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Toward Model Development and Property Prediction in Heterogeneous Materials

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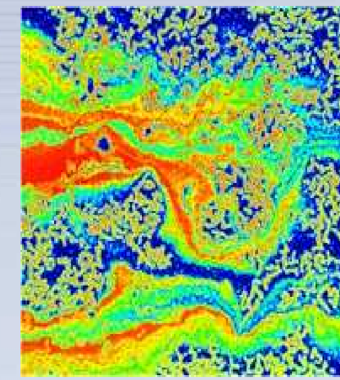
Outline

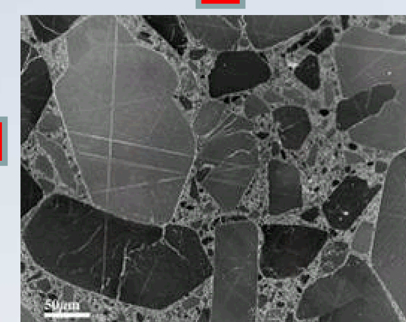
- **Background**
  - Transport of and through heterogeneous materials
    - General mass/charge, momentum, energy balances
    - "Anomalous" diffusion
- **Particle-based simulations**
  - Complex, discrete-particle kinematics
  - Deployment Mod-Sim tool a case study
- **Analysis Macro-scale models**
  - Continuous Time Random Walk (CTRW)
- **Toward a Meso-to-Macro framework for model development**
  - Non-equilibrium Statistical Physics/Thermodynamics
  - What are the component/process scale governing equations in complex, far-from-equilibrium systems?

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”
      - **Discrete particles** in polymer matrix or **suspending fluid**
      - Composites
- **Generalized, nonequil. continuum Transport**
  - **Generalized Diffusion**
    - **“Anomalous”**

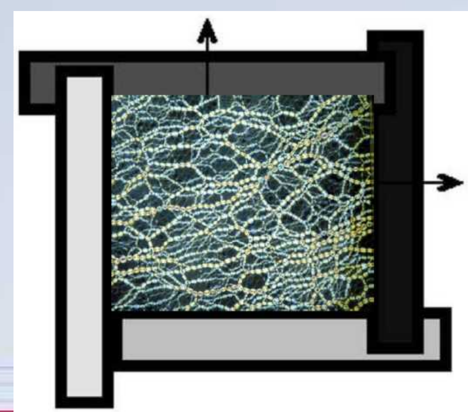


Static μstruct



dynamic

μstruct



LDRD

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Project Goals

- **Develop models that accurately model the underlying events/processes on range of scales**
  - Models must be amenable to math analysis
  - Constitutive relations required to close model equations should be directly accessible experimentally
  - To be predictive
    - Need access to range of length and time scales to close gaps between
      - Discrete constituents and component/process scale
      - Simulation and experimental run-time and product life span
    - Need workflow path to parameterize constitutive relations on relevant scales
- **Novel models push the boundary of V&V to become Discovery tools**
  - Advance experimental analysis capabilities and elucidate underlying phenomena

Technical Approach

- **Starting point**
  - Spatially nonlocal model: $\rho \frac{D}{Dt}\mathbf{u} + \nabla \cdot \boldsymbol{\sigma}_K(\mathbf{r};t) = \int_{\Re^3} g(\mathbf{r},\mathbf{r}')d\mathbf{r}'$
- **Extensions – what's new**
  - Model development
    - Stochastic nonlocal equation of motion

$$\rho D\mathbf{u} = [-\nabla \cdot \boldsymbol{\sigma}_K(\mathbf{r};t) + \int_{\Re^3} g_c(\mathbf{r},\mathbf{r}') + \underbrace{g_d(\mathbf{r},\mathbf{r}')}\, d\mathbf{r}']Dt + \underbrace{\mathbf{B}(\mathbf{r};t)d\mathbf{W}(t)}$$

FDR

    - Implement & Validate nonlocal constitutive relations
      - *Nonlocal time/history*
  - Model analysis of scale bridging (verification)
    - Microscopic stochastic process to macroscopic balance equations
    - Statistical analysis/data mining tool kit for quantitative "prediction"
  - Constitutive relations measured by probing range of scales (validation)

Classical Langevin and Diffusion Equations: Micro-Macro and "Nonlocal" Connections

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

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

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

- **Assume: Steady-state (no history) and Gaussian random force**

$$\left.\begin{aligned} \gamma(t-t') &= \gamma\delta(t-t') \\ \mathbf{f}(t) &= \mathbf{F}^B(t) \end{aligned}\right\}$$

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

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

  - Interactionless, Markovian, SDE → PDE

Diffusion in concentrated colloidal suspensions

Langevin Equation with Interations

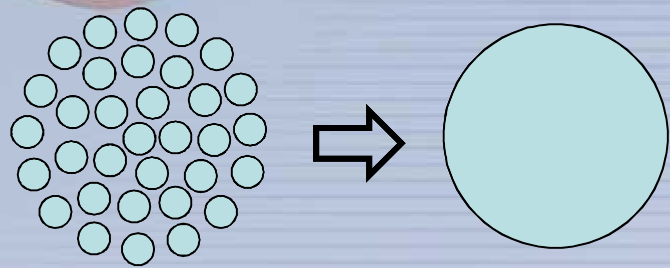
- **Brownian Dynamics Simulations**
  - Markov assumption

