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Diffusion of Monodisperse, Hard-Sphere Colloidal Fluids: Continuous-Time Random-Walks and Beyond

Jeremy Lechman et al.

Nanoscale and Reactive Processes Department
Engineering Sciences Center
Sandia National Laboratories

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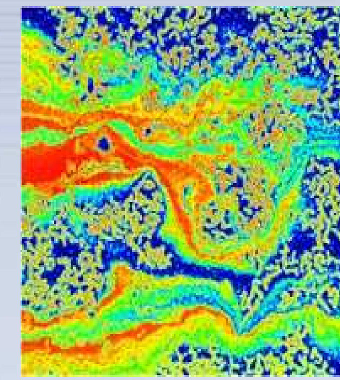
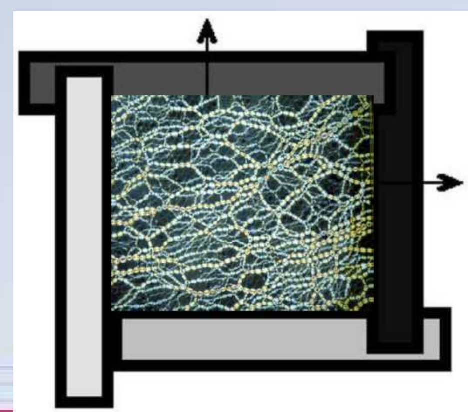
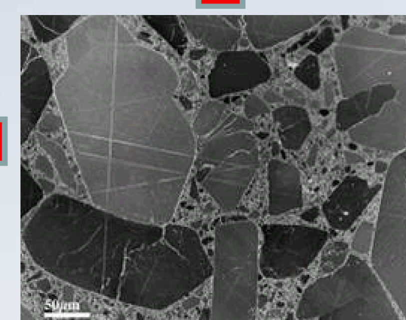
Background and Introduction

- **Need better prediction and control of**
  - Ion transport in composite electrodes (microstructure scale)
  - Durability of composite electrodes, etc.
- **Heterogeneous materials**
  - Inhomogeneous, “discontinuous”
    - material properties and microstructure
      - multi-phase, multi-material → interfaces
    - “dynamics” (i.e., kinematics of a particle or flux)
      - **Discrete particles** in polymer matrix or **suspending fluid**
      - Effective thermal (electrical, etc.) conductivity of composites



- **Generalized, nonequil. continuum Transport**
  - **Generalized Diffusion**
    - **“Anomalous”**
    - **Multi-fractal**





Project Goals

- **Develop models that accurately capture events/processes on *broad* range of scales**
  - What are the component/process scale governing equations in complex, far-from-equilibrium systems?
    - Models must be amenable to math analysis
    - Constitutive relations for closure of model equations should be directly accessible experimentally
  - To be predictive
    - Need access to **FULL** range of length and time scales to close gaps between
      - Discrete constituent and component/process scale
      - Simulation/experimental run-time and product/component life span and performance
    - Need workflow path for parameterizing constitutive relations across relevant scales
- **Novel models push the boundary of V&V to become Discovery tools**
  - Advance experimental and math analysis capabilities to elucidate underlying physical phenomena and path to innovation

Brownian Motion and Diffusion Equation: "Micro-Macro" Connection

- **Translation of *isolated* small sphere in Newtonian fluid**
  - Time dependent Stokes drag force on sphere
    - Nonlocal: space → time

$$\int_{\Omega} \nabla \cdot \boldsymbol{\sigma}_H(t) dV = \int_{\partial\Omega} \boldsymbol{\sigma}_H(t) \cdot \hat{\mathbf{r}} dS \to \int_{-\infty}^{t} \boldsymbol{\Gamma}(t-t') \cdot \mathbf{v}_i(t') dt'; \quad \boldsymbol{\Gamma}(t-t') = \gamma(t-t')\mathbf{I}$$

$$m^* \frac{d\mathbf{v}(t)}{dt} = -\int_{-\infty}^{t} \gamma(t-t')\mathbf{v}(t')dt' + \mathbf{f}(t)$$

- **Assume: Gaussian random force, long-time limit (i.e., ignore fluid and particle inertia)**

$$\left.\begin{aligned} \gamma(t-t') &= \gamma\delta(t-t') \\ \mathbf{f}(t) &= \mathbf{F}^B(t) \end{aligned}\right\} \boxed{\begin{aligned} &\frac{d\mathbf{r}_i(t)}{dt} = \frac{1}{\gamma}\mathbf{F}_i^B(t) \\ &\left\langle \mathbf{F}_i^B(t) \right\rangle = 0; \left\langle \mathbf{F}_i^B(t)\mathbf{F}_i^B(t') \right\rangle = 2k_B T\gamma\delta(t-t') \end{aligned}}$$

  - Interactionless, Markovian, SDE → PDE

$$\boxed{\frac{\partial \rho(x,t)}{\partial t} = D\nabla^2 \rho(x,t)}$$

“Whatever it is I think I see…”

- **Diffusion underlies all irreversible, non-equilibrium processes**
  - Linear, phenomenological Onsager coefficients
    - Fick’s (Second) Law (mass transport)
    - Fourier’s Law (thermal conduction)
    - Newton’s Law (momentum transport)
  - Applicable in the long-time limit (beyond correlation length/time scale)
- **Many systems present multiple, competing length and time scales**
  - Which ones are relevant to the microscopic dynamical processes that underlie macro-transport – what is the “ruler” (i.e., measure) that allows for actual characterization of the system/process
  - How to handle “meso-scale” regimes where correlations are still significant?

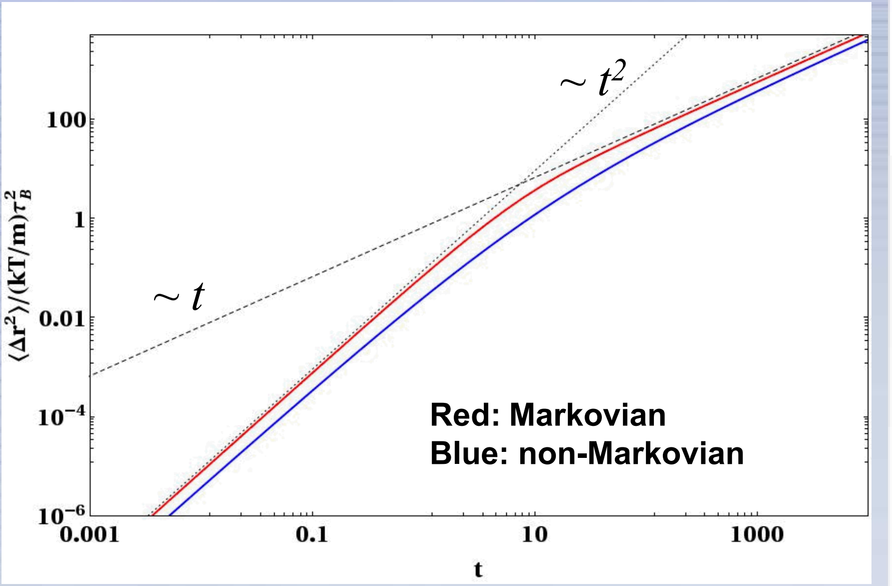
Revisiting the Classical Langevin Equation (OU Process)

- **"Microscopic" dynamics**

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i$$

$$\frac{d\mathbf{v}_i(t)}{dt} = -\frac{1}{\tau_B}\mathbf{v}_i(t) + \frac{1}{m}\mathbf{F}_i^B(t)$$

$$\left\langle \mathbf{F}_i^B(t) \right\rangle = 0; \left\langle \mathbf{F}_i^B(t)\mathbf{F}_i^B(t') \right\rangle = 2k_B T\gamma\delta(t-t')$$



- Solve (formally) and obtain

$$\left\langle \left|\Delta\mathbf{r}\right|^2 \right\rangle(t) = \frac{6kT}{m}\tau_B\left(t - \tau_B(1 - e^{-t/\tau_B})\right)$$

  - Defines/justifies long-time, $t >> \tau_B$
  - $MSD = f(t) \neq Dt^{\alpha};\ 0 \leq \alpha \leq 2$
    - Temptation: $D = D(t) \rightarrow MSD = D(t)t$
      - » What does this mean **physically**?

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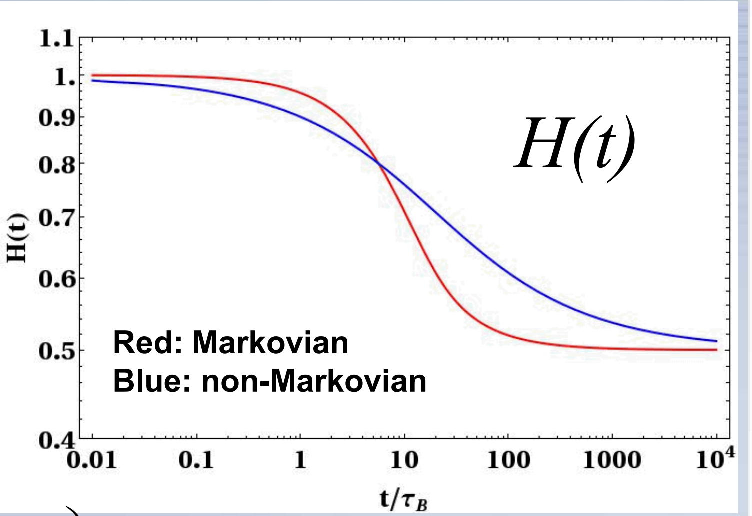
Scale-Invariant Diffusion Equation

- **Microscopic dynamics give**
  - $MSD = f(t)$
    - $MSD = Dt^{\alpha(t)};\ \alpha(t) = 2H(t)$
    - $MSD = D\tau_D(t);\ \dfrac{d\ln(\tau_D(t))}{d\ln(t)} = 2H(t)$



$$\left\langle |\Delta\mathbf{r}|^2 \right\rangle(t) = \frac{6kT}{m}\tau_B\left(t - \tau_B(1 - e^{-t/\tau_B})\right) = 6\left(\frac{kT}{m}\tau_B\right)\tau_D(t)$$

- **A density which gives above as the second moment is**
  - Gaussian assumption ➔ distribution is stationary and symmetric; no higher moments matter

$$\rho(\mathbf{x},\tau_D(t)) = \frac{1}{\sqrt{2\pi D\tau_D(t)}}\exp\left[-\frac{\mathbf{x}^2}{4D\tau_D(t)}\right]$$

  - Which is a solution to

$$\frac{\partial\rho(\mathbf{x},\tau_D)}{\partial\tau_D} = D\nabla^2\rho(\mathbf{x},\tau_D),\ \text{given}\ \rho(\mathbf{x},0) \sim \delta(\mathbf{x})$$

Generalized Diffusion-Relaxation Equation

- **Recall** $$\frac{\partial \rho(\mathbf{x},\tau_D(t))}{\partial \tau_D} = D\nabla^2 \rho(\mathbf{x},\tau_D(t))$$
  - Note $\partial \tau_D = \dfrac{d\tau_D(t)}{dt}\partial t$
- **So,** $$\frac{\partial \rho(\mathbf{x},\tau_D(t))}{\partial t} = \frac{d\tau_D(t)}{dt} D\nabla^2 \rho(\mathbf{x},\tau_D(t))$$
  - Here $\dfrac{\partial \tau_D(t)}{\partial t} = \left(1 - e^{-t/\tau_B}\right)$, so $\dfrac{\partial \rho(\mathbf{x},t)}{\partial t} = D\nabla^2 \rho(\mathbf{x},t) - e^{-t/\tau_B} D\nabla^2 \rho(\mathbf{x},t)$
  - Integrating gives,

$$\boxed{\rho(\mathbf{x},\tau_D(t)) = \rho(\mathbf{x},\tau_D(0)) + D\int_0^t \frac{d\tau_D(t-t')}{dt}\nabla^2 \rho(\mathbf{x},\tau_D(t'))\,dt'}$$

“Fractional” Diffusion?

