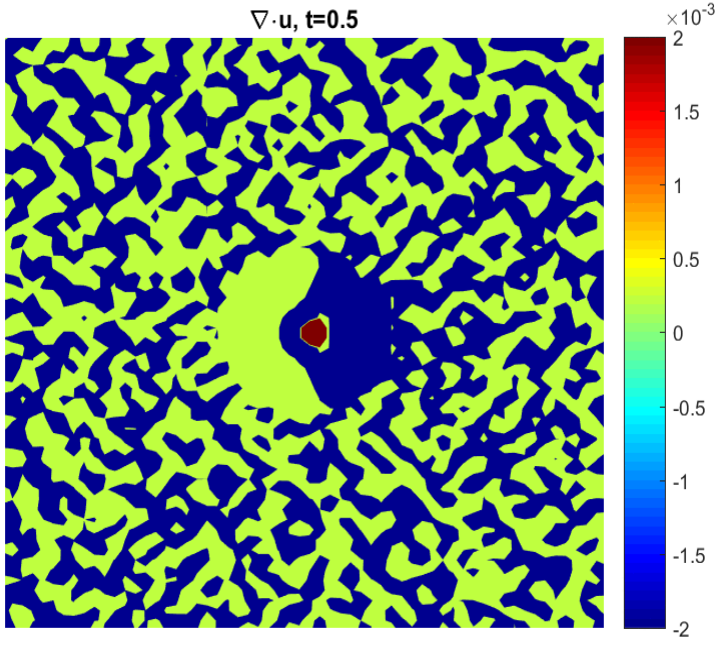


2D WCA fluid at $t = 4$

(2048 particles, density 0.6, temperature 1 in LJ units)

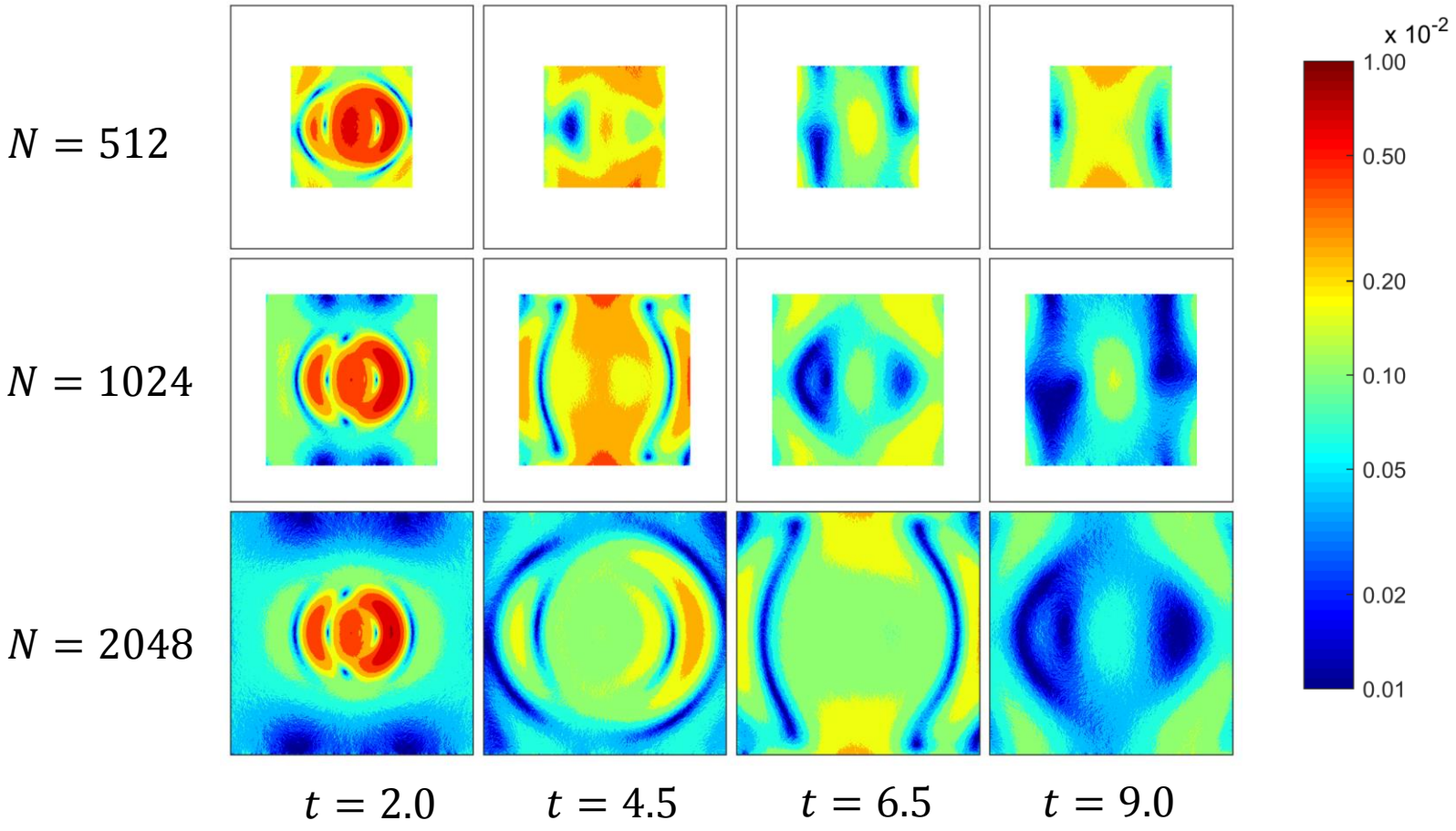

|u|, t=0.5
x 10^-1
1.000
0.500
0.200
0.100
0.050
0.020
0.010
0.005
0.002
0.001


∇×u, t=0.5
5
4
3
2
1
0
-1
-2
-3
-4
-5


∇·u, t=0.5
×10^-3
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2

Finite Size Effects

$|\mathbf{u}_{\parallel}|$



Heuristic Derivation of Algebraic Decay of VACF

$$\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle = \frac{(d-1)k_{\mathrm{B}}T}{m\rho}\frac{1}{[4\pi(D+\nu)]^{3/2}}t^{-d/2} \quad (t\to\infty)$$

$$\langle \mathbf{v}(t)|\mathbf{v}_0\rangle = \int d\mathbf{r}\,\rho_{\mathrm{tr}}(\mathbf{r},t|\mathbf{v}_0)\mathbf{u}_{\mathrm{tr}}(\mathbf{r},t|\mathbf{v}_0) \approx \int d\mathbf{r}\,P_{\mathrm{tr}}(\mathbf{r},t)\mathbf{u}_{\perp}(\mathbf{r},t|\mathbf{v}_0)$$

$$\frac{\partial P_{\mathrm{tr}}(\mathbf{r},t)}{\partial t} = D\nabla^2 P_{\mathrm{tr}}(\mathbf{r},t)$$

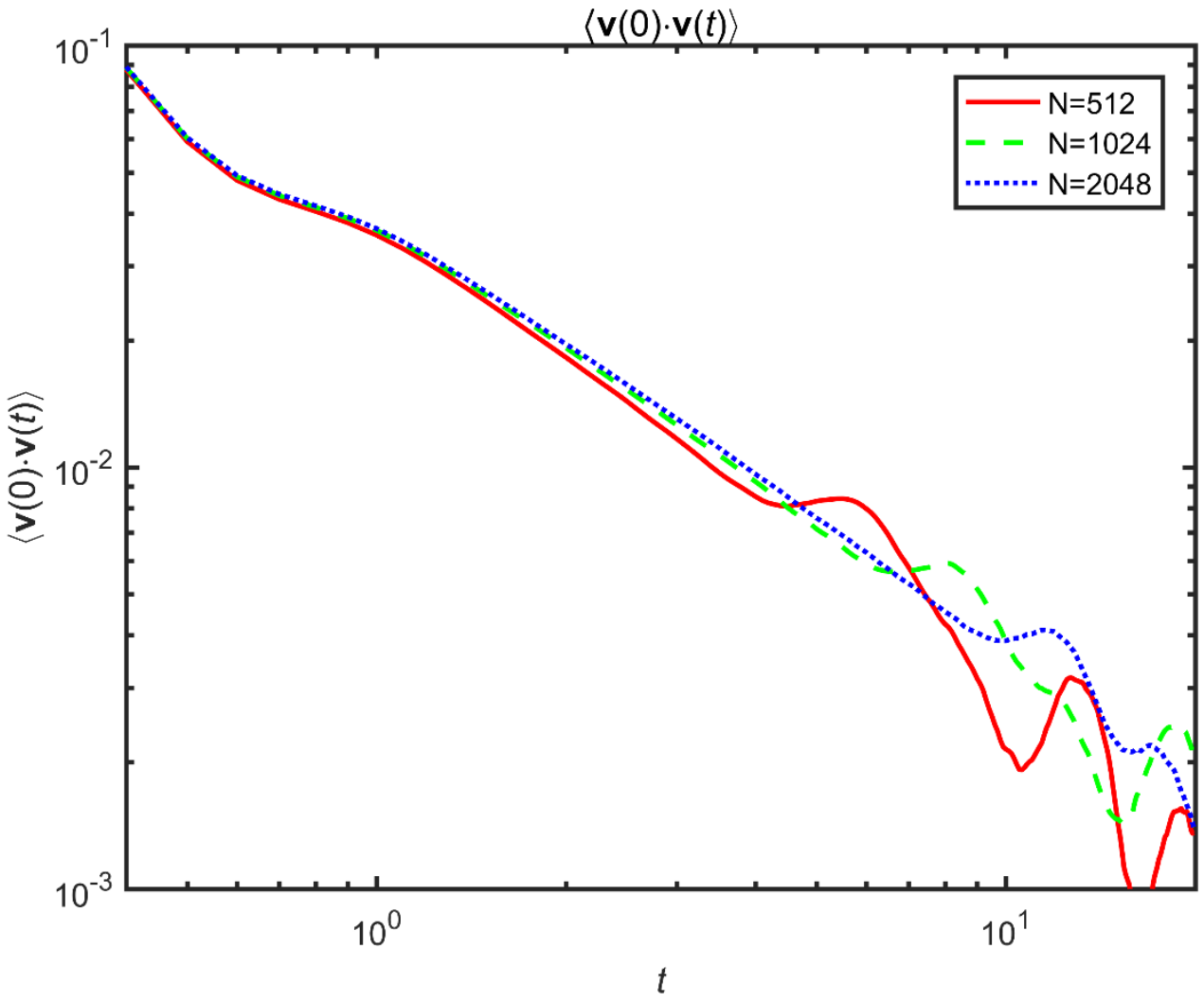
No dependence on $\mathbf{v}_0$?