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

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

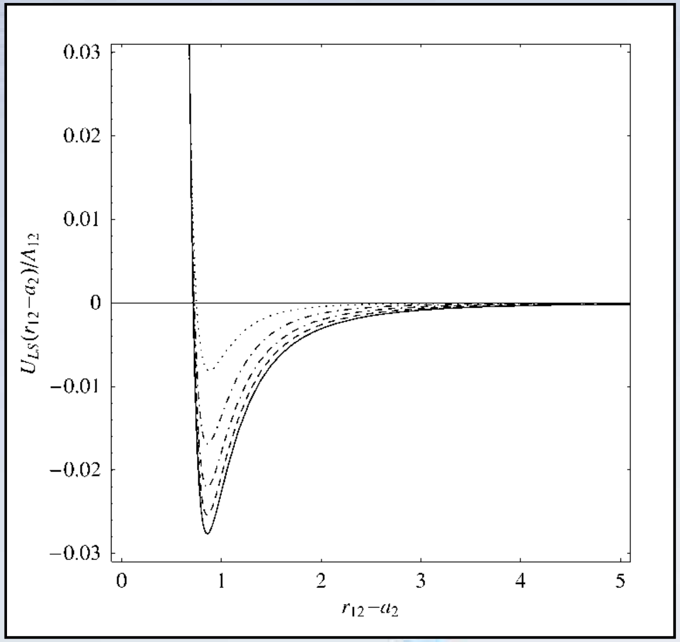
  - $\mathbf{F}^B$ assumed Gaussian distributed and self similar
  - Colloid inertia is often neglected (we don’t)
- **Can we transform spatial interactions into time (convolution) integral with memory kernel?**
  - This is a constitutive relation we can measure

Simulation Details: Colloid interactions



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

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



[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)*

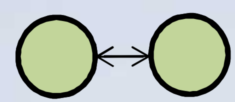
$$R = (I - \mathcal{R})^{-1} R_{1B} + R_{lub}$$

    - Fast Lubrication Dynamics
      - *O(N)*

$$R = R_0 + R_\delta$$

Isotropic Constant
(mean-field mobility)

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

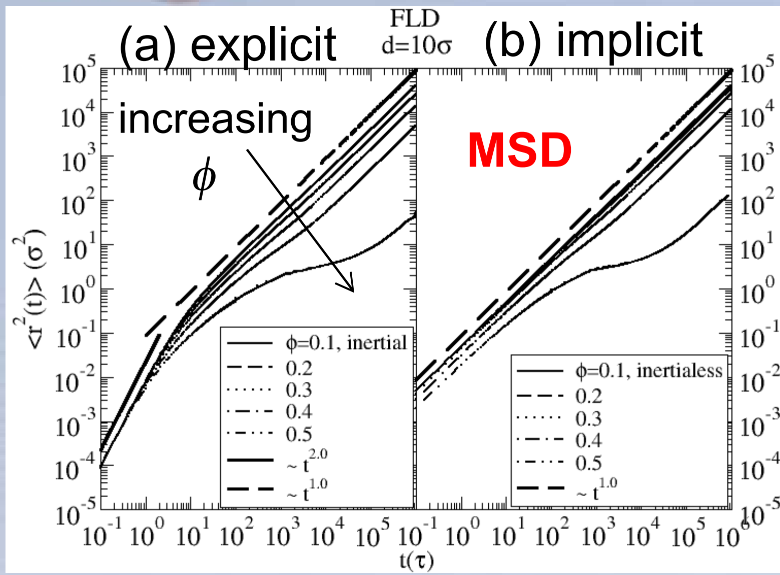


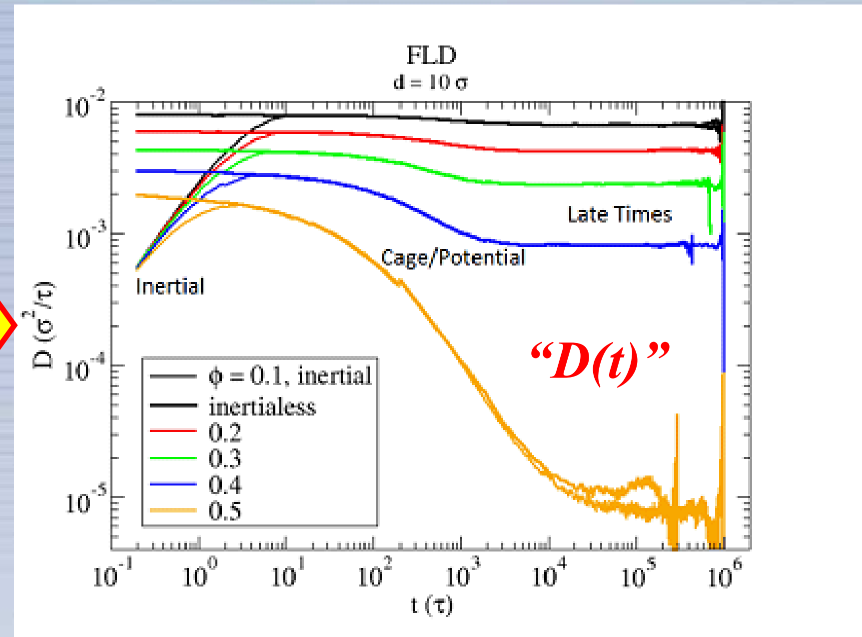
δ

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

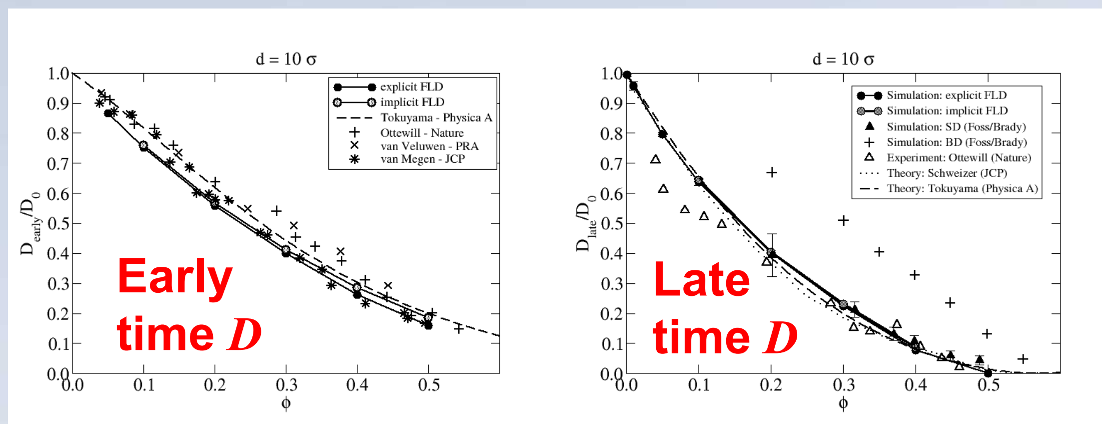
Kumar and Higdon, Phys Rev E, 82, 051401 (2010)
Ball and Melrose, Physica A, 247, 444-472 (1997)