- **Start with “diffusion-relaxation” equation**

$$\rho(\mathbf{x},\tau_D(t)) = \rho(\mathbf{x},\tau_D(0)) + D\int_0^t (1-e^{-(t-t')/\tau_B})\nabla^2\rho(\mathbf{x},\tau_D(t'))\,dt'$$

  – Take ***time*** derivative

$$\frac{\partial\rho(\mathbf{x},\tau_D(t))}{\partial t} = \frac{\partial\rho(\mathbf{x},\tau_D(0))}{\partial t} - D\frac{\partial\tau_D(0)}{\partial t}\nabla^2\rho(\mathbf{x},t) + D\int_0^t \frac{\partial^2\tau_D(t-t')}{\partial t^2}\nabla^2\rho(\mathbf{x},\tau_D(t'))\,dt'$$

- set $\frac{\partial\rho(\mathbf{x},\tau_D(0))}{\partial t}=0$ to get a “diffusion equation with memory”

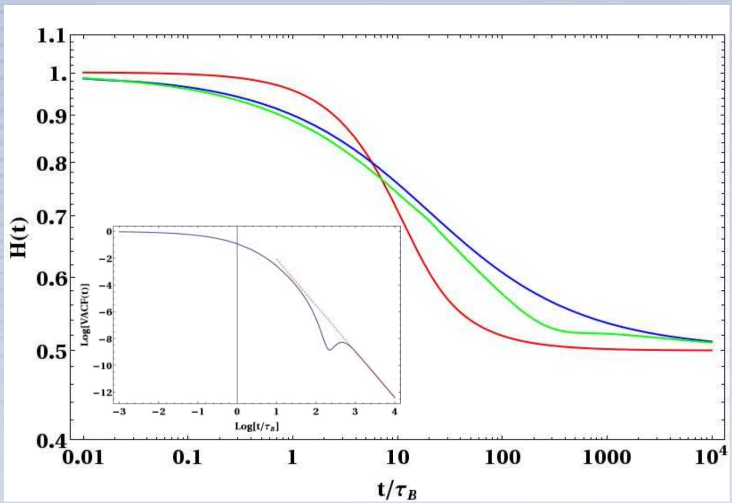
$$\frac{\partial\rho(\mathbf{x},\tau_D(t))}{\partial t} = \frac{kT}{m}\int_0^t e^{-(t-t')/\tau_B}\nabla^2\rho(\mathbf{x},\tau_D(t'))\,dt'$$

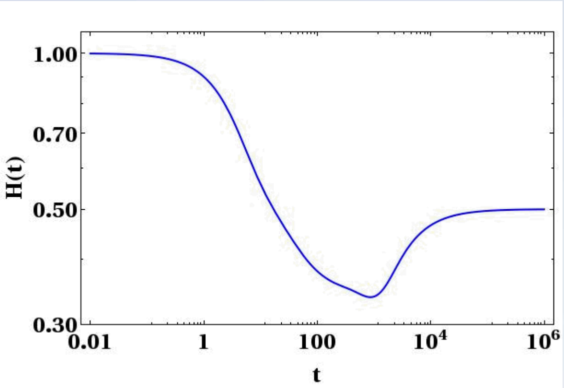
- Which is equivalent to

$$\tau_B\frac{\partial^2\rho(\mathbf{x},\tau_D(t))}{\partial t^2} + \frac{\partial\rho(\mathbf{x},\tau_D(t))}{\partial t} = D\nabla^2\rho(\mathbf{x},\tau_D(t))$$

Various Examples of $\tau_D(t)$

- **Have analytical forms for dilute particles ➔non-interacting random walkers**
  - Classical Damped Harmonic Oscillator
    - Under, over, critically damped
  - Classical GLE
    - Incompressible Newtonian Liquid
      - zero Re
    - Compressible Newtonian Fluid
      - Zero Re
      - High Re, Zero and moderate Ma
    - Incompressible/compressible Non-Newtonian
      - Zero Re
  - Nearly Classical Ideal Liquid
- **Can obtain from simulation**
  - Interacting particles (non-zero concentration)





The “Generalized Langevin Equation”

- Transient Brownian Dynamics (Interactionless)
  - NonMarkovian Langevin Equation

$$m^* \frac{d\mathbf{v}_i(t)}{dt} = -6\pi\mu a \int_0^t \underbrace{\left(\frac{(t-t')^{-3/2}}{2\Gamma(1/2)} + \delta(t-t') \right)}_{\xi(t-t')} \mathbf{v}_i(t')dt' + \mathbf{F}_i^R(t)$$

$$\left\langle \mathbf{F}_i^R(t) \right\rangle = 0$$

$$\left\langle \mathbf{F}_i^R(t)\mathbf{F}_i^R(t') \right\rangle = 2k_B T\xi(t-t')$$

  - If noise is modeled by Gaussian, stationary, self-similar processes, we have fBm
- Note Basset-Boussinesq

$$m^* \frac{d\mathbf{v}_i(t)}{dt} = 6\pi\mu a \int_0^t \left(\frac{(t-t')^{-1/2}}{\sqrt{\pi}} \right) \frac{d\mathbf{v}_i(t')}{dt'} dt' - 6\pi\mu a \mathbf{v}(t)$$

$$m^* = \left(m_p + \frac{1}{2} m_f \right)$$

Non-Markovian Example

- **Note, impulsive response of sphere in incompressible, Newtonian fluid**
  - sphere initially at rest, fluid at rest at infinity – i.e., dilute suspension

$$\mathbf{v}(t) = \frac{1}{2(q_1 - q_2)}\left[q_1 E_{1/2,1}(-t/\tau_1) - q_2 E_{1/2,1}(-t/\tau_2)\right]$$

$$q_{1,2} = \frac{1}{2Za}\left(1 \pm \sqrt{1-4Z}\right),\ Z = \frac{2m_p + m_f}{9m_f},\ \tau_{1,2} = (q_{1,2})^2 \nu$$

$$E_{\alpha,\beta}(y) = \sum_{k=0}^{\infty} \frac{y^k}{\Gamma(\alpha k + \beta)}$$

- **We can use this to derive MSD and**

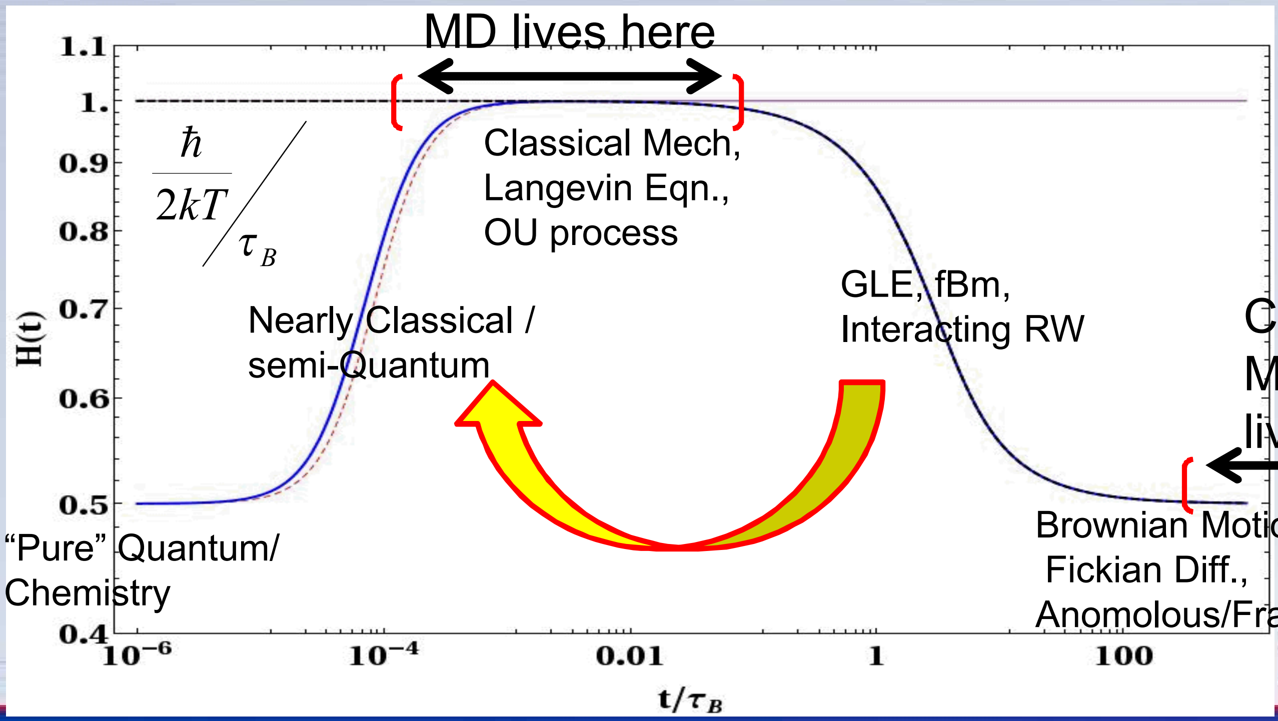
$$\tau_D(t) = \frac{\tau_B}{2(q_1 - q_2)}\left\{q_1 E_{1/2,3}[-(t/\tau_1)^2] - q_2 E_{1/2,3}[-(t/\tau_2)^2]\right\}$$

The Semi-Classical Limit and Defining Mesoscales

- **Nearly classical fluid (QM – Langevin equation)**
  - following De Bar 1963 (see also Vineyard 1958, van Hove 1954)

$$\tau_D^{Cl}(t) = \tau_B\left[\frac{t}{\tau_B} - \left(1 - e^{-t/\tau_B}\right)\right] \qquad \tau_D(t) = \tau_D^{Cl}(t) - i\frac{\hbar}{2kT}\left(\frac{d\tau_D^{Cl}(t)}{dt}\right) = t - \tau_B\left(1 - e^{-t/\tau_B}\right) - i\frac{\hbar}{2kT}\left(1 - e^{-t/\tau_B}\right)$$