$$\frac{\partial \mathbf{u}_{\perp}(\mathbf{r},t|\mathbf{v}_0)}{\partial t} = -\nu\,\nabla\times[\nabla\times\mathbf{u}_{\perp}(\mathbf{r},t|\mathbf{v}_0)]$$

$\mathbf{u}_{\mathrm{tr}} \approx \mathbf{u} \approx \mathbf{u}_{\perp}$?

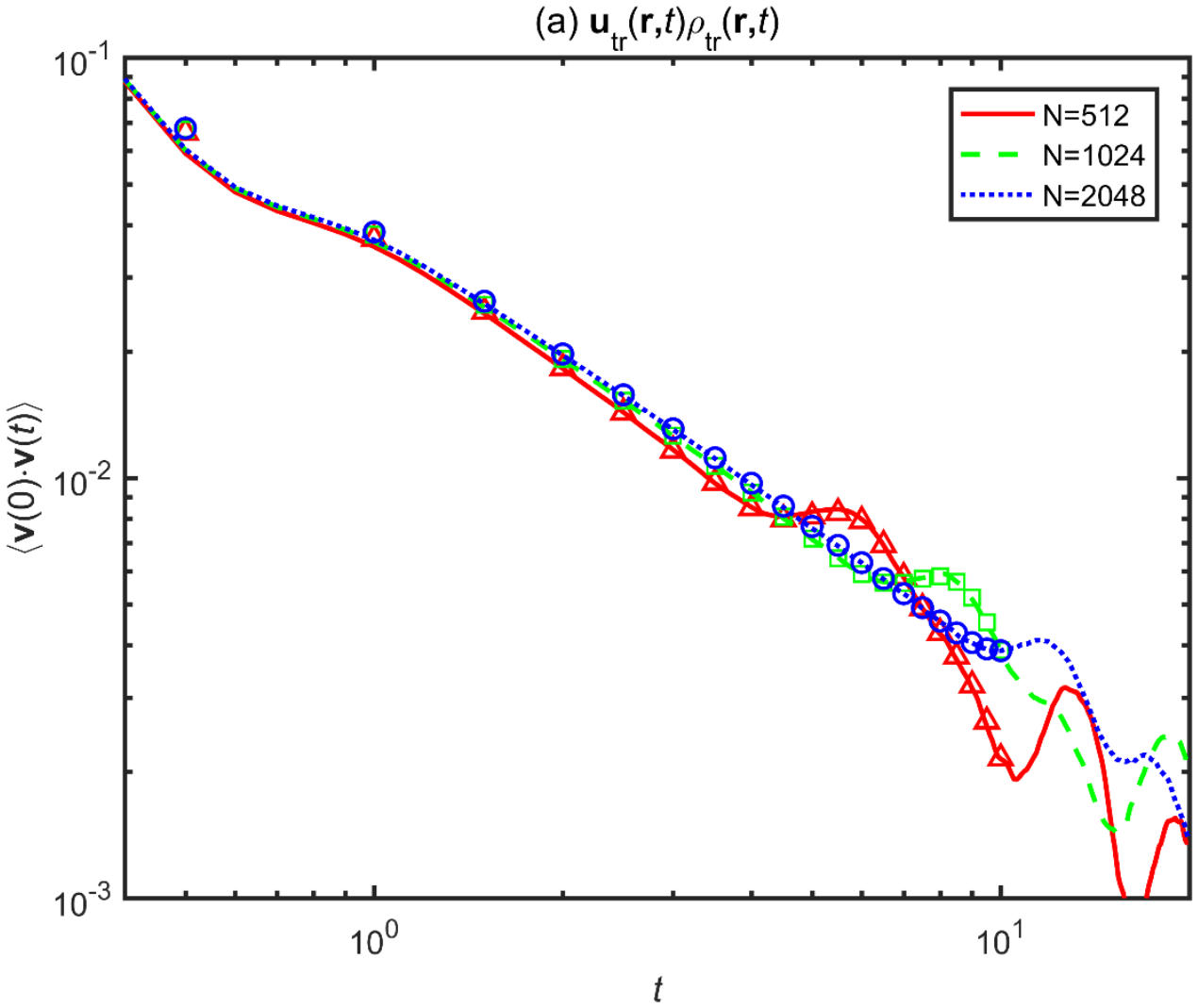
Compare the VACFs calculated from $\int d\mathbf{r}\,\rho_{\mathrm{tr}}(\mathbf{r},t)\mathbf{u}_{\mathrm{tr}}(\mathbf{r},t)$, $\int d\mathbf{r}\,\rho_{\mathrm{tr}}(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)$, $\int d\mathbf{r}\,\rho_{\mathrm{tr}}(\mathbf{r},t)\mathbf{u}_{\perp}(\mathbf{r},t)$, $\int d\mathbf{r}\,\boldsymbol{P}_{\mathrm{tr}}(\mathbf{r},t)\mathbf{u}_{\perp}(\mathbf{r},t)$ (in the order of more challenging assumptions).

VACF from Usual MD



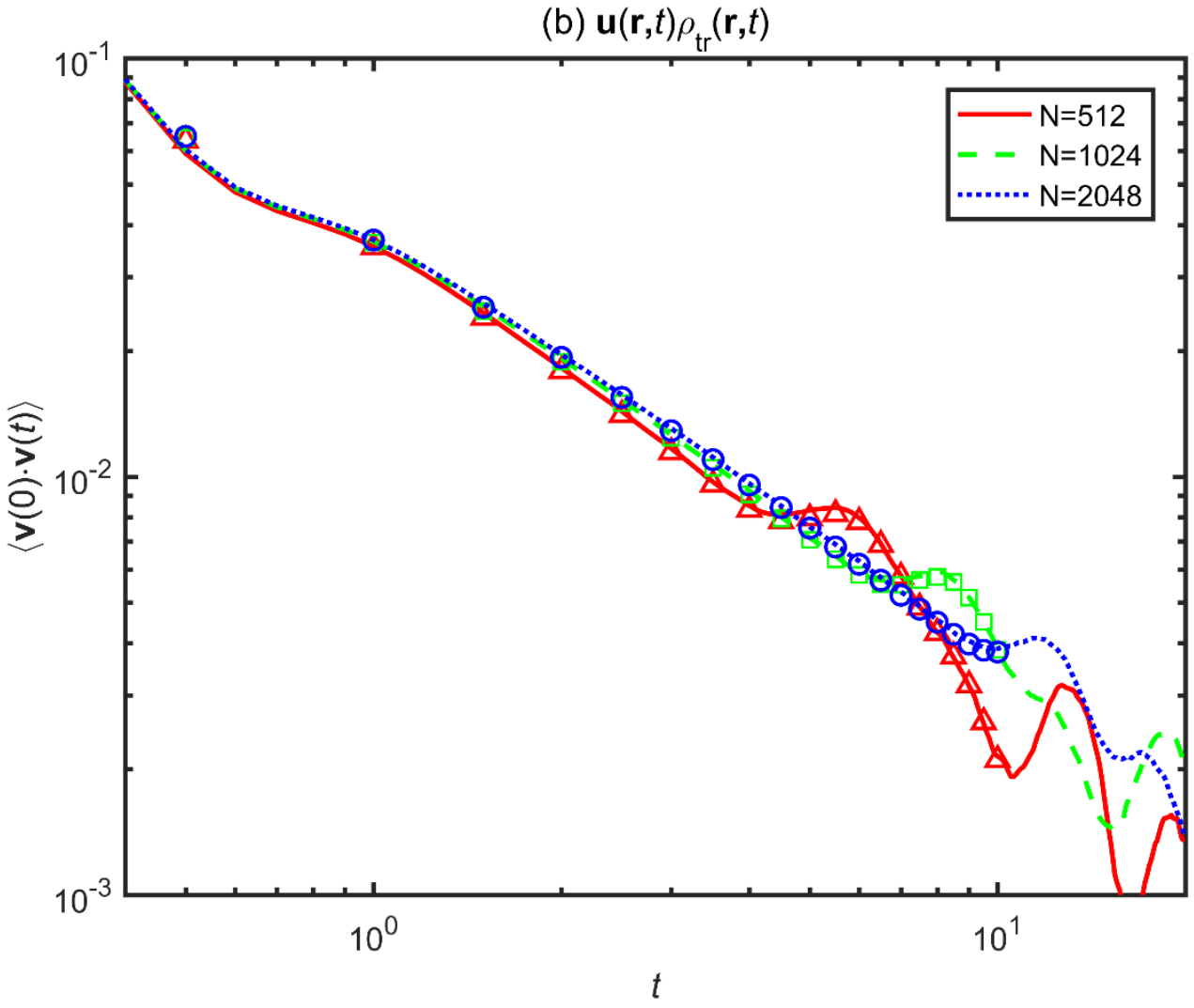
Bumps: finite-size-effect due to the acoustic wave.