Simulation Results: MSD and Validation





- $MSD = f(t) \neq Dt^{\alpha};\ \alpha \neq 1$
  - Engineer's temptation
    - $D = h(t) \rightarrow MSD = h(t)t$
  - What does this mean **physically** and mathematically?
    - **Validation** & Verification



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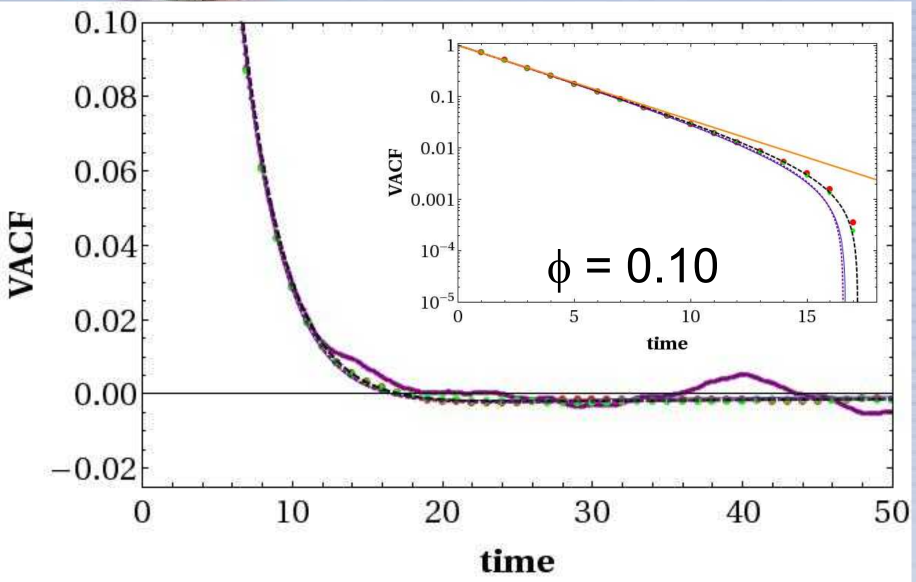
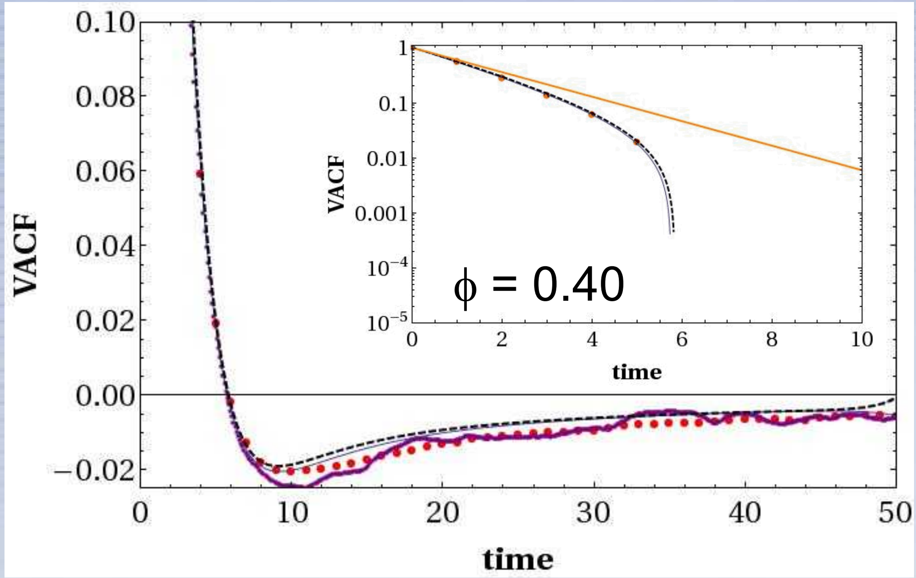
Simulation Resutls: VACF, Memory Kernel and "Microscopic Dynamics"





- **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**

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

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

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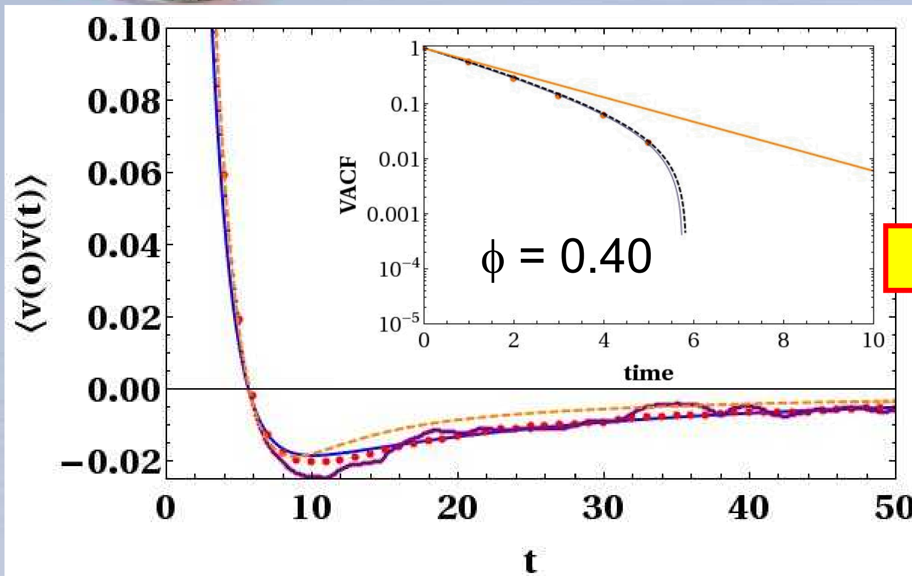
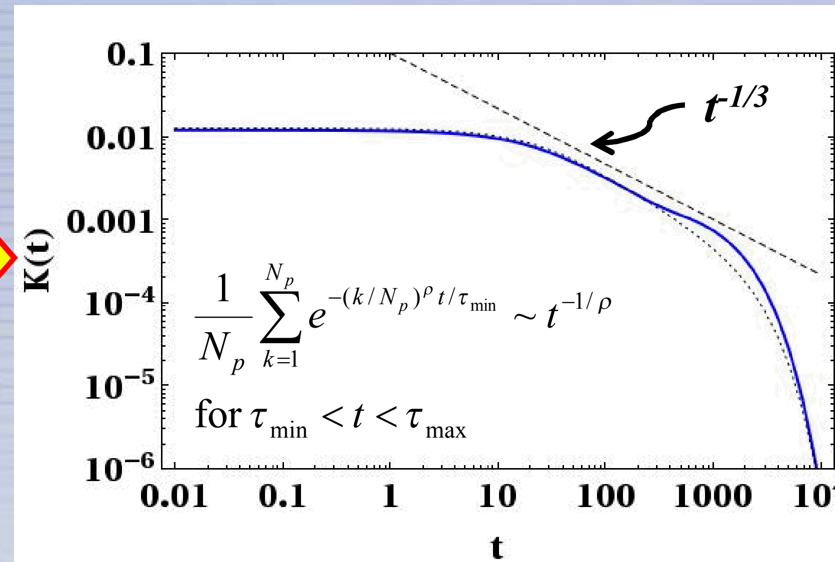
"Microscopic Dynamics": Alternate Form for VACF and Memory Kernel