  - Consider the "average trajectory" of a particle, $\rho_i(x,t)$

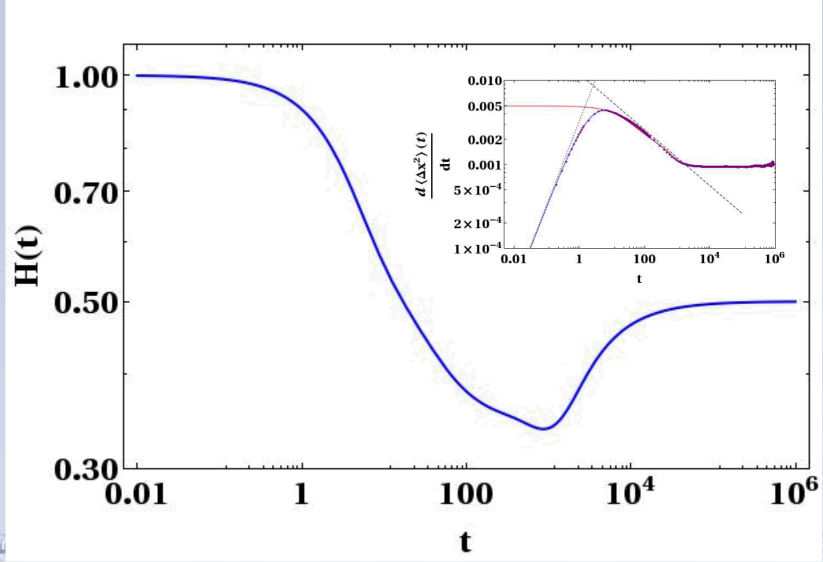


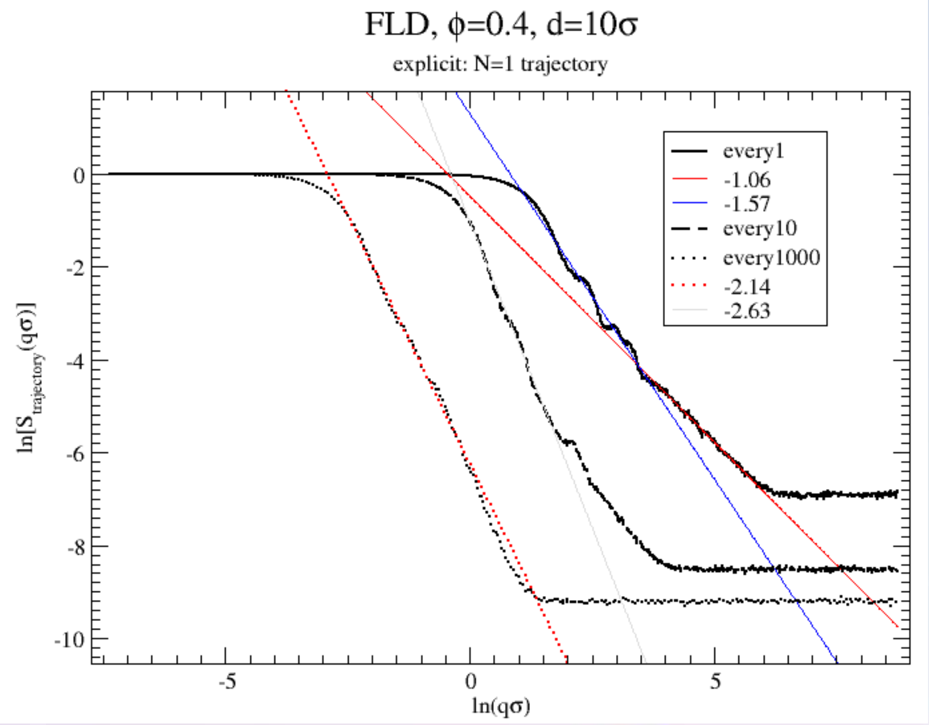
Space/Time structure of Probability Densities for Particle Trajectories

- **Single particle density (kinematics) of hard-sphere colloid**

$$\rho_i(\mathbf{r},t) = \left\langle m\delta(\mathbf{r}-\mathbf{R}_i(t)); f^N(\mathbf{R}^N,\mathbf{P}^N;t)\right\rangle = \lim_{t\to\infty}\frac{1}{t}\int_{t_0}^{t} m\delta(\mathbf{r}-\mathbf{R}_i(t'))dt' \approx \frac{1}{M_t}\sum_{k=0}^{M_t} m\delta(\mathbf{r}-\mathbf{R}_i(t_0+k\Delta t))$$

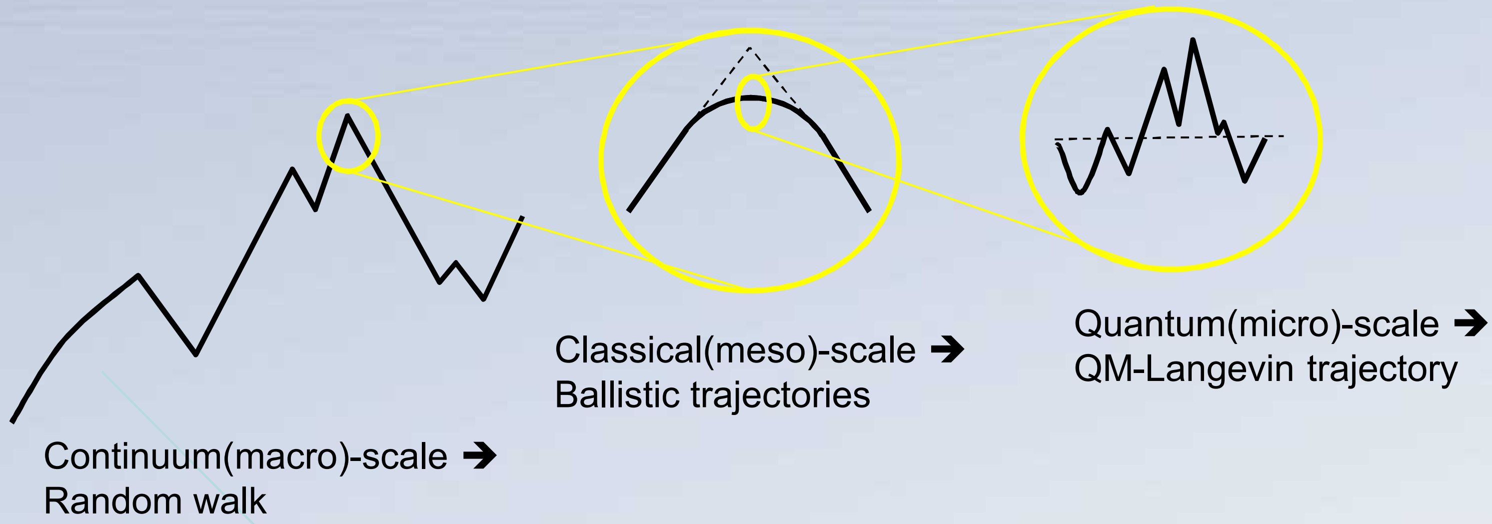
  - "Light scattering" of single particle trajectory, $\mathbf{R}_i(t_k)$
    - Self-affine record → self-similar fractal "trail"
      - Multiple length and time scales
      - Multifractal: $d_{f,D}(t) \sim 1/H(t)$
      - Change "ruler": $d_{f,D}(\tau_D) = 2$





Schematic of Scale Dependent Processes

- **Complex heterogeneity implies Multi-fractal functions**
  - Generalized Trajectories (mass, momentum, energy), $r(t)$
    - Non-differentiable
    - Hierarchy of scaling exponents
    - Fundamentally, no derivatives (e.g., particle velocity) can be defined in the classical delta-epsilon, limit sense



Scale Consistent "Diffusion" (at *Very* Small Scale)

- **For "Quantum-Mechanical" Markovian Langevin Eqn. (OU process)**

$$\tau_D^{Cl}(t) = \tau_B\left[\frac{t}{\tau_B} - \left(1 - e^{-t/\tau_B}\right)\right] \qquad \tau_D(t) = \tau_D^{Cl}(t) - i\frac{\hbar}{2kT}\left(\frac{d\tau_D^{Cl}(t)}{dt}\right) = t - \tau_B\left(1 - e^{-t/\tau_B}\right) - i\frac{\hbar}{2kT}\left(1 - e^{-t/\tau_B}\right)$$

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

$$\frac{\partial\rho(\mathbf{x},\tau_D(t))}{\partial t} = \frac{d\tau_D(t)}{dt}\left(\frac{kT}{m}\tau_B\right)\nabla^2\rho(\mathbf{x},\tau_D(t))$$

$$\frac{\partial\rho(\mathbf{x},\tau_D(t))}{\partial t} = \left(\frac{kT}{m}\tau_B\right)\left(1 - e^{-t/\tau_B}\right)\nabla^2\rho(\mathbf{x},\tau_D(t)) - i\frac{\hbar}{2m}e^{-t/\tau_B}\nabla^2\rho(\mathbf{x},\tau_D(t))$$

  - Take limit of $t \rightarrow 0$; keeping leading order term

$$\frac{\partial\rho(\mathbf{x},\tau_D(t))}{\partial t} \approx -i\frac{\hbar}{2m}\nabla^2\rho(\mathbf{x},\tau_D(t)) \qquad \lim_{t\rightarrow 0}\tau_D(t) = \frac{t^2}{2\tau_B} - i\frac{\hbar}{2kT}\left(\frac{t}{\tau_B}\right)$$

What is the “density” at small t?

- **Recall** $$\frac{\partial \rho(\mathbf{x},\tau_D(t))}{\partial \tau_D} = \frac{kT}{m}\tau_B \nabla^2 \rho(\mathbf{x},\tau_D(t))$$

$$\rho(\mathbf{x},\tau_D(t)) = \frac{1}{\sqrt{2\pi D\tau_D(t)}}\exp\left[-\frac{\mathbf{x}^2}{4D\tau_D(t)}\right]$$

$$\lim_{t\to 0}\tau_D(t) \approx \frac{t^2}{2\tau_B} - i\frac{\hbar}{2kT}\left(\frac{t}{\tau_B}\right) \approx -i\frac{\hbar}{2m}\left(\frac{t}{D}\right)$$

$$\lim_{t\to 0}\rho(\mathbf{x},\tau_D(t)) \approx \frac{1}{\sqrt{-\pi i\frac{\hbar}{m}t}}\exp\left[-\frac{\mathbf{x}^2}{-2i\frac{\hbar}{m}t}\right]$$

$$\lim_{t\to 0}\rho(\mathbf{x},\tau_D(t)) = \psi(\mathbf{x},-t) = \psi^*(\mathbf{x},t) \rightarrow$$ Gaussian wave function

$$\frac{\partial \psi^*(\mathbf{x},t)}{\partial t} = -i\frac{\hbar}{2m}\nabla^2\psi^*(\mathbf{x},t)$$

Routes to the scale-consistent or scale-invariant diffusion equation

Diffusion Equation for Wiener process (i.e., overdamped Langevin dynamics)

- **Consider phase-space density** $f^N(\mathbf{r}^N;t)$
  - Velocity not defined for these dynamics

$$d\mathbf{r}_i = \frac{1}{\gamma}\mathbf{F}_i^B dt$$

$$\left\langle \mathbf{F}_i^B(t) \right\rangle = 0; \left\langle \mathbf{F}_i^B(t)\mathbf{F}_j^B(t') \right\rangle = 2k_B T\gamma\delta(t-t')\delta_{ij}$$

  - Conservation of phase space volume implies Ito’s Formula

$$\frac{df^N}{dt} = \left[\frac{\partial f^N}{\partial t} + \sum_{i=1}^{N}\frac{kT}{\gamma}\frac{\partial^2}{\partial \mathbf{r}_i^2} f^N\right] = 0$$

    - Now, $\rho_k(\mathbf{x},t) = \left\langle \delta(\mathbf{x}-\mathbf{r}_k(t)); f^N(\mathbf{r}^N;t) \right\rangle$
    - and $$\frac{\partial \rho_k(\mathbf{x},t)}{\partial t} = \frac{kT}{\gamma}\left(\frac{\partial^2 \rho_k}{\partial \mathbf{x}^2}\right)$$

Kramers-Klein Equation for OU process (i.e., Langevin dynamics)

- **Consider Liouville phase-space density** $f^N(\mathbf{r}^N, \mathbf{p}^N; \tau_d(\Delta t))$
  - Conservation of phase space volume implies

$$\frac{d}{d\tau_D} f^N(\mathbf{r}^N, \mathbf{p}^N; \tau_d(t)) = \frac{df^N}{dt}\frac{dt}{d\tau_D} = 0$$

From Ito's Lemma

$$\frac{df^N}{dt} = \frac{d\tau_D}{dt}\left[\frac{\partial f^N}{\partial t}\frac{\partial t}{\partial \tau_D} + \sum_{i=1}^{N}\frac{\partial}{\partial \boldsymbol{\chi}_i}\cdot\left(f^N \frac{\partial \boldsymbol{\chi}_i}{\partial t}\frac{\partial t}{\partial \tau_D}\right) + \sum_{i=1}^{N}\gamma kT\frac{\partial^2}{\partial \mathbf{p}_i^2} f^N\right] = 0$$