From $\int d\mathbf{r}\, \rho_{\mathrm{tr}}(\mathbf{r},t)\mathbf{u}_{\mathrm{tr}}(\mathbf{r},t)$



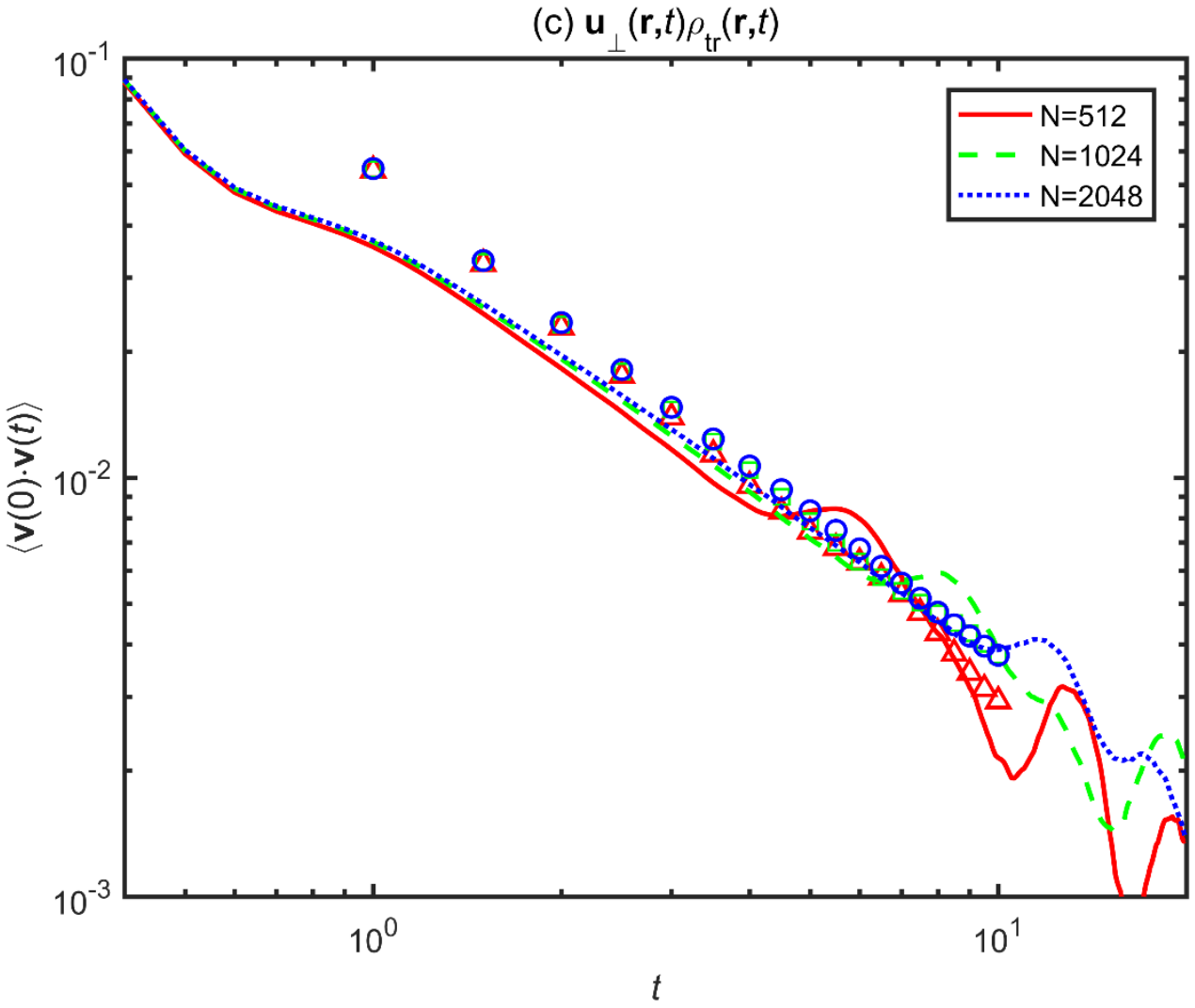
Perfect agreement (as expected)

From $\int d\mathbf{r}\, \rho_{\mathrm{tr}}(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)$



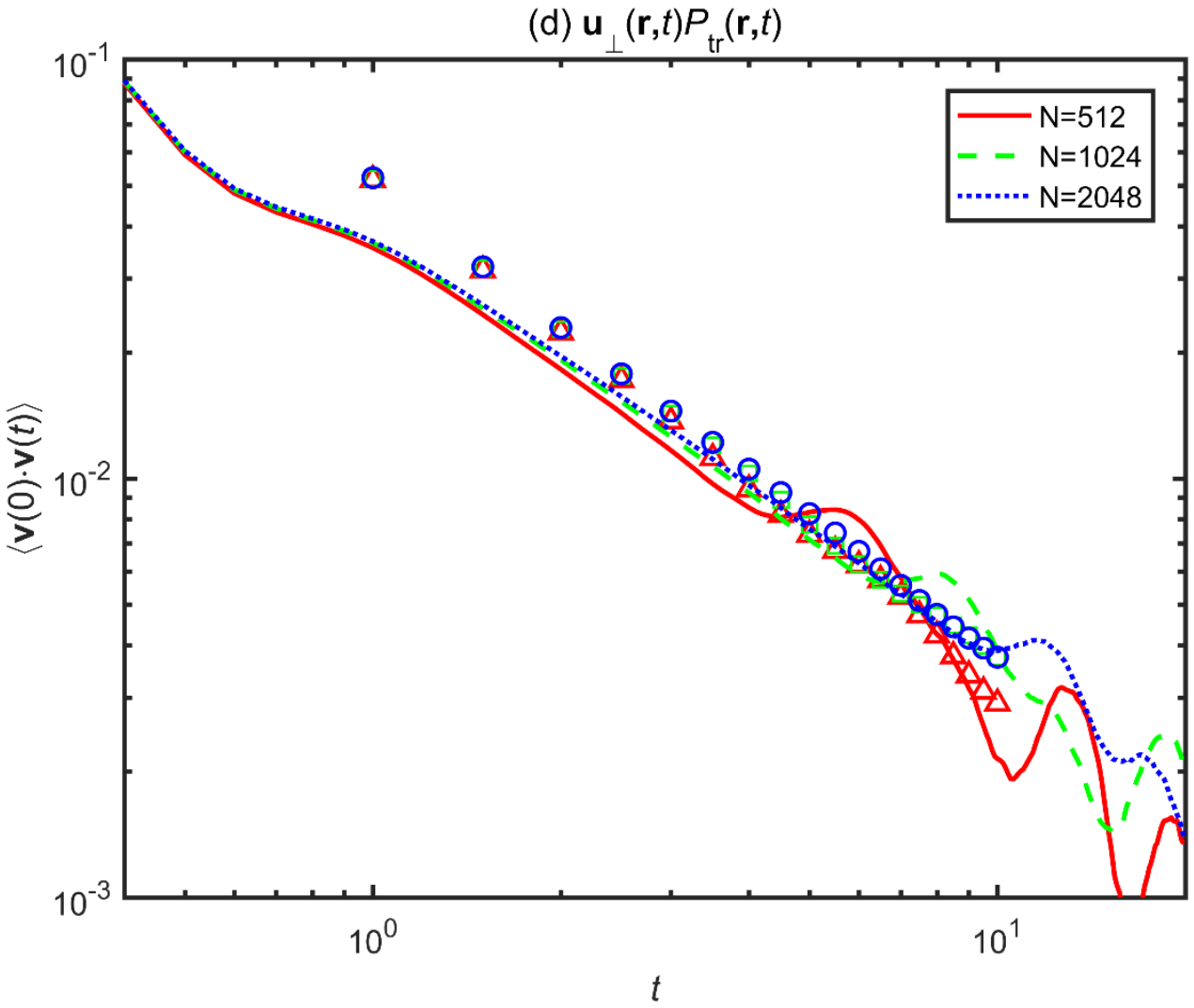
Remarkably good agreement

From $\int d\mathbf{r}\, \rho_{\mathrm{tr}}(\mathbf{r},t)\mathbf{u}_{\perp}(\mathbf{r},t)$