- **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**

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

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

Summary: Langevin 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”**

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Validation: DWS

Micro-rheology to Macro-rheology

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

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

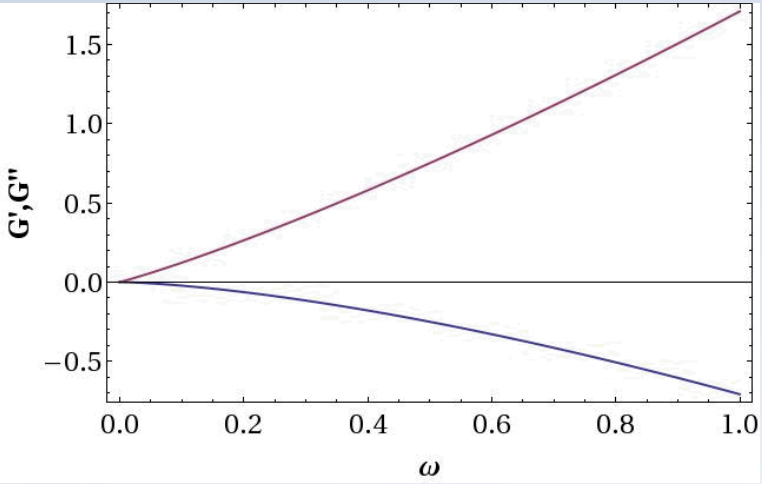
- **Relaxation Modulus for Transient BD**

$$\tilde{G}_r(s) \approx \frac{\tilde{K}(s)}{6\pi a} =$$

- **Viscoelastic (complex) modulus**

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

$$G^*(\omega) \sim$$



Linear, Oscillatory Macro-rheology

- **Prescribe deformation measure stress**

$$\boldsymbol{\sigma}(t) = 2\int_0^\infty \mu(t-t')\dot{\boldsymbol{\varepsilon}}dt' = -2\int_0^\infty \frac{d\mu(t-t')}{dt'}\boldsymbol{\varepsilon}dt' + c$$

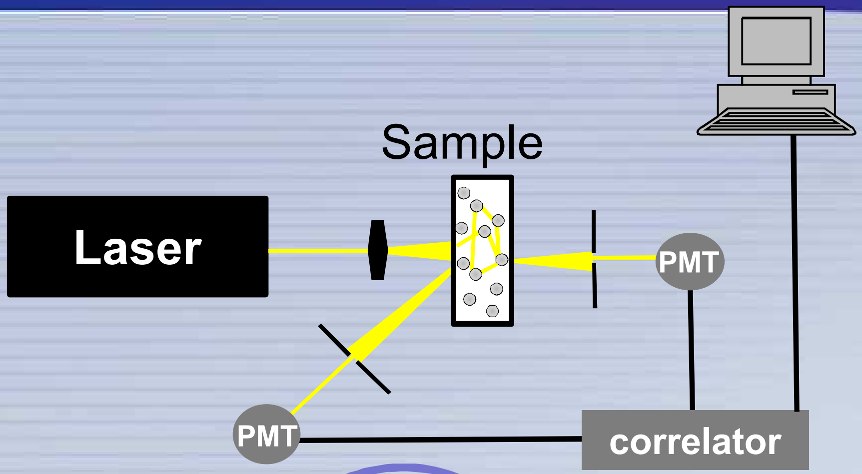
- **Green-Kubo – linear response**

$$\mu(t) = \frac{1}{Vk_BT}\int_0^t \left\langle J_{xy}(t')J_{xy}(0)\right\rangle dt'$$

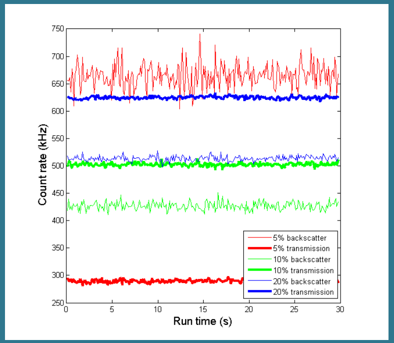
$$G(t) = \frac{d\mu(t)}{dt} = \frac{1}{Vk_BT}\left\langle J_{xy}(t')J_{xy}(0)\right\rangle$$

Validation: Diffusing-Wave Spectroscopy

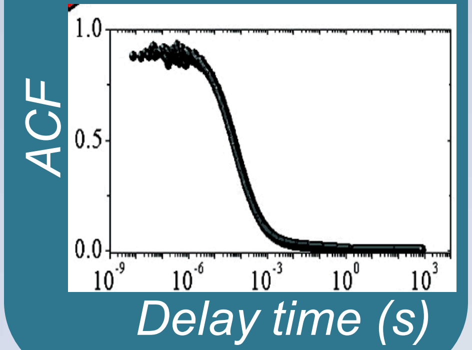
- **Diffusivity of turbid suspensions**
- **Connect stochastic colloidal dynamics to rheology**