- Where, $\boldsymbol{\chi}_i(t) = \begin{Bmatrix} \mathbf{r}_i(t) \\ \mathbf{p}_i(t) \end{Bmatrix}$
- and $\rho_i(\mathbf{x}, \mathbf{v}, \tau_D(t)) = \left\langle m\delta(\mathbf{x} - \mathbf{r}_i(t))\delta(\mathbf{v} - \frac{\mathbf{p}_i(t)}{m}); f^N(\mathbf{r}^N, \mathbf{p}^N; \tau_D(t))\right\rangle$

$$\frac{\partial \rho_i(\mathbf{x}, \mathbf{v}, \tau_D(t))}{\partial t} = -\frac{\partial}{\partial \mathbf{x}}\cdot(\rho_i \mathbf{v}) + \frac{\partial}{\partial \mathbf{v}}\cdot\left(\frac{\gamma}{m}\rho_i \mathbf{v}\right) + \frac{\gamma kT}{m^2}\frac{d\tau_D}{dt}\left(\frac{\partial^2 \rho_i}{\partial \mathbf{v}^2}\right)$$

Non-dimensionalized Kramer's Equation

- **Choose the following non-dimensionalization**

$$\hat{\mathbf{x}} = \mathbf{x}/\lambda \;;\; \hat{\mathbf{v}} = \mathbf{v}\Big/\sqrt{kT/m} \;;\; \tau = t/\tau_B$$

  – Where $\lambda = \tau_B \sqrt{kT/m}$

  – Now, write

$$\frac{\partial \rho_i(\hat{\mathbf{x}}, \hat{\mathbf{v}}, \tau_D(\tau))}{\partial \tau} = -\frac{\partial}{\partial \hat{\mathbf{x}}} \cdot (\rho_i \hat{\mathbf{v}}) + \frac{\partial}{\partial \hat{\mathbf{v}}} \cdot (\rho_i \hat{\mathbf{v}}) + \frac{d\tau_D(\tau)}{d\tau} \left(\frac{\partial^2 \rho_i}{\partial \hat{\mathbf{v}}^2} \right)$$

Now reduce

- **Note, from microscopic equations of motion**

$$\frac{\partial \langle \hat{\mathbf{r}}_i(t) \rangle_t}{\partial t} = -\frac{\partial \langle \hat{\mathbf{p}}_i(t)/m \rangle_t}{\partial t} \Rightarrow \partial \hat{\mathbf{x}} = -\partial \hat{\mathbf{v}}$$

$$\frac{\langle \hat{\mathbf{r}}_i(t) \rangle_t - \hat{\mathbf{r}}_i(0)}{\langle \hat{\mathbf{p}}_i(t)/m \rangle_t - \hat{\mathbf{p}}_i(0)/m} = -1 = \tan\theta \,;\ \theta = -\frac{\pi}{4}$$

$$\frac{\partial \rho_i(\hat{\mathbf{x}}, \hat{\mathbf{v}}, \tau_D(\tau))}{\partial \tau} = -2\frac{\partial}{\partial \hat{\mathbf{x}}} \cdot \left(\rho_i \hat{\mathbf{v}}\right) + \frac{d\tau_D(\tau)}{d\tau}\left(\frac{\partial^2 \rho_i}{\partial \hat{\mathbf{x}}^2}\right)$$

- **Now, Integrate over v ($\langle \mathrm{v} \rangle = 0$ at equilibrium) to get**

$$\frac{\partial \rho_i(\hat{\mathbf{x}}, \tau_D(\tau))}{\partial \tau} = \frac{d\tau_D(\tau)}{d\tau}\left(\frac{\partial^2 \rho_i}{\partial \hat{\mathbf{x}}^2}\right)$$

Path Integral – Preliminaries

- **Choose the non-dimensionalization**

$$\hat{\mathbf{x}} = \mathbf{x}/\lambda\,;\ \hat{\mathbf{v}} = \mathbf{v}\Big/\sqrt{kT/m}\,;\ \tau = t/\tau_B$$

  - Where $\lambda = \tau_B \sqrt{kT/m}$

- **Consider Transition Probability for Markov Process**

$$\rho(\hat{\mathbf{q}}) = \frac{1}{\left(\sqrt{2\pi}\right)^3} \exp\left[-\frac{\hat{\mathbf{q}}^2}{2}\right] \qquad \hat{\mathbf{q}} = \hat{\mathbf{x}}\Big/\sqrt{\hat{\tau}_D}\,;\ \hat{\tau}_D = \tau_D/\tau_B$$

  - Gives recursion relation

$$P_n(\hat{\mathbf{q}}) = \frac{1}{\left(\sqrt{2\pi}\right)^{3n}} \int d^3\hat{q}_1 d^3\hat{q}_2 \ldots d^3\hat{q}_{n-1} e^{-S(\hat{\mathbf{q}}_0, \hat{\mathbf{q}}_2, \ldots, \hat{\mathbf{q}}_n)}$$

$$S(\hat{\mathbf{q}}_0, \hat{\mathbf{q}}_2, \ldots, \hat{\mathbf{q}}_n) = \frac{1}{2} \sum_{l=1}^{n} (\hat{\mathbf{q}}_l - \hat{\mathbf{q}}_{l-1})^2$$

$$\hat{\mathbf{q}}_0 = 0;\ \hat{\mathbf{q}}_n = \hat{\mathbf{q}}$$

Path Integral (1) a la Standard Approach

- **Introduce macroscopic time variables**

$$\varepsilon = \frac{\hat{\tau}_D}{n} \qquad \hat{\tau}_l = l\varepsilon\,,\ \hat{\tau}_n = n\varepsilon = \hat{\tau}_D$$

- **Define piecewise continuous path**

$$\hat{\mathbf{x}}(\hat{\tau}'_D) = \sqrt{\varepsilon}\left[\hat{\mathbf{q}}_{l-1} + \frac{\hat{\tau}'_D - \hat{\tau}_{l-1}}{\hat{\tau}_l - \hat{\tau}_{l-1}}\left(\hat{\mathbf{q}}_l - \hat{\mathbf{q}}_{l-1}\right)\right] \qquad \hat{\tau}_{l-1} < \hat{\tau}'_D < \hat{\tau}_l$$

  - Note scaling/conversion pre-factor on RHS?

- **Now** $\dfrac{d\hat{\mathbf{x}}}{d\hat{\tau}'_D} = \dfrac{1}{\sqrt{\varepsilon}}\left(\hat{\mathbf{q}}_l - \hat{\mathbf{q}}_{l-1}\right) = \dfrac{\hat{\mathbf{x}}_l - \hat{\mathbf{x}}_{l-1}}{\varepsilon}$ $\qquad \hat{\mathbf{x}}(0) = 0;\ \hat{\mathbf{x}}(\hat{\tau}_D) = \sqrt{\varepsilon}\,\hat{\mathbf{q}} = \hat{\mathbf{x}}$

$$S(\hat{\mathbf{q}}_0, \hat{\mathbf{q}}_2, \ldots, \hat{\mathbf{q}}_n) \approx S(\hat{\mathbf{x}}(\hat{\tau}_D)) = \frac{1}{2}\int_0^{\hat{\tau}_D}\left(\frac{d\hat{\mathbf{x}}(\hat{\tau}'_D)}{d\hat{\tau}'_D}\right)^2 d\hat{\tau}'_D$$

  - Which leads to

$$P_n(\hat{\mathbf{q}}) = \frac{1}{\left(\sqrt{2\pi}\right)^3}\int\prod_{l=1}^{n-1}\frac{d^3\hat{x}(\hat{\tau}_l)}{\left(\sqrt{2\pi}\sqrt{\varepsilon}\right)^3}\exp\left[-S(\hat{\mathbf{x}})\right]$$

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Continuum Limit (1)

- **Now let** $n \to \infty \Rightarrow \varepsilon \to 0$ **for fixed** t

$$P_n(\hat{\mathbf{q}}) \to \Pi(\hat{\mathbf{x}}, \hat{\tau}_D) = \int \left[d\hat{\mathbf{x}}(\hat{\tau}_D)\right] \exp\left[-S(\hat{\mathbf{x}}(\hat{\tau}_D))\right]$$

$$\Pi(\mathbf{x}, \tau_D) = \mathrm{N}(\tau_D) e^{-\mathbf{x}^2 / 4\frac{kT}{m}\tau_B \tau_D} = \rho(\mathbf{x}, \tau_D)$$

  - Notice this limit is perfectly justified even for finite correlation time
  - Also, recall

$$\rho_i(\mathbf{r}, t) = \left\langle m\delta(\mathbf{r} - \mathbf{R}_i(t)); f^N(\mathbf{R}^N, \mathbf{P}^N; t) \right\rangle = \frac{1}{t}\int_0^t m\delta(\mathbf{r} - \mathbf{R}_i(t'))dt' \approx \frac{1}{M_t}\sum_{k=0}^{M_t} m\delta(\mathbf{r} - \mathbf{R}_i(t_k))$$

$$\to \Pi(\mathbf{r}, t) = \int \left[d\mathbf{r}(t)\right] \exp\left[-S(\mathbf{r}(t))\right]$$

$$\Rightarrow \frac{1}{2kT\tau_B}\int_0^t S(t')dt' = \frac{m}{2kT\tau_B}\int_0^t \left(\frac{d\mathbf{R}_i(t')}{dt'}\right)^2 dt' \approx \frac{m}{2kT\tau_B}\sum_{k=0}^{M_t}\left(\frac{\mathbf{R}_i(t_k) - \mathbf{R}_i(t_{k-1})}{\Delta t}\right)^2 \Delta t$$

Diffusion in Inhomogeneous Fluids: Dynamic, Classical DFT

- **Consider continuity equation of concentration**

$$\frac{d}{dt}P(\mathbf{r}^N,t)=\frac{\partial P(\mathbf{r}^N,t)}{\partial t}+\sum_{i=1}^{N}\nabla_i\cdot\left[\mathbf{v}_iP(\mathbf{r}^N,t)\right]=0$$

  – Recall for steady drag $\mathbf{v}_i(t)=v_{0,i}e^{-t/\tau_B}+\frac{1}{m}\int_0^t e^{-(t-t')/\tau_B}\mathbf{F}_i(t')dt'$

    - Assume force *independent of time* and initial velocity is zero

$$\mathbf{F}_i=-\nabla_iV\left(\mathbf{r}^N\right)=-kT\nabla_i\ln\left[P\left(\mathbf{r}^N\right)\right]-\nabla_iV^{ex}\left(\mathbf{r}^N\right)$$

$$\mathbf{v}_i(t)=\frac{\mathbf{F}_i}{m}\int_0^t e^{-(t-t')/\tau_B}dt'=\frac{\tau_B}{m}\left(1-e^{-t/\tau_B}\right)\mathbf{F}_i$$

    - Which gives

$$\frac{\partial P(\mathbf{r}^N,t)}{\partial t}=\frac{1}{\gamma}\left(1-e^{-t/\tau_B}\right)\sum_{i=1}^{N}\nabla_i\cdot\left[P(\mathbf{r}^N,t)\nabla_iV(\mathbf{r}^N)\right]$$

    - Integrating over *N-1* particles yields

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t}=\frac{1}{\gamma}\left(1-e^{-t/\tau_B}\right)\nabla\cdot\left[\rho(\mathbf{r},t)\nabla\mu(\mathbf{r})\right]$$

$$\nabla\mu(\mathbf{r})\equiv\nabla\left[\frac{\delta F\left[\rho^{eq}(\mathbf{r})\right]}{\delta\rho^{eq}(\mathbf{r})}\right]$$

$$\nabla\mu(\mathbf{r})=kT\nabla\ln\left[\rho(\mathbf{r})\right]+\nabla\mu^{ex}(\mathbf{r})$$

Diffusion in moderately concentrated colloidal suspensions in thermal equilibrium