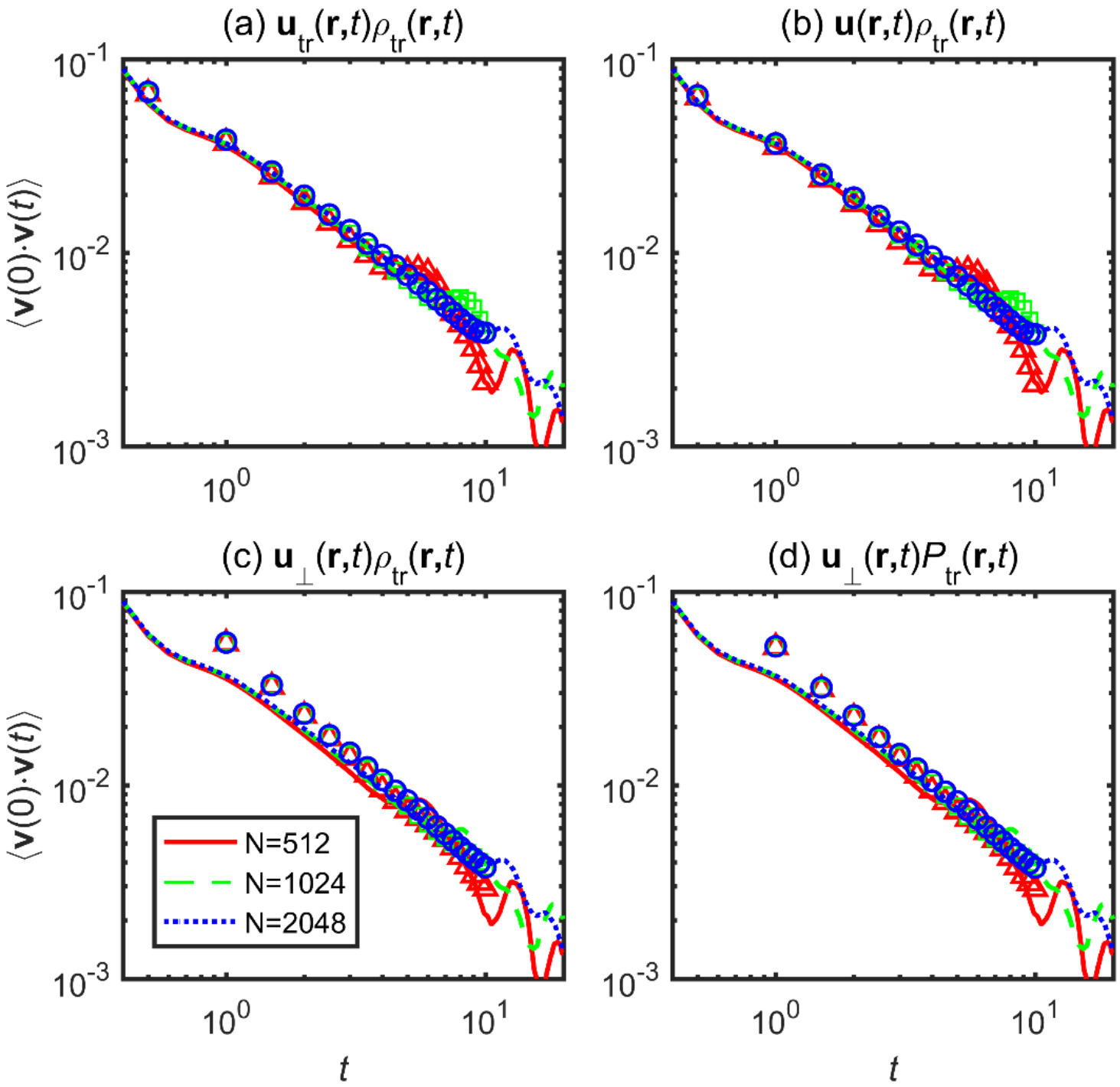


Better agreement for larger time; No bumps

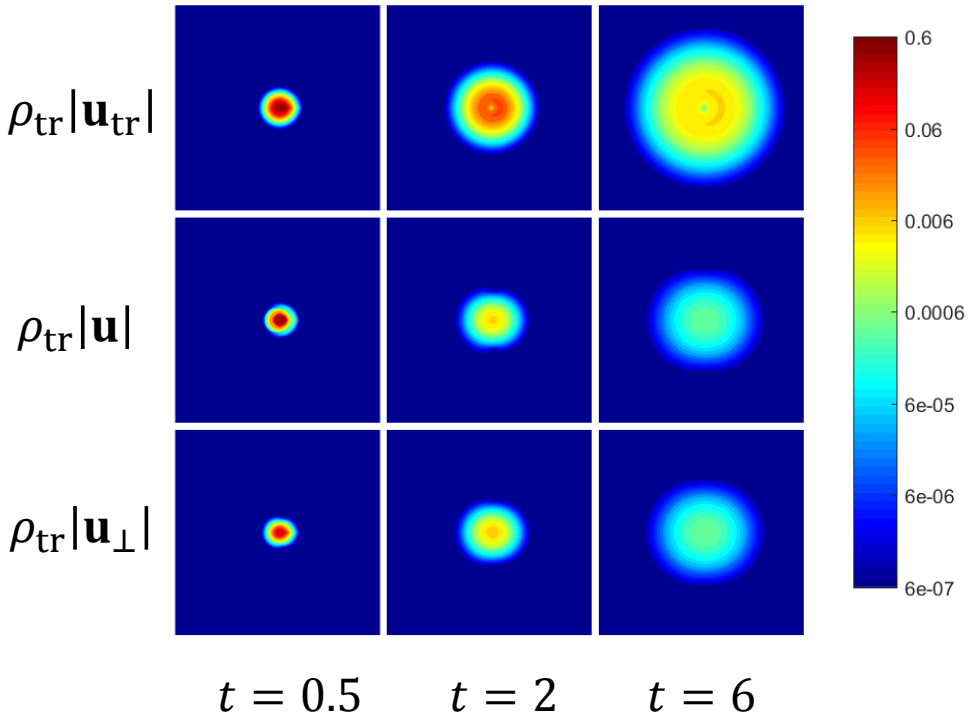
From $\int d\mathbf{r}\, \boldsymbol{P}_{\mathrm{tr}}(\mathbf{r},t)\mathbf{u}_{\perp}(\mathbf{r},t)$

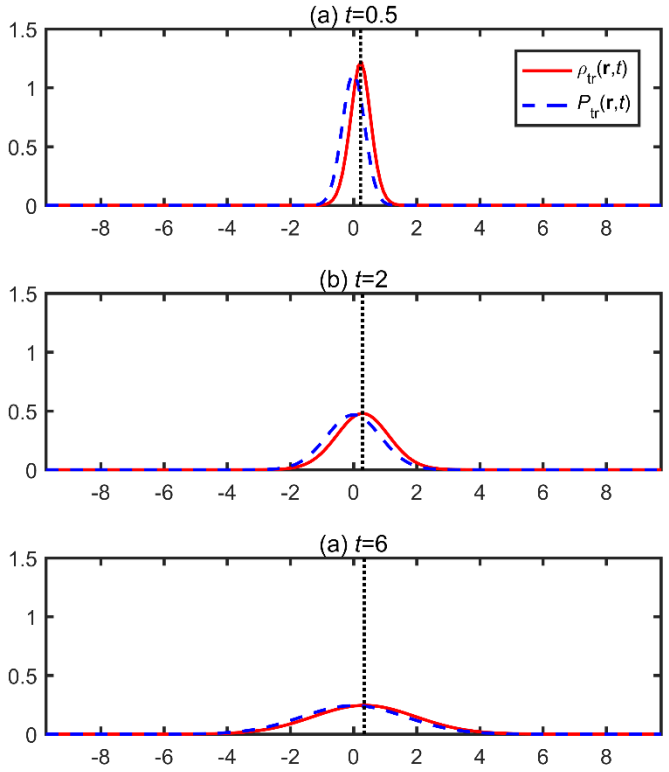


Still agrees for large time


(a) $\mathbf{u}_{tr}(\mathbf{r},t)\rho_{tr}(\mathbf{r},t)$
(b) $\mathbf{u}(\mathbf{r},t)\rho_{tr}(\mathbf{r},t)$
(c) $\mathbf{u}_{\perp}(\mathbf{r},t)\rho_{tr}(\mathbf{r},t)$
(d) $\mathbf{u}_{\perp}(\mathbf{r},t)P_{tr}(\mathbf{r},t)$
$\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle$
10^{-1}
10^{-2}
10^{-3}
10^{0}
10^{1}
t
N=512
N=1024
N=2048