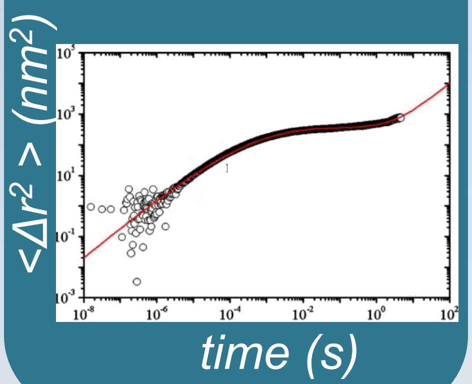
Measure:
intensity fluctuations vs. time



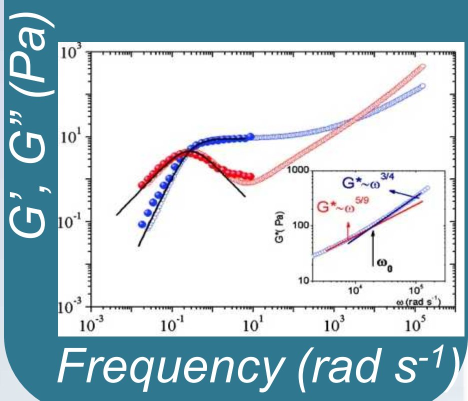
Autocorrelation :
Transmission-> f(τ, l*)
Backscatter-> f(τ)



Mean square displacement



Rheology



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Analysis of Macro models: CTRW