Langevin Equation with Interations

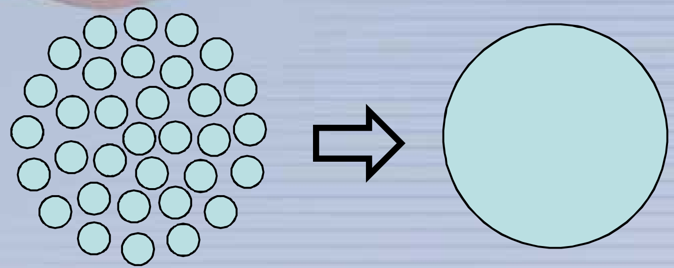
- **Brownian Dynamics Simulations**
  - Markov assumption

$$m\frac{d\mathbf{v}_i}{dt} = -\mathbf{R}\cdot\mathbf{v}_i + \sum_{j\neq i}\mathbf{F}_{ij}^{colloid}\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right) + \mathbf{F}_i^B(t)$$

$$\left\langle \mathbf{F}_i^B(t)\right\rangle = 0; \left\langle \mathbf{F}_i^B(t)\mathbf{F}_j^B(t')\right\rangle = 2\mathbf{R}_{FU}k_B T\delta_{ij}\delta(t-t')$$

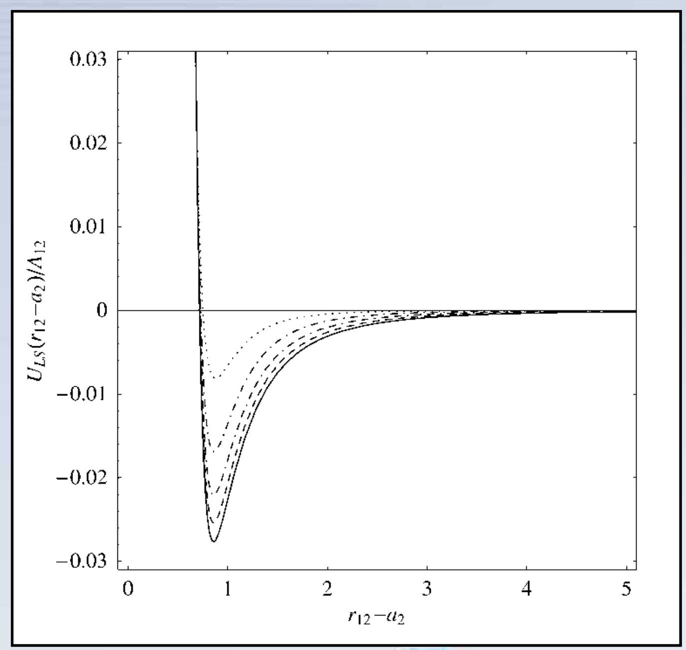
  - $\mathbf{F}^B$ assumed Gaussian distributed and self similar
  - Colloid inertia is often neglected (we don't)
- **Can we transform spatial interactions into time (convolution) integral with memory kernel?**
  - This is a constitutive relation we can measure

Simulation Details: Colloid interactions



- Integrated Lennard-Jones potential[1]
  - Repulsive soft-sphere
    - $a_1 = a_2 = 5\sigma$
    - $A_{12} = 1$
    - $r_c = r_{min} = 30^{-1/6}\sigma$

$$
\begin{aligned}
U_A &= -\frac{A_{12}}{6}\Bigg[\\
&\qquad \frac{2a_1a_2}{r_{12}^2-(a_1+a_2)^2} + \frac{2a_1a_2}{r_{12}^2-(a_1-a_2)^2} + \ln\left(\frac{r_{12}^2-(a_1+a_2)^2}{r_{12}^2-(a_1-a_2)^2}\right)\Bigg] \\
U_R &= \frac{A_{12}}{37800}\frac{\sigma^6}{r_{12}}\Bigg[\\
&\qquad \frac{r_{12}^2-7r_{12}(a_1+a_2)+6\left(a_1^2+7a_1a_2+a_2^2\right)}{(r_{12}-a_1-a_2)^7} \\
&\qquad + \frac{r_{12}^2+7r_{12}(a_1+a_2)+6\left(a_1^2+7a_1a_2+a_2^2\right)}{(r_{12}+a_1+a_2)^7} \\
&\qquad - \frac{r_{12}^2+7r_{12}(a_1-a_2)+6\left(a_1^2-7a_1a_2+a_2^2\right)}{(r_{12}+a_1-a_2)^7} \\
&\qquad - \frac{r_{12}^2-7r_{12}(a_1-a_2)+6\left(a_1^2-7a_1a_2+a_2^2\right)}{(r_{12}-a_1+a_2)^7}\Bigg] \\
U &= U_A + U_R, \qquad r_{12} < r_c
\end{aligned}
$$



[1]R. Everaers and M.R. Ejtehadi, Phys. Rev. E ***67***, 41710 (2003)

Simulation Details: Hydrodynamic Interactions

- **Markovian assumption**
  - Steady state (quasistatic) incompressible Newtonian flow
    - Stokesian Dynamics
      - PME
        - » *O(NlogN)*

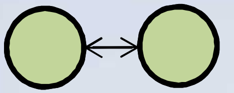
$$R = (I - \mathcal{R})^{-1} R_{1B} + R_{lub}$$

    - Fast Lubrication Dynamics
      - *O(N)*

$$R = R_0 + R_\delta$$

Isotropic Constant
(mean-field mobility)

$$\mathbf{R}_0 = 3\pi\mu d(1+2.16\phi)\mathbf{I}$$

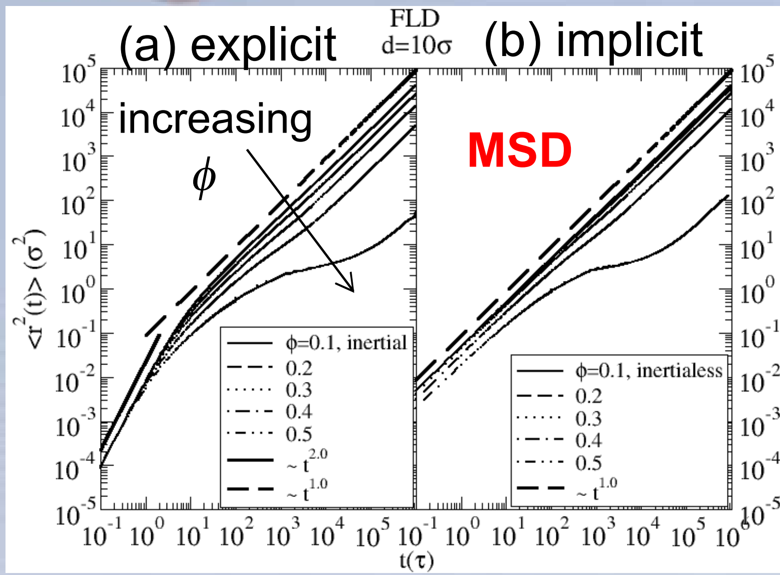


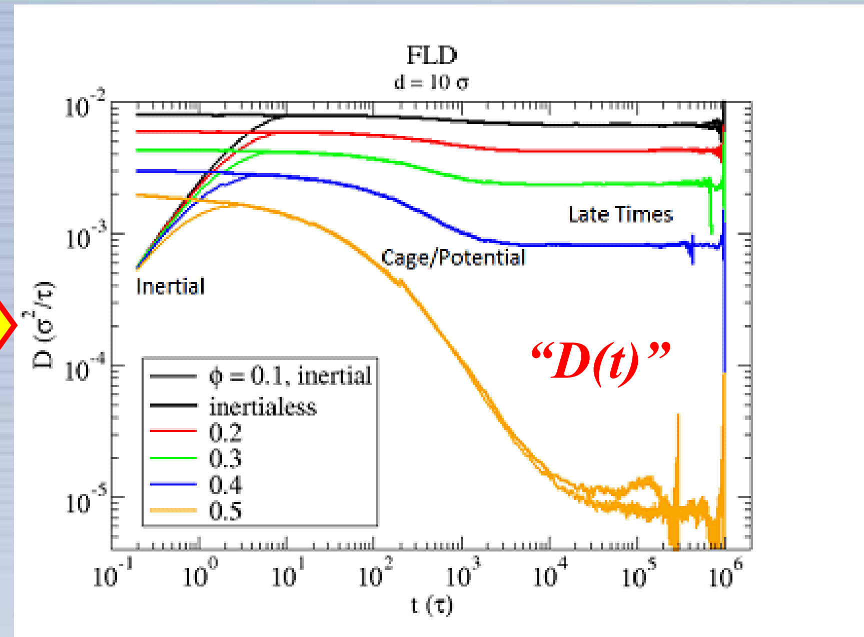
δ

δ^{-1} or $\delta^{-1}+log(\delta^{-1})$

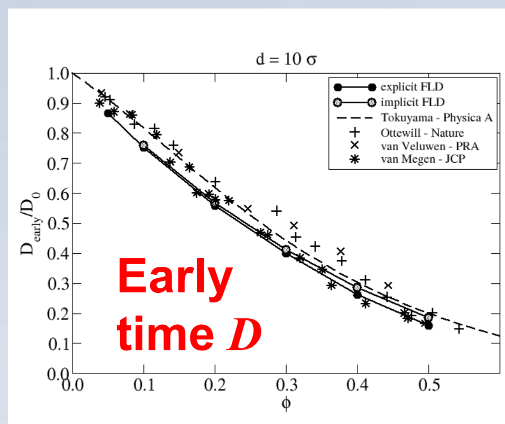
Kumar and Higdon, Phys Rev E, 82, 051401 (2010)
Ball and Melrose, Physica A, 247, 444-472 (1997)