Further Investigation





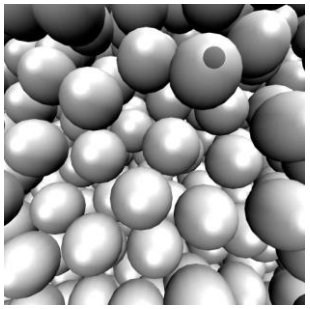
Only the center part $\left(\frac{L}{3} \times \frac{L}{3}\right)$ is displayed

Uncertainty Quantification in MD (and Particle-Based) Simulations: Statistical Errors and Finite-System-Size Effects

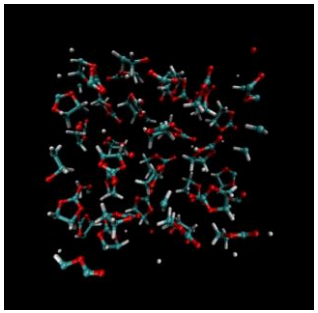
Collaboration with

Kang-Sahn Kim, Prof. Eok Kyun Lee (Chemistry, KAIST)

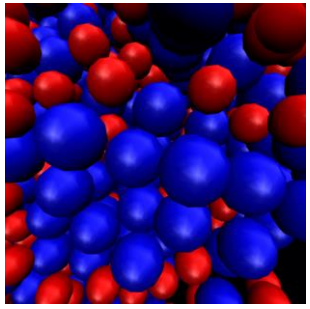
Prof. George Karniadakis (Applied Mathematics, Brown University)



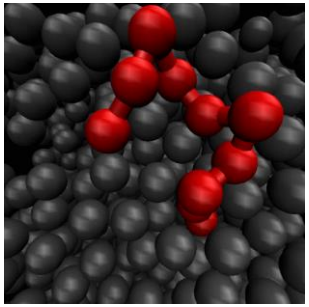
LJ fluid



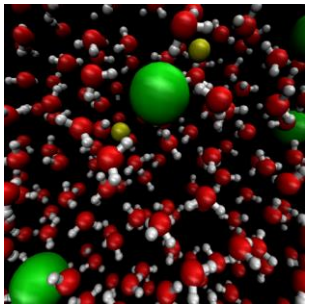
Ethylene carbonate liquid



Ar/Kr mixture



FENE chains in a WCA fluid



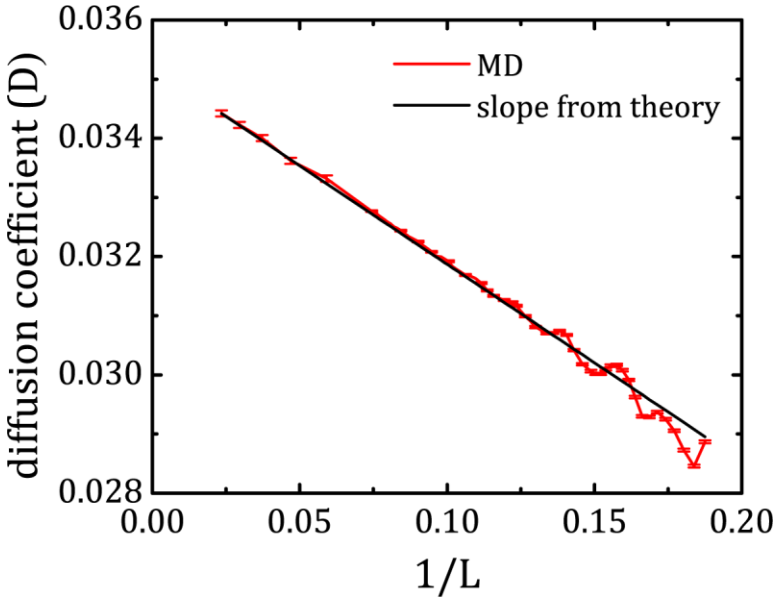
H_2O + NaCl

Overview

Two types of intrinsic uncertainty in MD simulation results

Statistical errors
Sampling error
(precision)

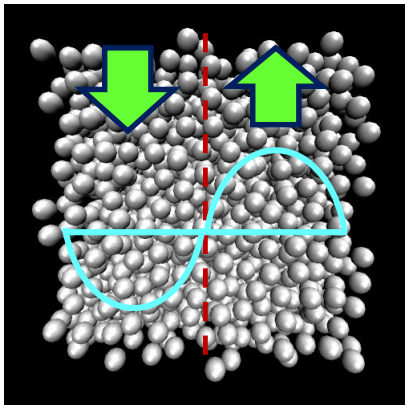
Finite-system-size effects
Systematic error
(accuracy)



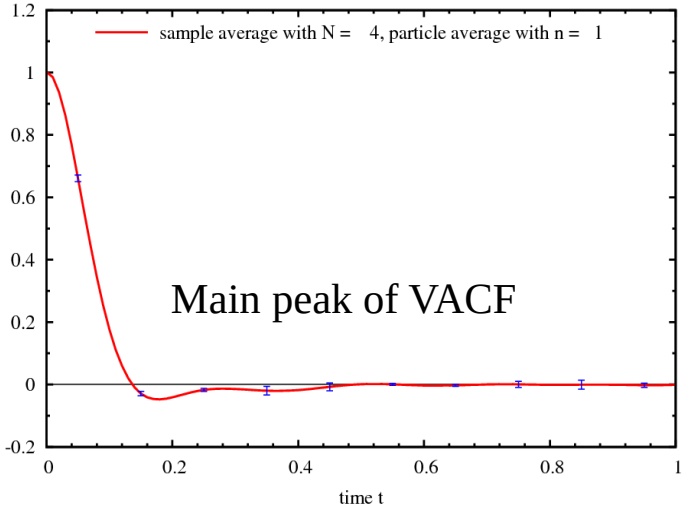
Estimation of transport coefficient

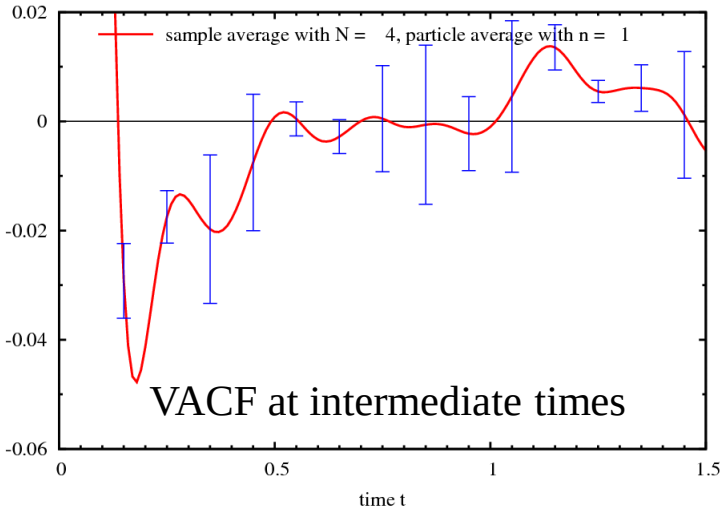
- Diffusion coefficient: MSD method / VACF method
- Shear viscosity
  - Green-Kubo method (EqMD)
  - Reverse Poiseuille method (NEMD)

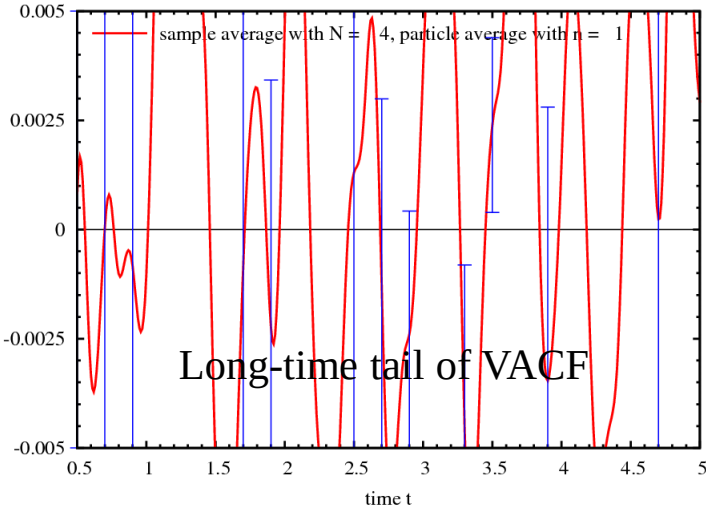
$$\eta = \frac{V}{k_B T}\int_0^\infty \langle p_{xy}(0)p_{xy}(t)\rangle dt$$