Generalized Diffusion Equation

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

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

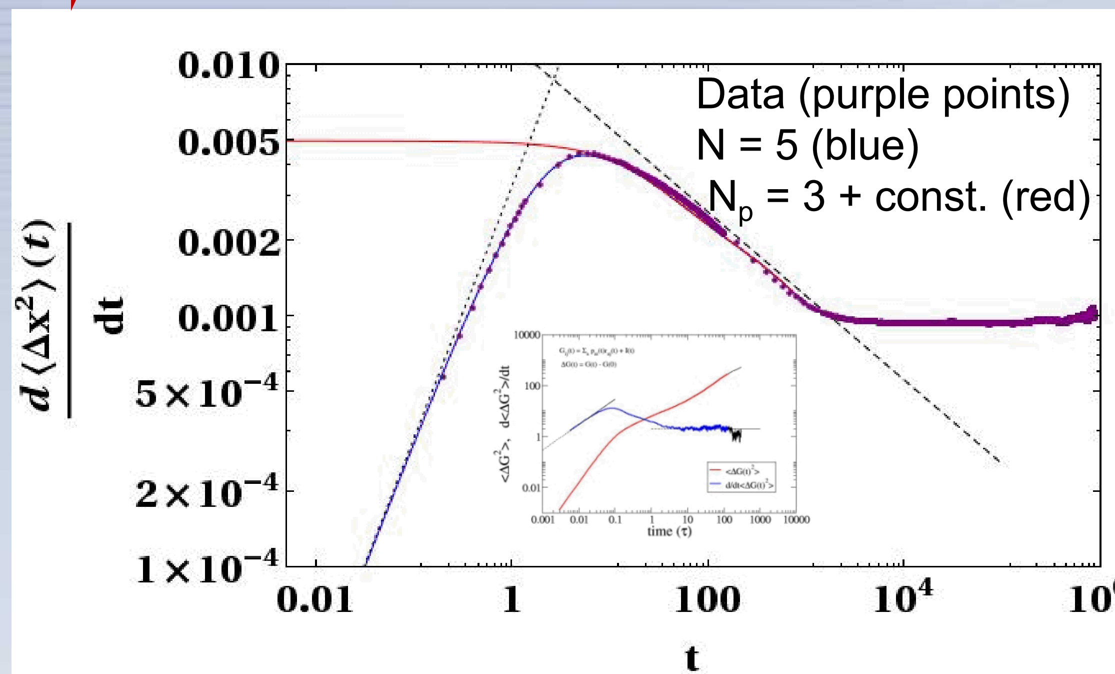
- **CTRW**
  - **Solution**

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

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

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

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

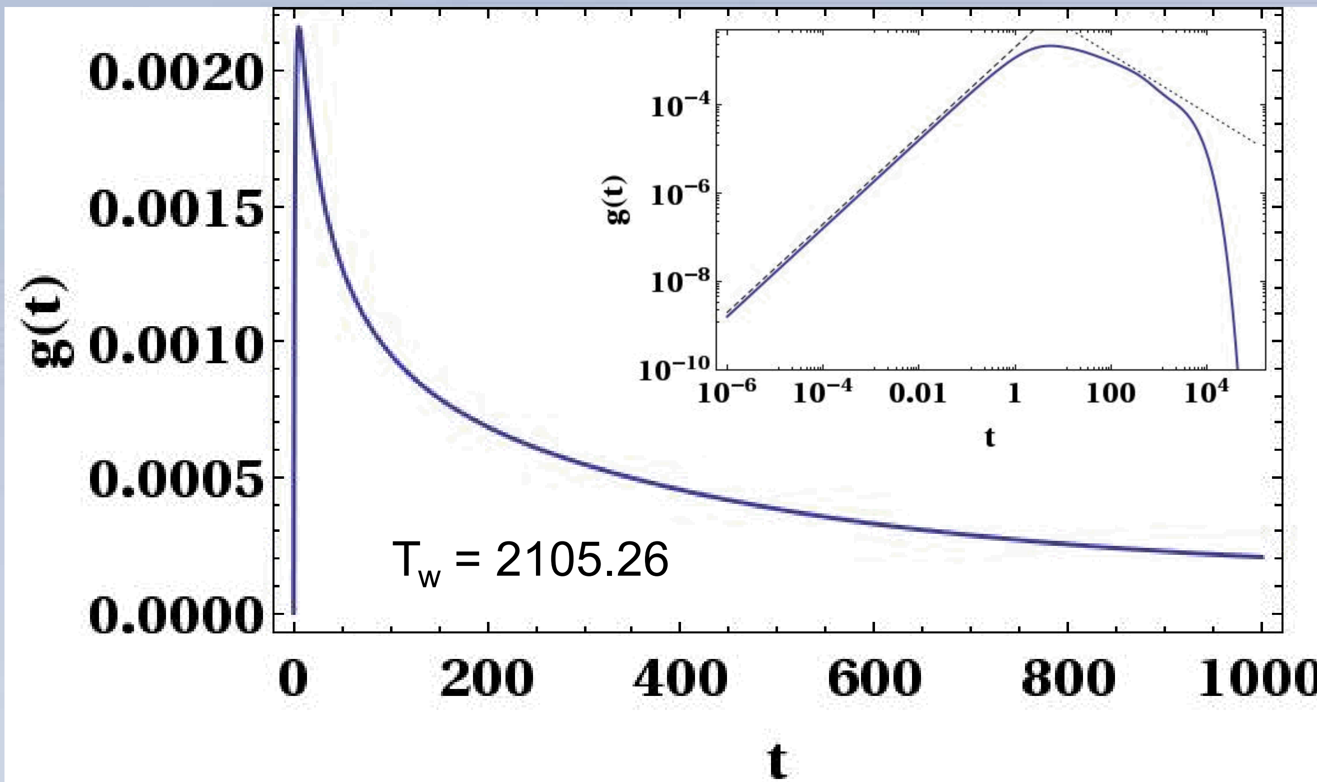


  - **Note:**

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

Waiting Time Distribution

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

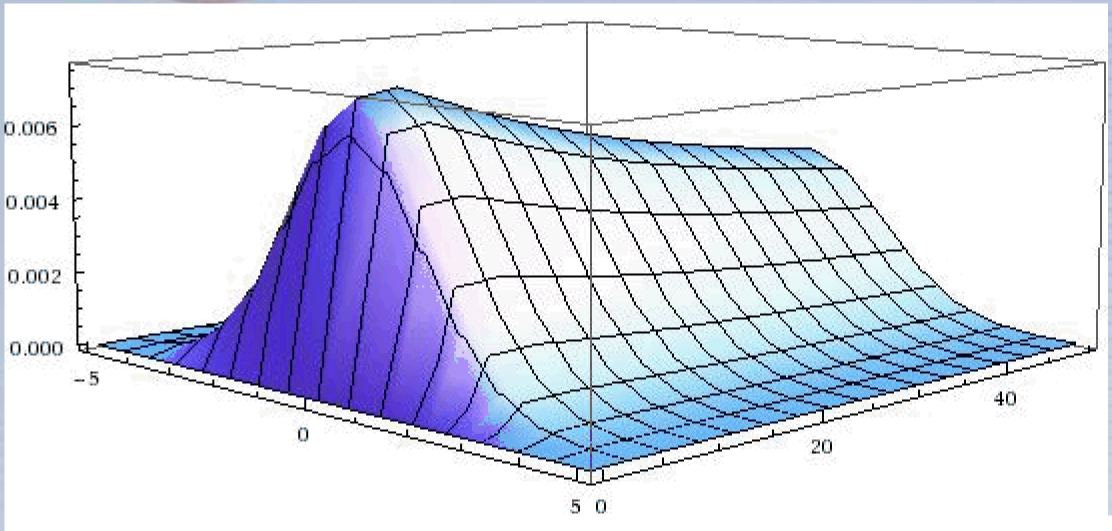


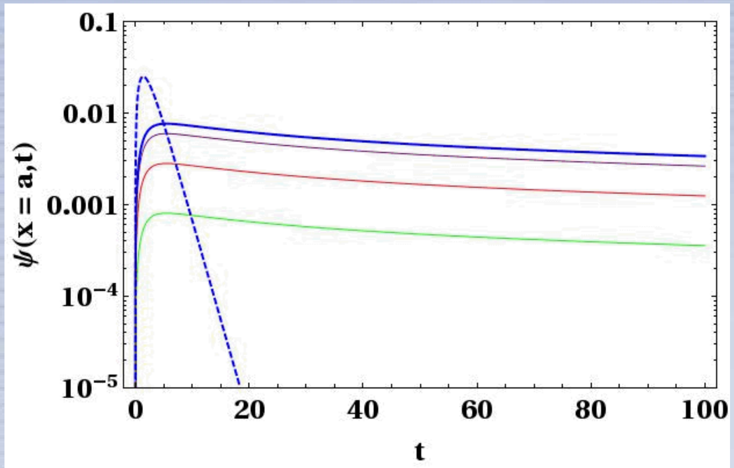
$$g(t) = A_N \sum_{i=0}^{N} c_i e^{-\lambda_i t}$$