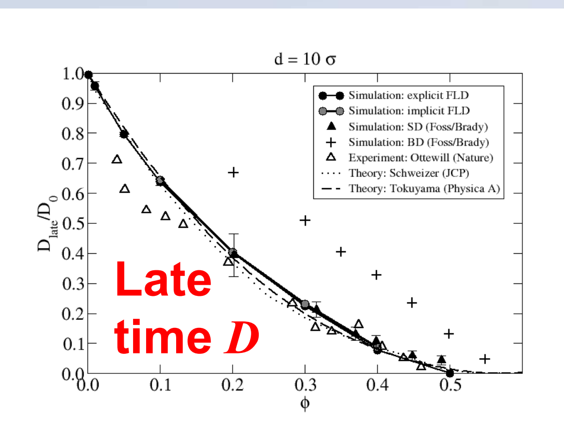
Simulation Results: MSD and Validation



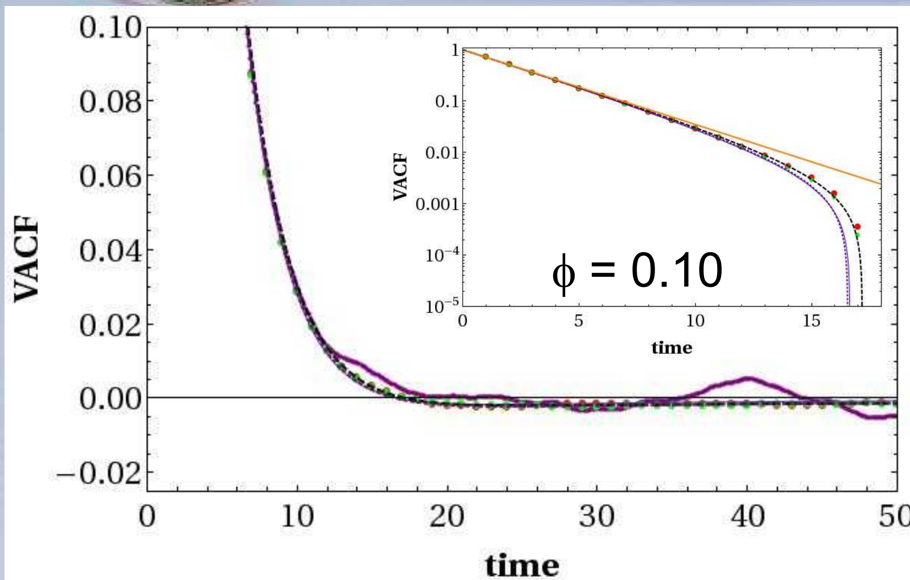


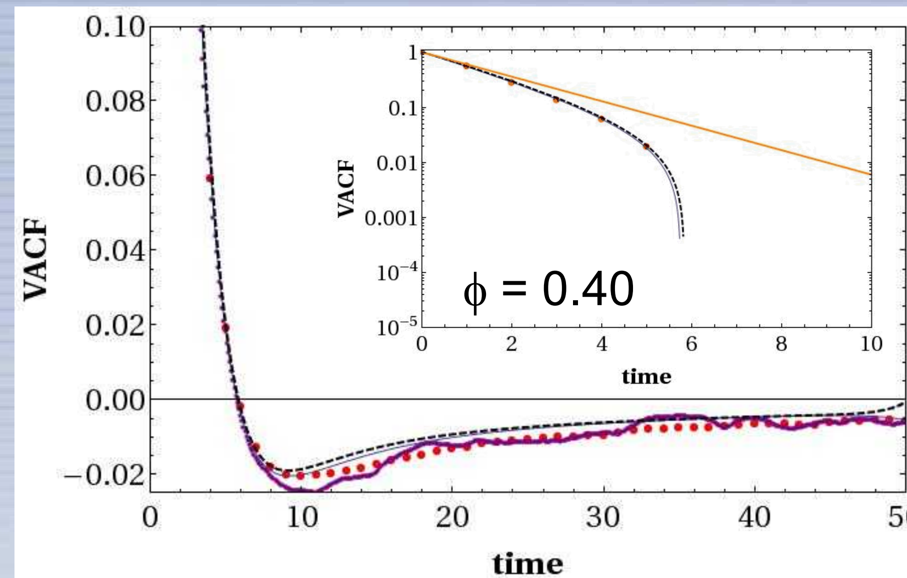
- $MSD = f(t) \neq Dt^{\alpha};\ \alpha \neq 1$
  - "Early" and "Late" time D compare well with experiments
  - Engineer's temptation
    - $D = D(t) \rightarrow MSD = D(t)t$





Simulation Resutls: VACF, Memory Kernel and "Microscopic Dynamics"





- **Fit VACF with**

$$f(t/\tau_B;\tau_{coll},\theta)\propto\sum_{n=0}^{\infty}\frac{(-1)^n(t/\tau_{coll})^{2(n+1)-\theta n-2}}{n!}\sum_{k=0}^{\infty}\frac{(k+n)!(-1)^k}{k!\Gamma(1+2n+k-\theta n)}(t/\tau_B)^k$$

- **Which is a fundamental solution of fBm-type equation**

$$\frac{d\mathbf{v}_i(t)}{dt}=-\frac{1}{\tau_B}\mathbf{v}_i(t)-\frac{1}{\tau_{coll}^{2-\theta}}\int_0^t(t-t')^{-\theta}\mathbf{v}_i(t')dt'+\frac{1}{m_i}\left(\mathbf{F}_i^B(t)+\mathbf{F}_i^{fBm}(t)\right);\quad 0<\theta<1$$

$$\left\langle\mathbf{F}_i^{fBm}(t)\right\rangle=0;\left\langle\mathbf{F}_i^{fBm}(t)\mathbf{F}_i^{fBm}(t')\right\rangle=\frac{2k_BT\gamma}{\tau_{coll}}\left(\frac{t-t'}{\tau_{coll}}\right)^{-\theta}$$

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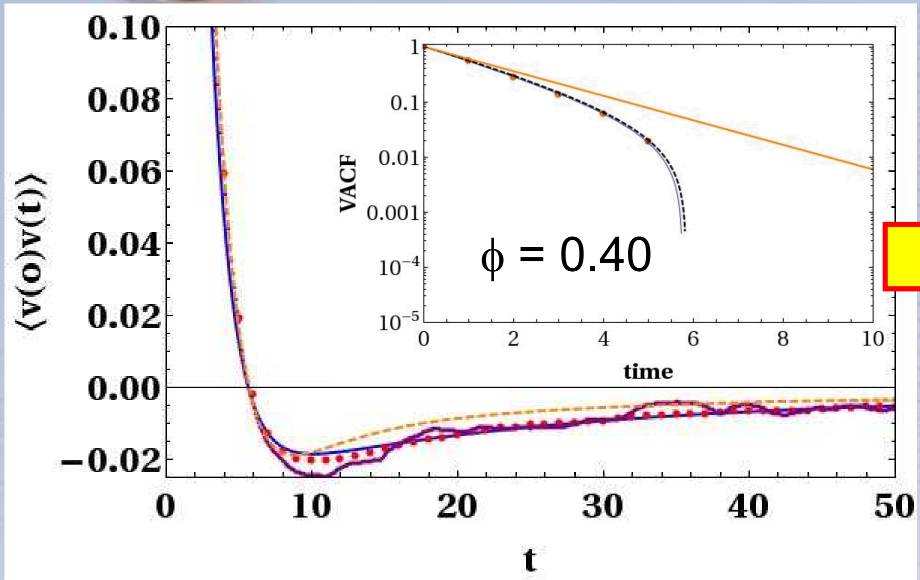
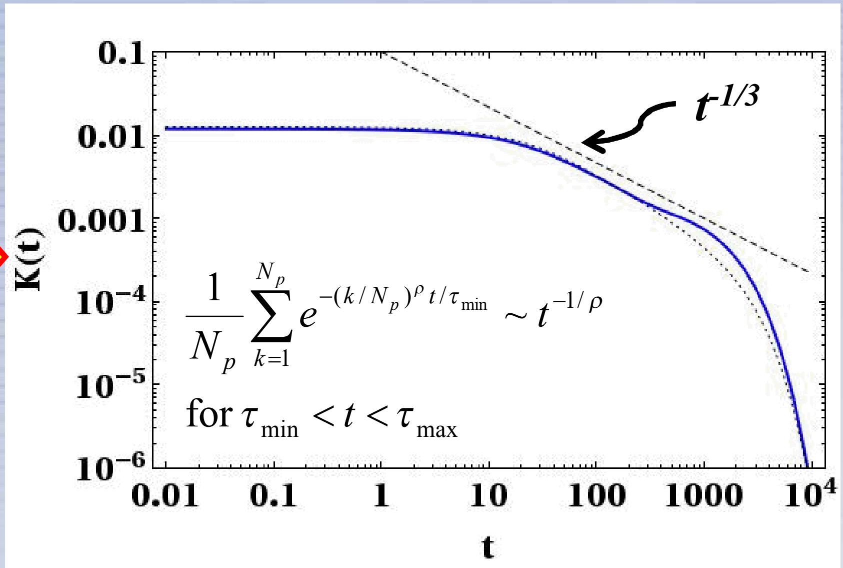
"Microscopic Dynamics": Alternate Form for VACF and Memory Kernel





- **Or, fit VACF with**

$$f(t) = -A_N \sum_{i=0}^{N} c_i \lambda_i e^{-\lambda_i t} \qquad A_N = \frac{1}{\sum_{i=0}^{N} c_i / \lambda_i}$$

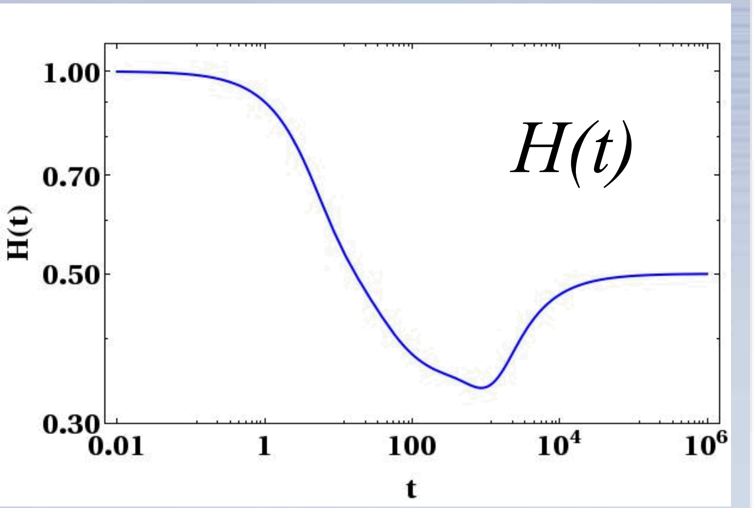
- **Which leads to**

$$m_i \frac{d\mathbf{v}_i(t)}{dt} = -\int_0^t K(t-t')\mathbf{v}_i(t')dt' + \mathbf{F}_i^R(t) \qquad K(t) \sim \delta(t) + \frac{1}{N}\sum_{k=1}^{N} e^{-(k/N)^\rho t/\tau_{coll}}$$

$$0.00574\, e^{-0.0436\, t} + 0.00446\, e^{-0.0105\, t} + 0.00165\, e^{-0.000811\, t} + 0.664\, \delta(t)$$

Relaxation-Diffusion Equation for Colloids

- $MSD = f(t) = Dt^{\alpha(t)};\ \alpha(t) = 2H(t)$
  - Or, $= D\tau_D(t);\ \dfrac{d\tau_D(t)}{dt} = 2H(t)$



$$\left\langle \left|\Delta \mathbf{r}\right|^2 \right\rangle(t) = 6\left(\frac{kT}{m}\tau_B\right)\tau_D(t)$$

$$\tau_D(t) \rightarrow \frac{t}{\tau_B} + \frac{\tau_{coll}}{N\tau_B}\sum_{k=1}^{N}\left(\frac{N}{k}\right)^{\beta_{coll}}\left(1 - e^{-(k/N)^{\beta_{coll}}\, t/\tau_{coll}}\right) - 2(1 - e^{-t/\tau_B});\tau_B < \tau_{coll}$$

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

$$\boxed{\rho(\mathbf{x}, t) = \rho(\mathbf{x}, 0) + D\int_0^t \frac{d\tau_D(t - t')}{dt}\nabla^2 \rho(\mathbf{x}, t')dt'}$$

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Summary: Langevin Equations to Generalized Diffusion Equations

- **Brownian Dynamics Simulations**
  - Markovian: Langevin with interactions

$$m\frac{d\mathbf{v}_i}{dt} = -\mathbf{R}\cdot\mathbf{v}_i + \sum_{j\neq i}\mathbf{F}_{ij}^{colloid}\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right) + \mathbf{F}_i^B(t)$$

$$\left\langle \mathbf{F}_i^B(t)\right\rangle = 0; \left\langle \mathbf{F}_i^B(t)\mathbf{F}_j^B(t')\right\rangle = 2\mathbf{R}_{FU}k_B T\delta_{ij}\delta(t-t')$$

  - Non-Markovian: Generalized Langevin

$$m_i\frac{d\mathbf{v}_i(t)}{dt} = -\int_0^t K(t-t')\mathbf{v}_i(t')dt' + \mathbf{F}_i^R(t)$$

$$K(t) \sim \delta(t) + \frac{1}{N}\sum_{k=1}^{N} e^{-(k/N)^{\rho}\, t/\tau_{coll}}$$

$$\left\langle \mathbf{F}_i^R(t)\right\rangle = 0; \left\langle \mathbf{F}_i^R(t)\mathbf{F}_j^R(t')\right\rangle = 2k_B T\delta_{ij}K(t-t')$$

- **Can transform spatial interactions into convolution integral + "noise"**
  - Then can obtain relaxation-diffusion equation

Micro-rheology to Macro-rheology

- **Mason and Weitz**
  - microscopic memory function proportional to macroscopic bulk frequency-dependent viscosity (mean-field approximation)

$$\frac{d\mathbf{v}_i(t)}{dt} = \int_0^t K(t-t')\mathbf{v}_i(t')dt' + \mathbf{F}_i^R(t) \qquad \tilde{\mu}(s) = \frac{\tilde{K}(s)}{6\pi a} \qquad \tilde{\mu}(s) \approx \tilde{G}_r(s)$$