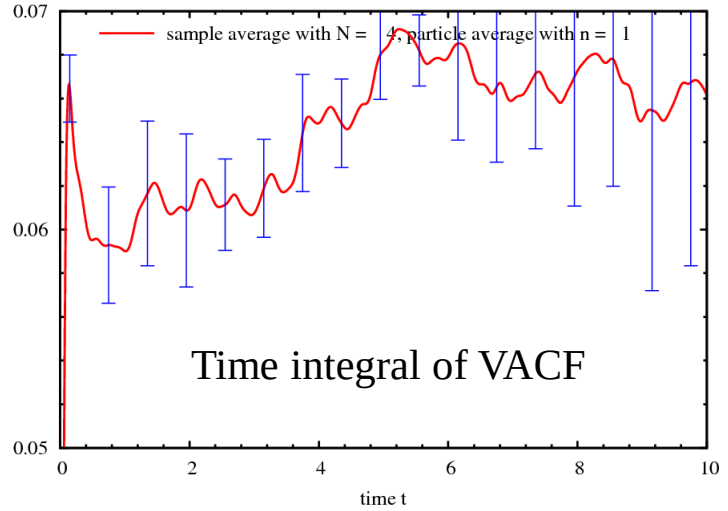


Sampling Size and Quality of MD Data



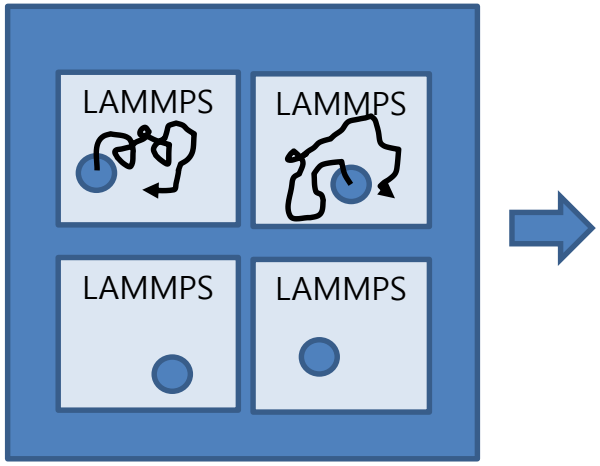






Sample size increases up to by factor of 2^{18}
Standard error decreases up to by factor of $2^9 = 512$

Large MD Ensemble Run



Average over the ensemble
with statistical errors

Running `LAMMPS` with multi-partition mode

```
mpirun -n 1024 lmp -p 64x16 -in uloop.lmp
```

```
label abc
variable sampid uloop 64
  include md.lmp  # run actual script with a given sampid
next sampid
jump SELF abc
```

Example of md.lmp

Time-averaging calculation of $\langle p_{xy}(0) p_{xy}(10i\Delta t) \rangle$ $(i = 0, \ldots, 1000)$

```
include read_equil_sample.lmp

variable mypxy equal pxy
fix scf all ave/correlate 10 1000 10000 v_mypxy ave running &
  file res.scf${sampid} overwrite

run 1000000
```

Time-averaging calculation of VACF

```
variable vx1 equal vx[1]          # need "atom_modify map array"
variable vy1 equal vy[1]
variable vz1 equal vz[1]

fix vcf all ave/correlate 10 1000 10000 v_vx1 v_vy1 v_vz1 auto &
  ave running file res.vcf${sampid} overwrite
```

❖ Calculation of the ensemble average → post-processing

LMP_ENS (LAMMPS ENSEMBLE)

LAMMPS wrapper program for large ensemble MD run and uncertainty quantification

Usage 1

```
#! INCLUDE read_equil_sample.lmp

variable mypxy equal pxy
fix scf all ave/correlate 10 1000 10000 v_mypxy
run 1000000

#! FIX_STAT get scf
#! FIX_STAT stat a3 intg(a3)
#! FIX_STAT print res.pxy0pxyt
```

Usage 2

```
#! INCLUDE read_equil_sample.lmp
#! VACF_ATOM vacf1 10 1000 res.vacf Na 100 xyz --intg --sum
#! RUN 1000000
```

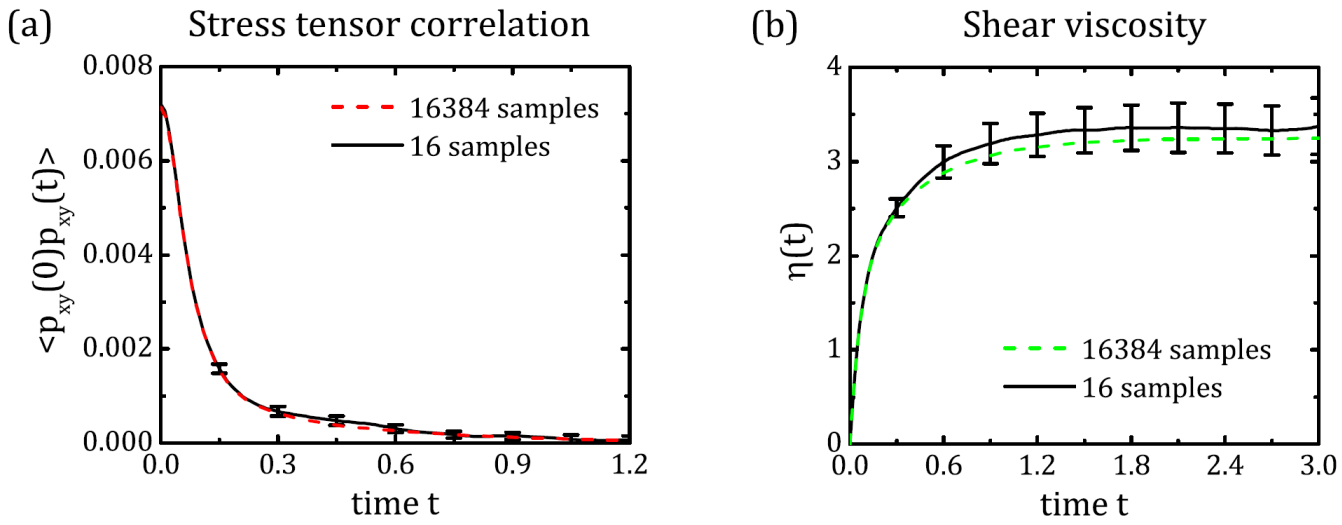
- VACF_MOL, MSD_ATOM, MSD_MOL, TCF, TCF_ATOM, AVE_TIME, …

- LMP_ENS script can share variables with LAMMPS

```
variable Nstep equal ${n1}*${n2}
#! RUN ${Nstep}
```

Standard Errors in a Time Autocorrelation Function and Its Time Integral

Theoretical error estimates for sampling errors in a time autocorrelation function and its time integral



X_i i.i.d. with mean μ and variance σ^2

$$\bar{X} = \frac{1}{N}\sum_{i=1}^{N} X_i \quad \rightarrow \quad \varepsilon = \sqrt{\langle (\bar{X} - \mu)^2 \rangle} = \frac{\sigma}{\sqrt{N}}$$

$$\sqrt{\langle \varepsilon^2(t) \rangle} = \frac{a(t)}{\sqrt{\mathcal{T}\mathcal{N}}}$$

$\mathcal{T}$ = length of MD trajectory

$\mathcal{N}$ = number of MD samples

$a(t)$ = normalized standard error

Gaussian Process Approximation

Statistical errors in a time correlation function and its time integral can be estimated from the correlation function under the GPA.

$$\langle p(0)p(t_1)p(t_2)p(t_3)\rangle =$$
$$\langle p(0)p(t_1)\rangle\langle p(t_2)p(t_3)\rangle + \langle p(0)p(t_2)\rangle\langle p(t_1)p(t_3)\rangle + \langle p(0)p(t_3)\rangle\langle p(t_2)p(t_4)\rangle$$

Error correlation function for $c(t) = \langle p(0)p(t)\rangle$

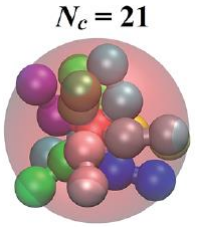
$$\langle \varepsilon_c(t')\varepsilon_c(t'')\rangle = \frac{1}{\mathcal{N}\mathcal{T}}\int_{-\infty}^{\infty} d\alpha\,[c(\alpha)c(\alpha + t'' - t') + c(\alpha - t')c(\alpha + t'')]$$