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

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

Full Jump Distributions

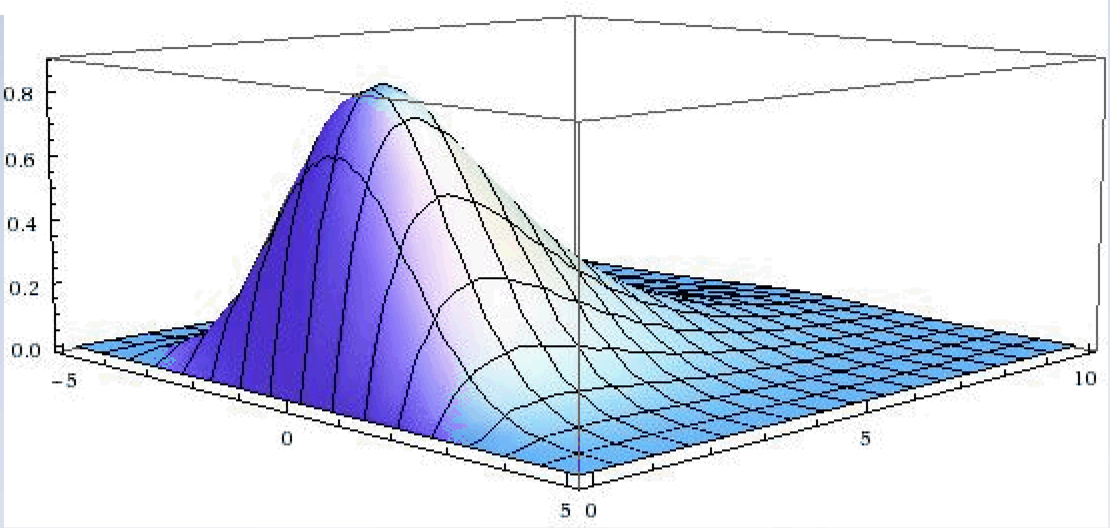




- **Recall**

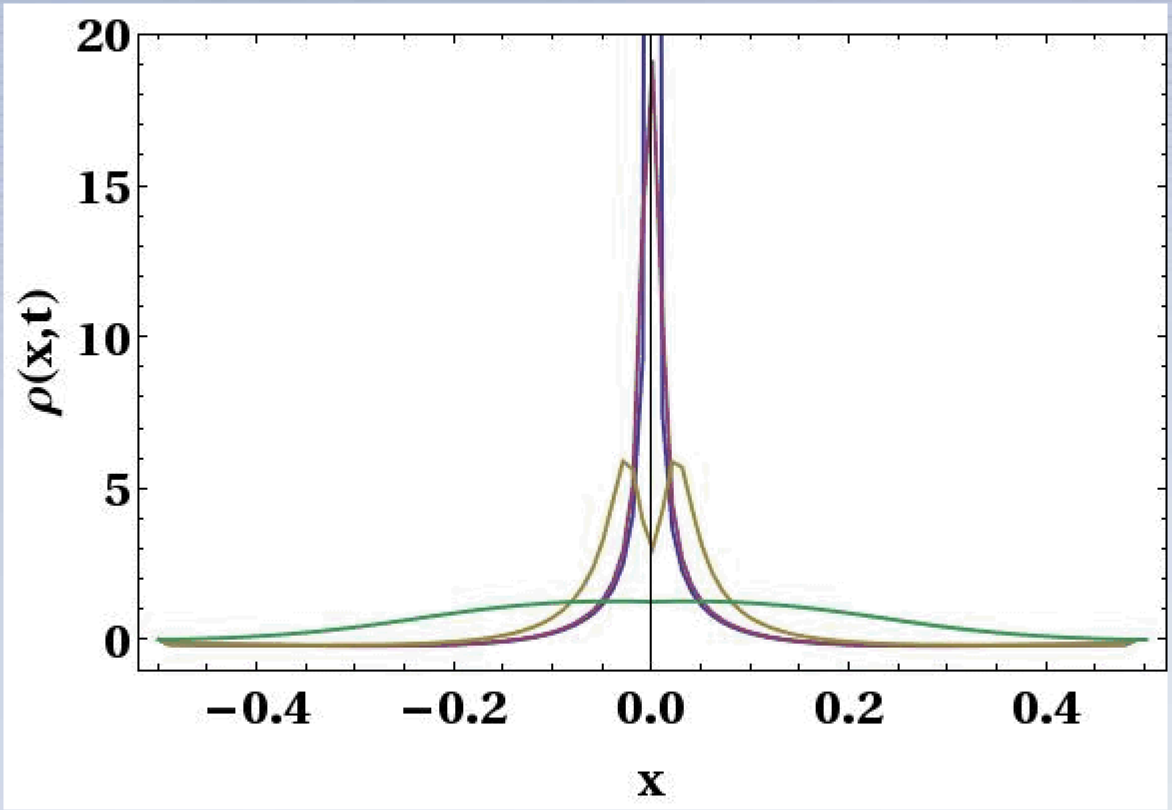
$$\psi(k,s) = g(s)\phi(k)$$

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



Green's Function for CTRW

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



Developing a Scale Consistent Meso-to-Macro Model Development Framework

Defining the Meso-scale: an Example

- **"Microscopic" dynamics**

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

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

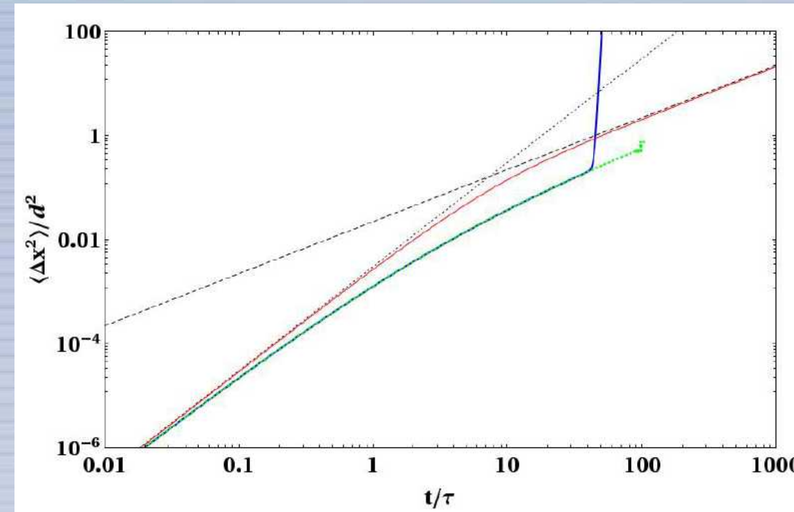
$$\left\langle \mathbf{F}_i^B(t) \right\rangle = 0; \left\langle \mathbf{F}_i^B(t)\mathbf{F}_i^B(t') \right\rangle = 2k_B T\gamma\delta(t-t')$$

  - Solve and obtain statistics

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

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

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



- **Recall**
  - $MSD = f(t) \neq Dt^{\alpha};\ \alpha \neq 1$
  - Engineer's temptation
    - $D = h(t) \rightarrow MSD = h(t)t$
  - What does this mean **physically** and mathematically?