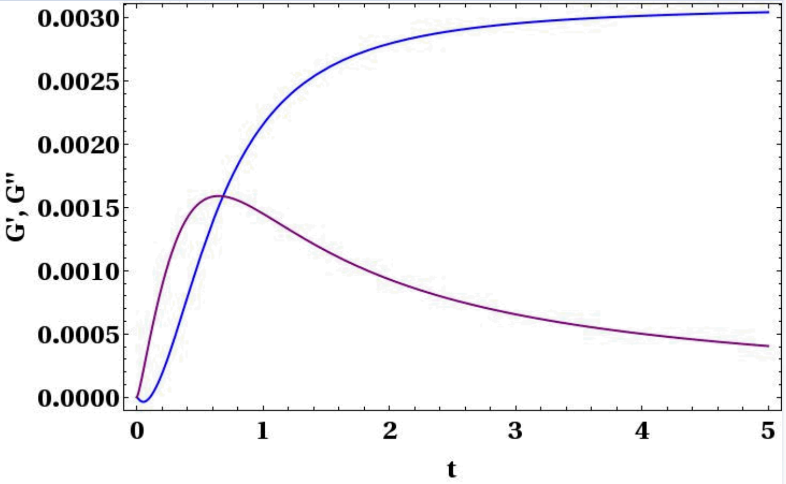
- **Relaxation Modulus for Transient BD**

$$\tilde{G}_r(s) \approx \frac{\tilde{K}(s)}{6\pi a} \sim \frac{1}{6\pi N a} \sum_{k=1}^{N} \frac{\tau_{coll}}{s\tau_{coll} + (k/N)^\rho} \qquad K(t) \sim \frac{1}{N}\sum_{k=1}^{N} e^{-(k/N)^\rho\, t/\tau_{coll}}$$

- **Viscoelastic (complex) modulus**

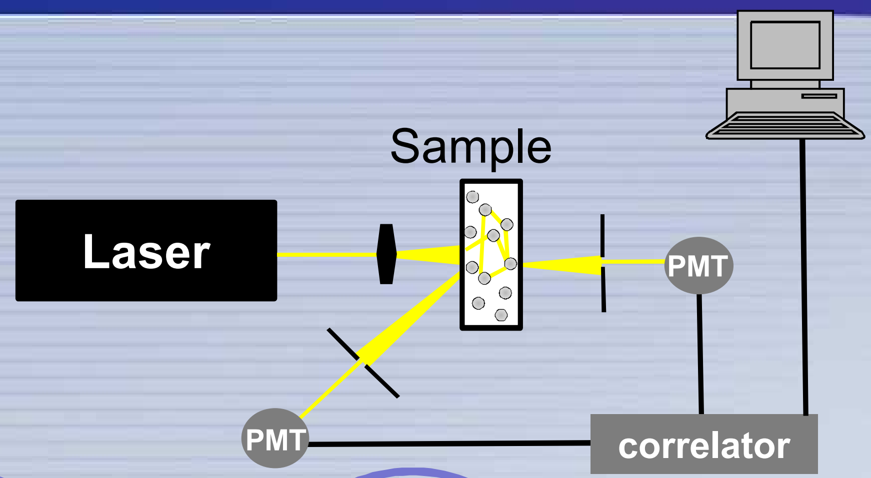
$$\tilde{G}(s) = s\tilde{G}_r(s); \quad s \to i\omega$$

$$G^*(\omega) \sim \frac{1}{6\pi N a} \sum_{k=1}^{N} \frac{\tau_{coll}}{i\omega\tau_{coll} + (k/N)^\rho}$$

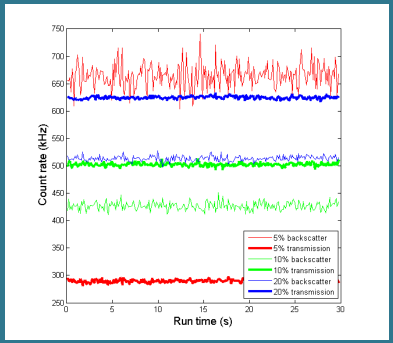


Validation: Diffusing-Wave Spectroscopy

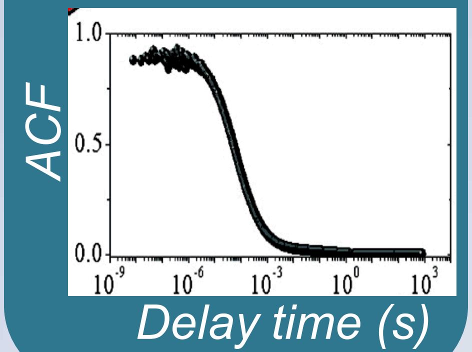
- **Diffusivity of turbid suspensions**
- **Connect stochastic colloidal dynamics to rheology**



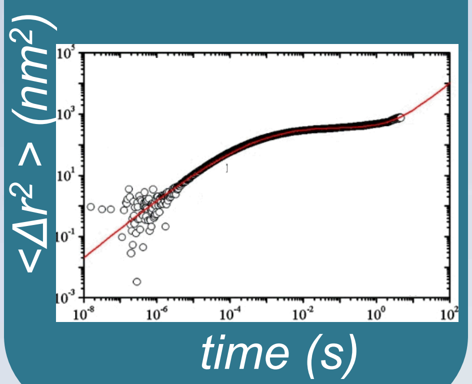
Measure:
intensity fluctuations vs. time



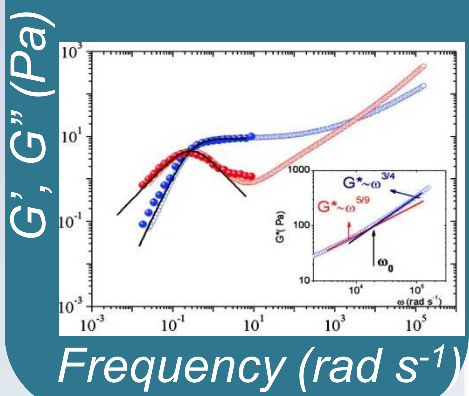
Autocorrelation :
Transmission-> f(τ, l*)
Backscatter-> f(τ)



Mean square displacement



Rheology



Analysis of Macro models: CTRW

Generalized ("Anomolous") Diffusion

- **Some *possible* models – nonlinear FPE, FFPE, etc.**
- **Consider CTRW with multiple time scales of the form**

$$\frac{\partial \rho(x,t)}{\partial t} - \int_0^t g(t-t')\frac{\partial \rho(x,t')}{\partial t'}dt' = D\frac{\partial}{\partial t}\int_0^t g(t-t')\frac{\partial^2 \rho(x,t')}{\partial x^2}dt' \quad [1]$$

  - Assume jump pdf can be decoupled into jump length pdf and waiting time pdf

$$\psi(k,s) = \phi(k)g(s)$$

  - Assume jump length pdf is Gaussian
    - true for long times in any finite variance jump length distribution

$$\phi(k) \sim 1 - Dk^2 + O(k^4)$$

  - Waiting time distribution, *g(t)*

$$\rho(k,s) = \frac{1-g(s)}{s}\frac{\rho_0(k)}{1-(1-Dk^2)g(s)}$$

[1] Fa and Mendes (2010), *J. Stat. Mech.*

Macroscopic, Deterministic Equation for NonMarkovian Stochastic Dynamics

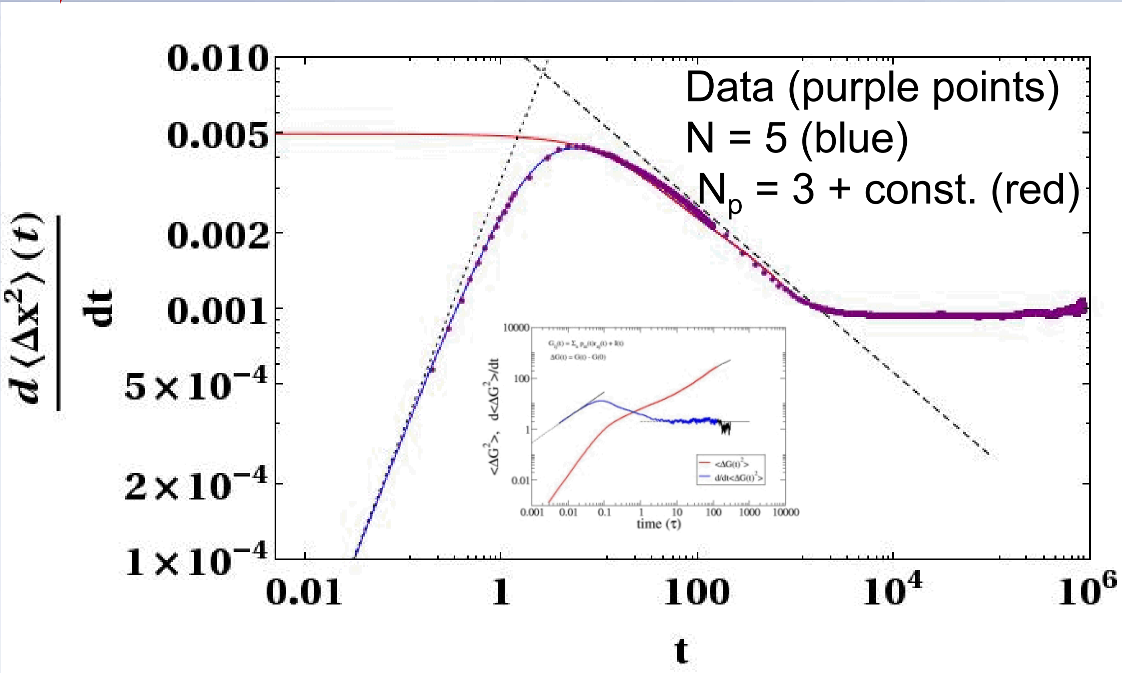
- **CTRW**
  - **Solution**

$$\rho(k,s) = \frac{1-g(s)}{s}\frac{\rho_0(k)}{1-(1-Dk^2)g(s)} \quad \Rightarrow \quad s\left\langle \Delta\tilde{x}^2(s)\right\rangle - \left\langle \Delta x^2(0)\right\rangle = \frac{2Dg(s)}{1-g(s)}$$