Standard error estimate for the time integral of $c(t)$

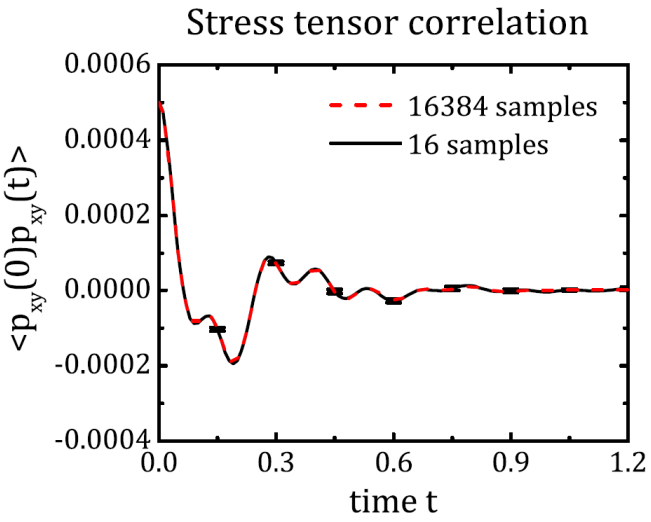
$$\varepsilon_{\text{intg}}(t) = \sqrt{\frac{1}{\mathcal{N}\mathcal{T}}\int_{-\infty}^{\infty} d\alpha\left[c(\alpha)\int_0^t dt'\int_{\alpha}^{\alpha+t} dt''\,c(t'-t'') + \int_{\alpha}^{\alpha+t} c(t')dt'\int_{\alpha-t}^{\alpha} c(t')dt'\right]}$$

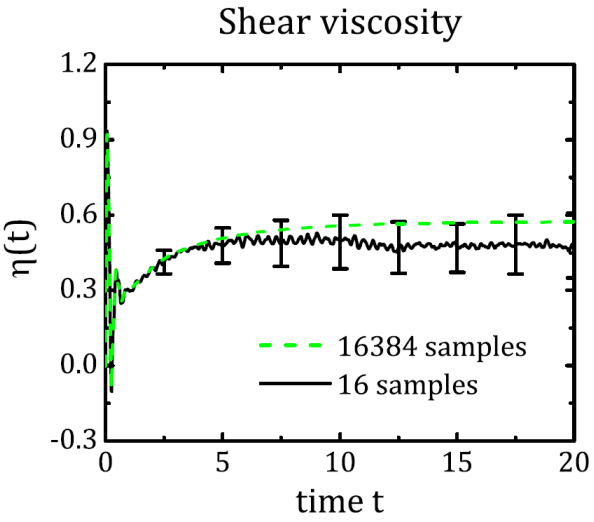
Kim, Borodin, Karniadakis, "Quantification of sampling uncertainty for molecular dynamics simulation: Time-dependent diffusion coefficient in simple fluids", *J. Comput. Phys.* **302**, 485 (2015)

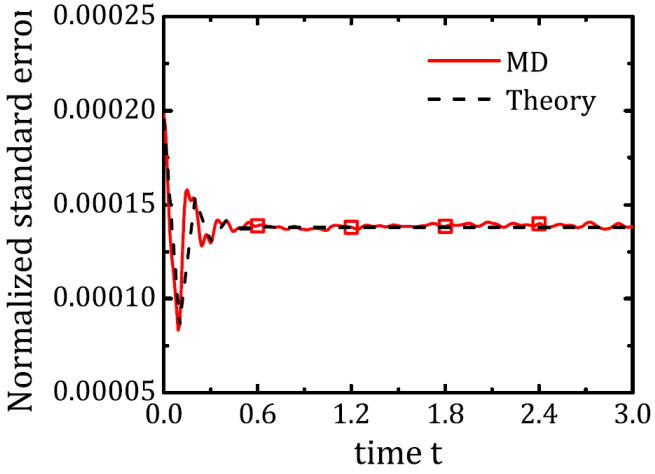
Star Polymer Melt Result

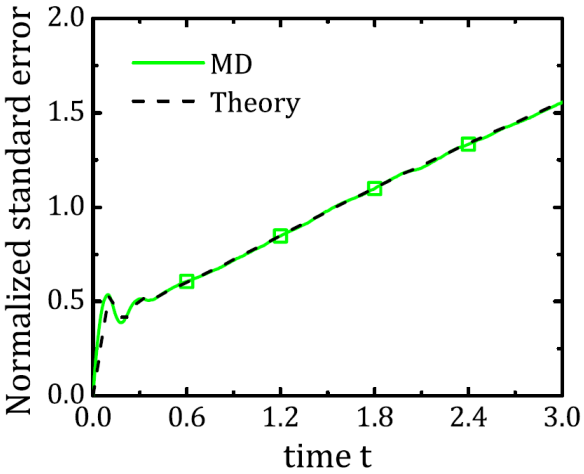


Soft Matt. **10**, 8659 (2014)

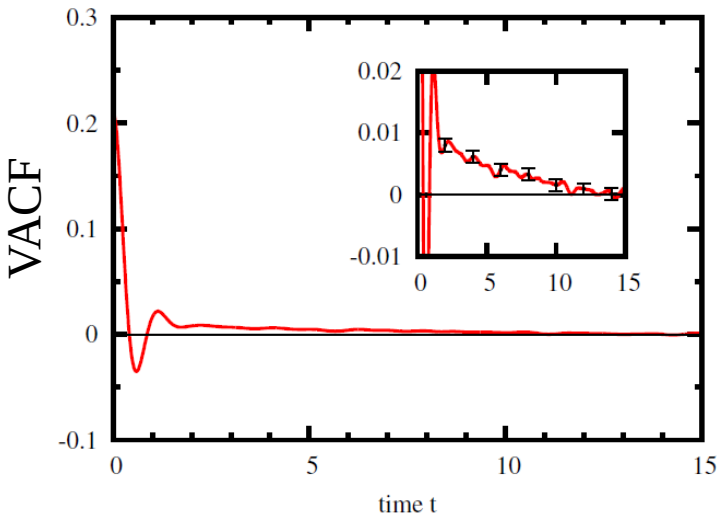


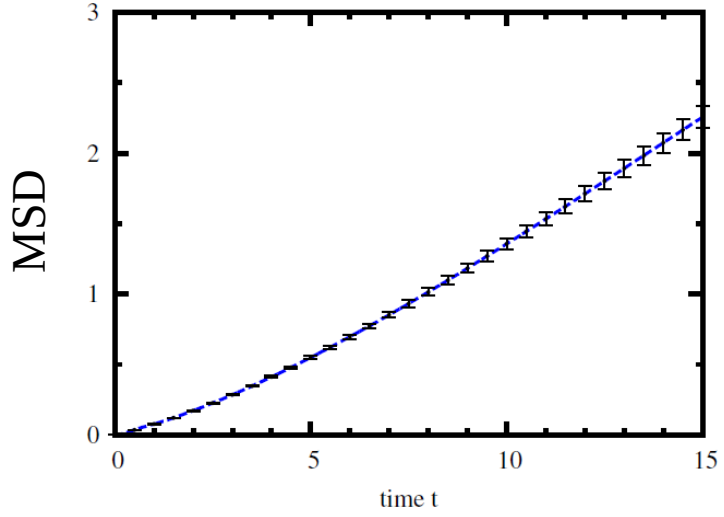






Statistical Errors in VACF, MSD, and $D(t)$





A colloidal particle suspended in a simple molecular fluid

VACF method

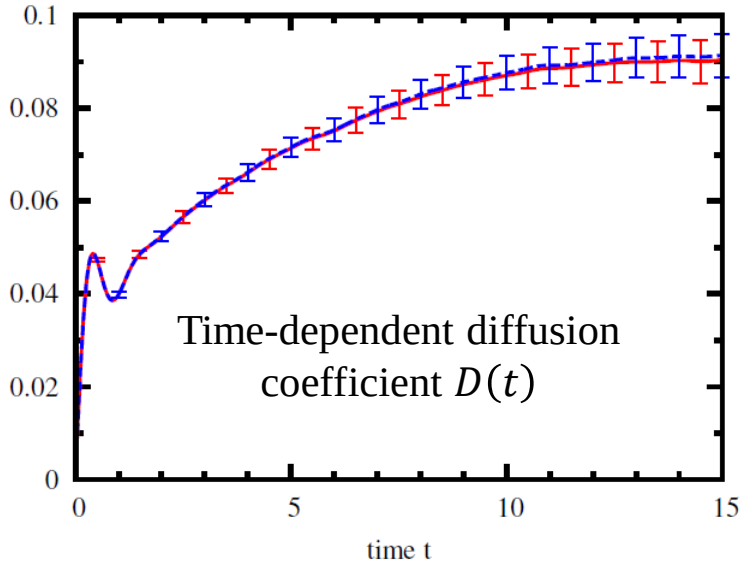
integration

$$D(t) = \int_0^t \langle v(0)v(t')\rangle dt'$$

MSD method

differentiation

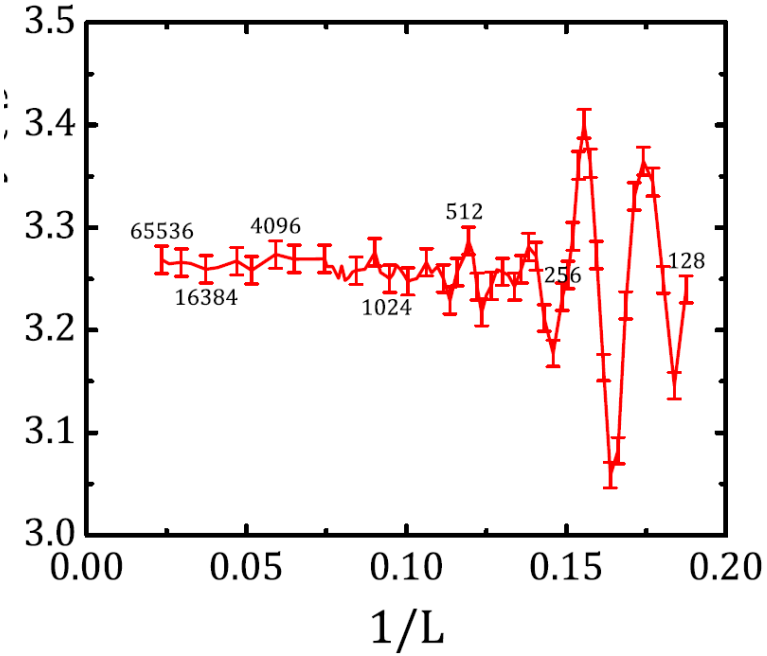
$$D(t) = \frac{1}{2}\frac{d}{dt}\langle [x(t) - x(0)]^2 \rangle$$