  - **Choose *g(t)***

$$g(t) = A_N \sum_{i=0}^{N} c_i e^{-\lambda_i t}$$

$$A_N = \frac{1}{\sum_{i=0}^{N} c_i / \lambda_i}$$

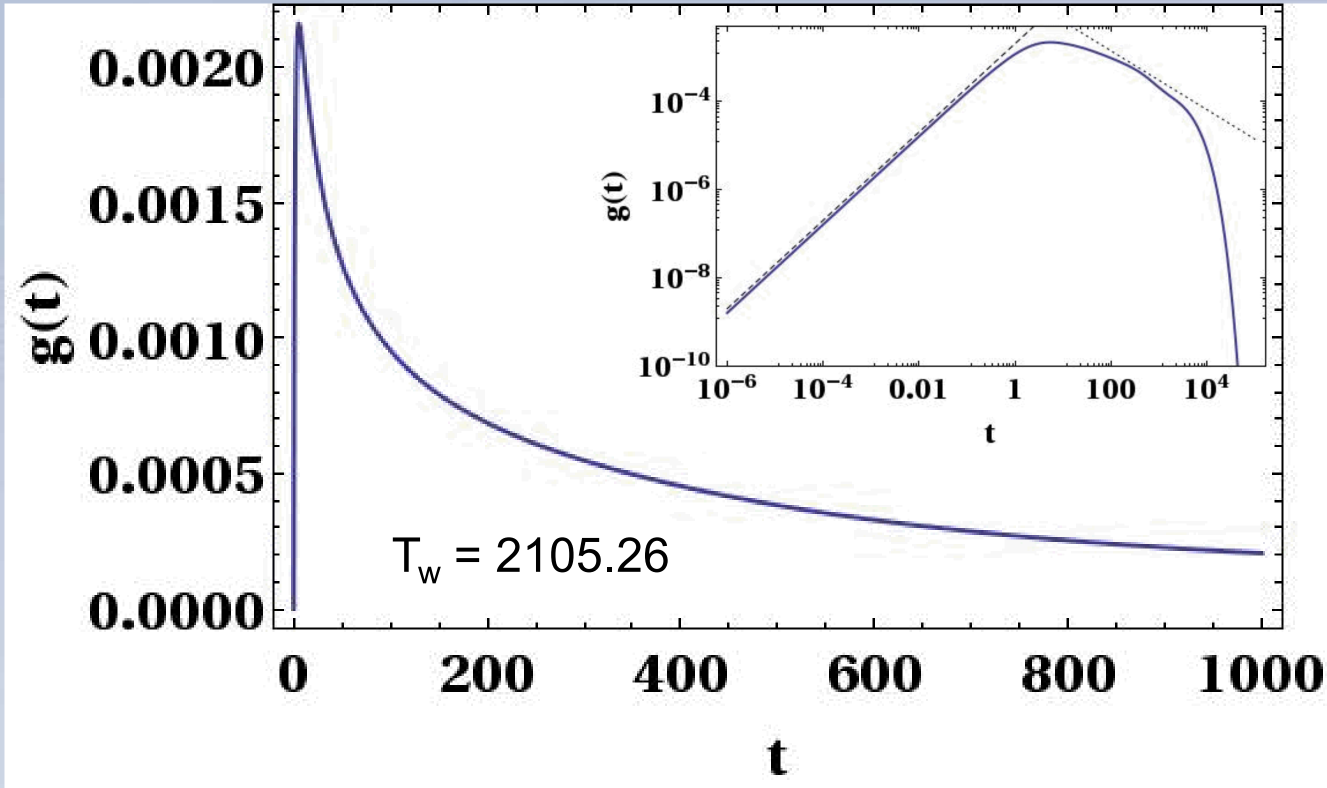


  - **Note:**

$$\frac{1}{N_p}\sum_{k=1}^{N_p} e^{-(k/N_p)^{\rho} t/\tau_{\min}} \sim t^{-1/\rho} \quad \text{for } t > \tau_{\min}$$

Waiting Time Distribution

- **Note:** $s\left\langle \Delta\tilde{x}^2(s)\right\rangle - \left\langle \Delta x^2(0)\right\rangle = \dfrac{2Dg(s)}{1-g(s)}$

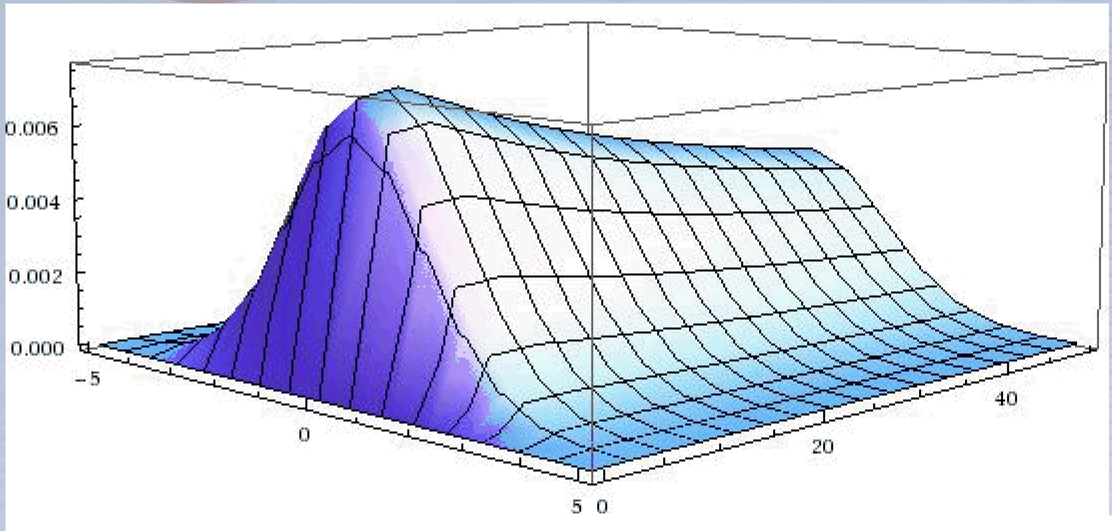


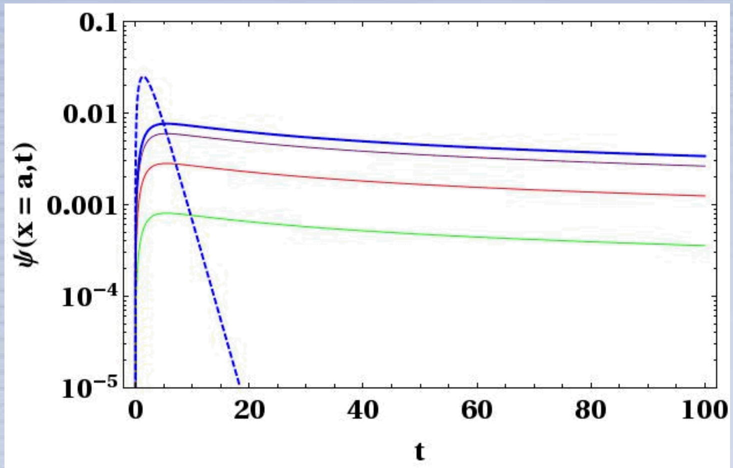
$$g(t) = A_N \sum_{i=0}^{N} c_i e^{-\lambda_i t}$$

$$A_N = \frac{1}{\sum_{i=0}^{N} c_i / \lambda_i}$$

$$-0.00249419\, e^{-0.664182\, t} + 0.000725312\, e^{-0.0562511\, t} + 0.00074885\, e^{-0.0171688\, t} + 0.000801025\, e^{-0.00280788\, t} + 0.000219001\, e^{-0.000330834\, t}$$

Full Jump Distributions

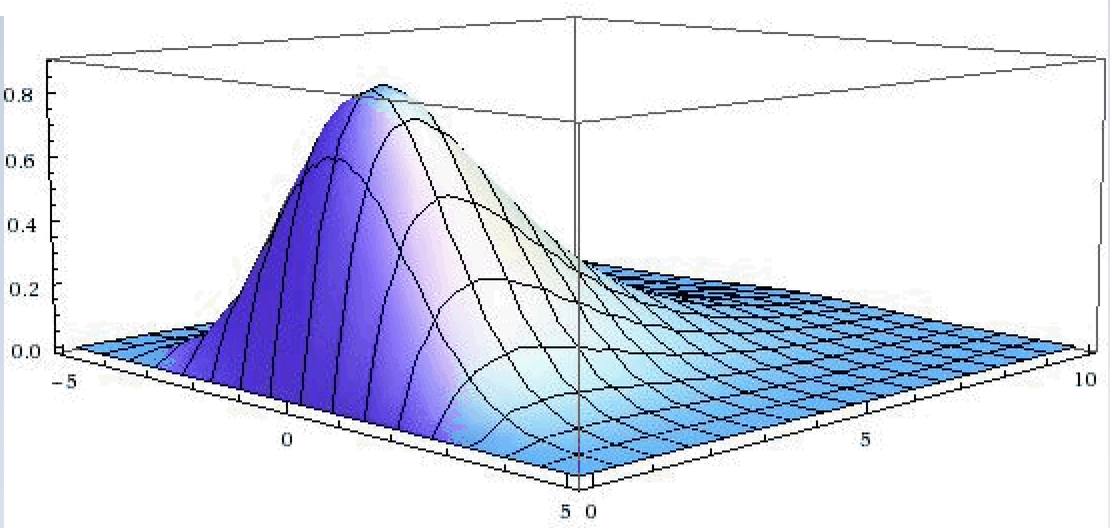




- **Recall**

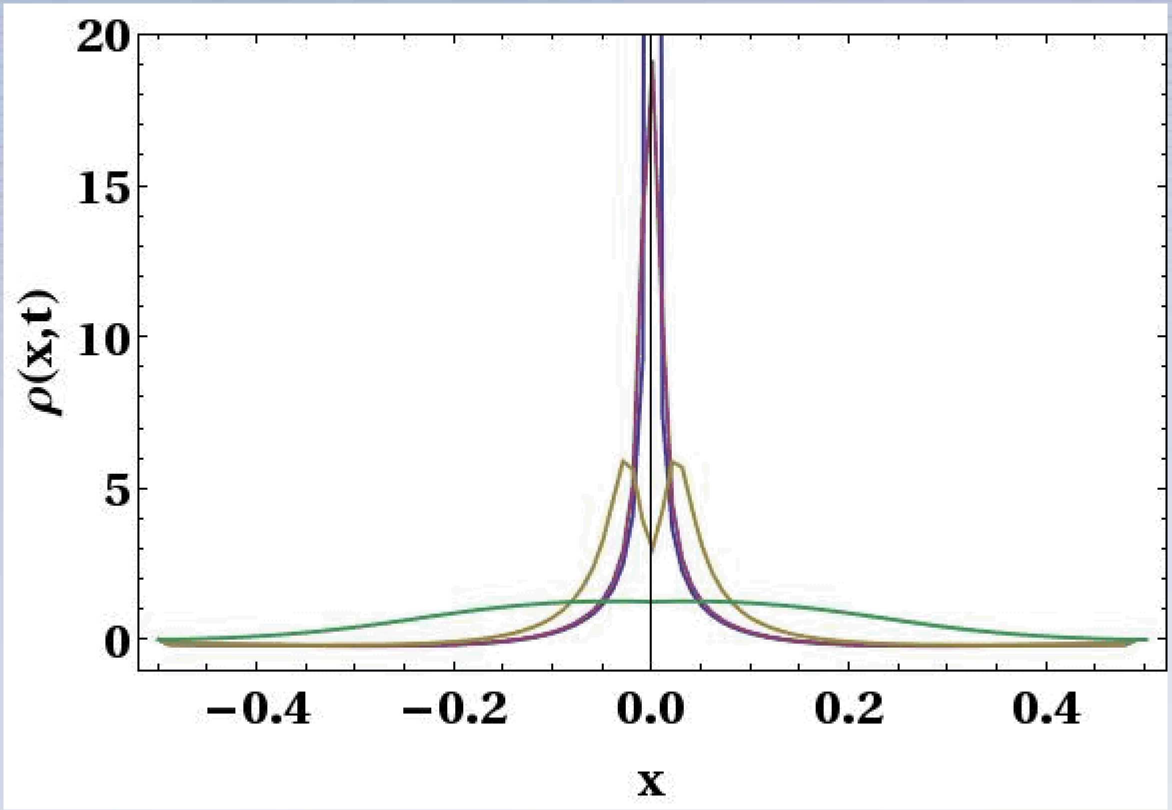
$$\psi(k,s) = g(s)\phi(k)$$

$$\phi(k) = 1 - \sigma^2 k^2$$



Green's Function for CTRW

- **Note:** $\rho(k,s) = \dfrac{1-g(s)}{s} \dfrac{W_0(k)}{1-\psi(k,s)}$



Conclusions

- **Developing Meso-to-Macroscale Modeling framework**
  - Nonequilibrium Statistical Physics/Thermodynamics
- **Solution of Langevin Equation with interactions leads to GLE**
  - Can obtain Memory Kernel of “reasonable” form via VACF
  - Leads to rheology
    - Comparison to Experiments forthcoming
- **Can determine waiting time distribution for CTRW**
  - Assuming Gaussian Jumps
  - Leads to Generalized diffusion equation
    - However, CTRW framework not consistent in dilute limit!?
    - Sum of exponentials may be “degenerate”

Acknowledgements

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