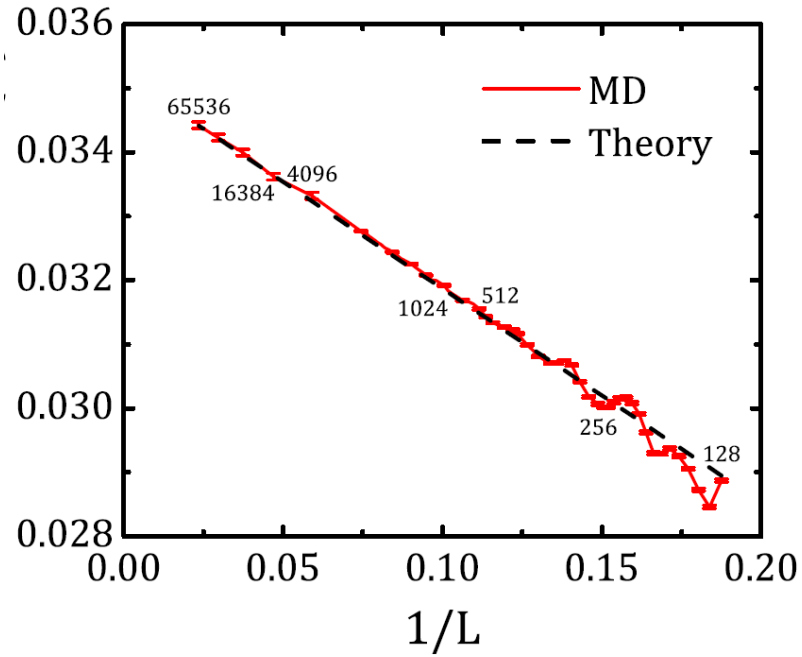
Two methods are equivalent: the same mean with the same standard error.

Finite-System-Size Effect (LJ Fluid)

Shear viscosity η

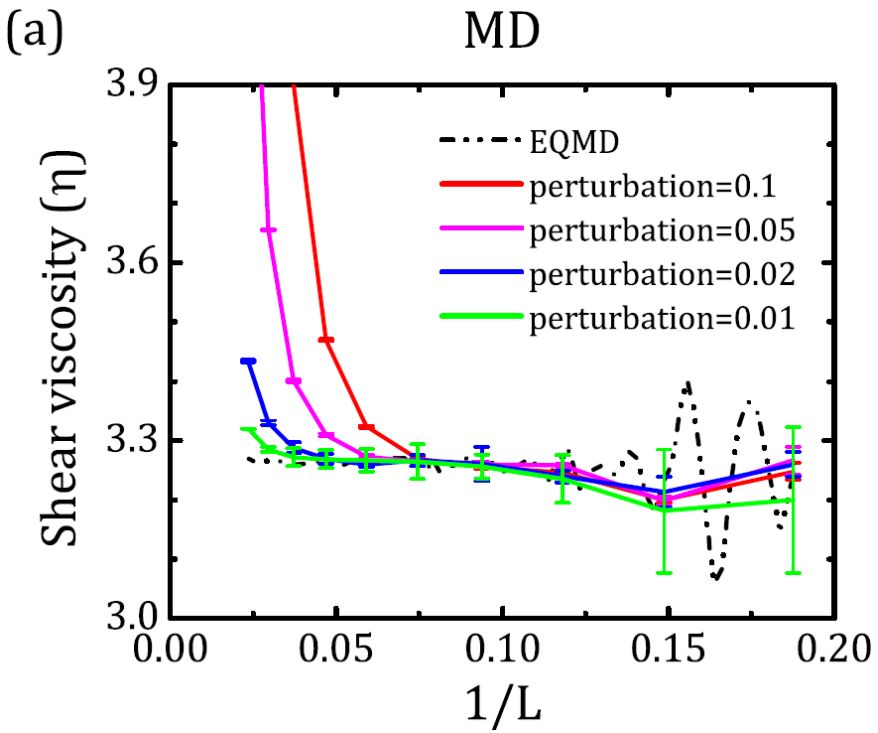


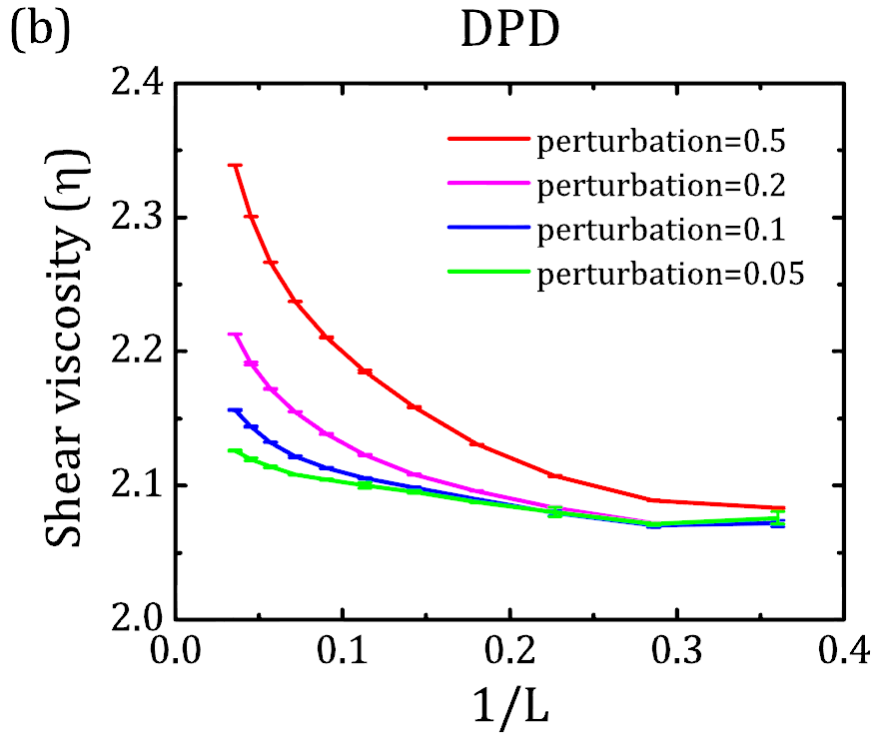
Diffusion Coefficient D

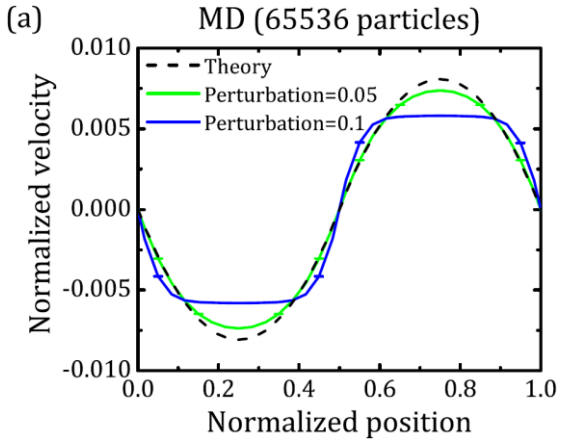


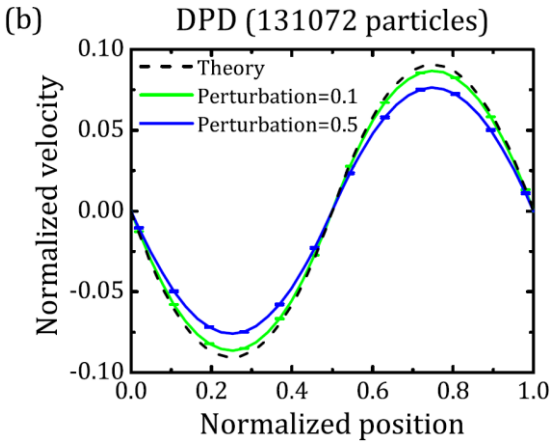
$$D_\infty = D_L + \frac{2.837 k_B T}{6\pi\eta L}$$

Reverse Poiseuille Method









THANK YOU!!!