Mass Balance

- **Meso-scale**

$$\rho_i(\mathbf{x},\mathbf{v},t) = \left\langle m\delta(\mathbf{x}-\mathbf{r}_i(t))\delta(\mathbf{v}-\mathbf{v}_i(t)); f^N(\mathbf{r}^N,\mathbf{p}^N;t)\right\rangle$$

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

- **Macroscopic continuity**

$$\rho(\mathbf{x},t) = \left\langle \sum_{i=1}^{N} m\delta(\mathbf{x}-\mathbf{r}_i(t)); f^N(\mathbf{r}^N,\mathbf{p}^N;t)\right\rangle$$

$$\frac{\partial\rho(\mathbf{x},t)}{\partial t} = \frac{\partial}{\partial\mathbf{x}}\cdot\left(\rho(\mathbf{x},t)\mathbf{u}(\mathbf{x},t)\right)$$

where, $\rho(\mathbf{x},t)\mathbf{u}(\mathbf{x},t) = \int \mathbf{v}\rho(\mathbf{x},\mathbf{v},t)d\mathbf{v}$

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Conclusions

- **Solution of Langevin Equation with interactions leads to GLE**
  - Can obtain Memory Kernel of “reasonable” form from VACF
- **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”
- **Developing Meso-to-macroscale Modelling framework**
  - Nonequilibrium Statistical Physics/Thermodynamics

Outlook

- **Prediction – the crystal ball**
  - Relationship of near equilibrium to far from equilibrium
    - Space-time formulations of
  - Statistical analysis tool-kit for numerical and experimental data mining
    - Stochastic model development from “rare” events
- **Validation**
  - DSC, DWS, Impedance/dielectric Spectroscopy, …
- **Applications**
  - Design and analysis of energy storage/conversion devices
    - Electrochemistry and Thermo-mechanics of composite electrodes
    - Ionic liquids
  - Processing of energetic materials
    - Processing-Product/Property-Performance
    - Aging

Acknowledgements

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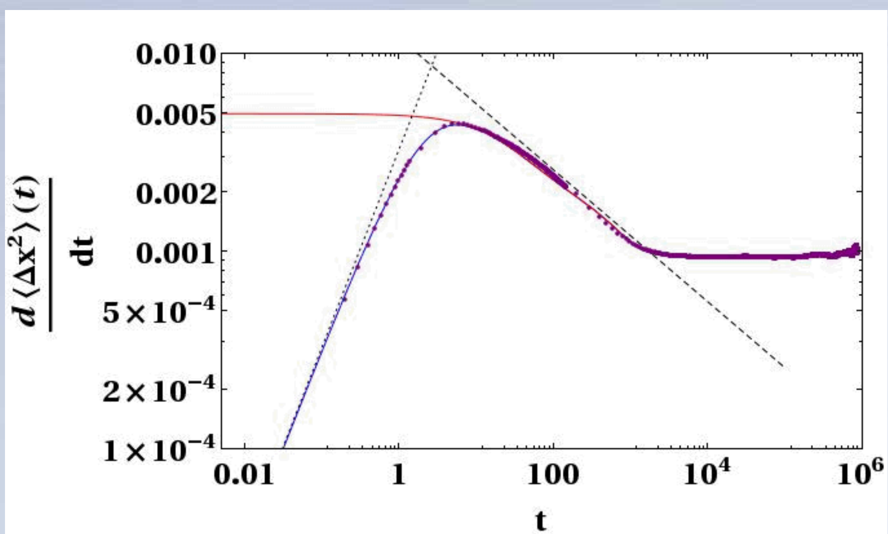
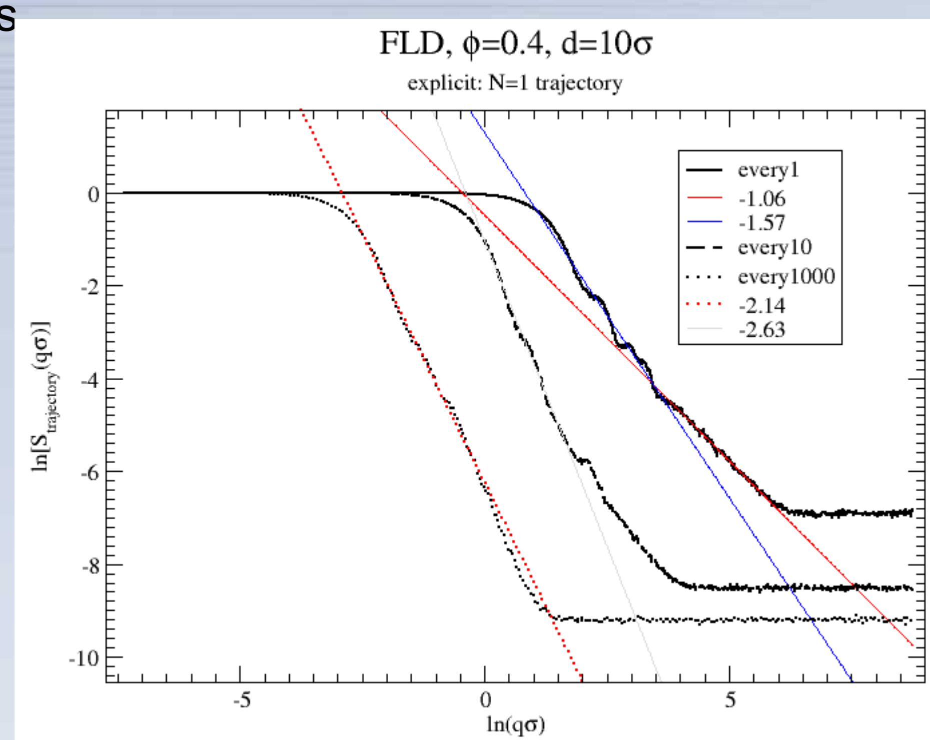
So what?

- **Single particle density of hard-sphere colloid**

$$\rho_i(\mathbf{r},t) = \left\langle m\delta(\mathbf{r}-\mathbf{R}_i(t)); f^N(\mathbf{R}^N,\mathbf{P}^N;t) \right\rangle$$

  – "Light scattering" of single particle trajectory…
    - Multiple length and time scales
    - ~ Multifractal





– $\rho(r) \sim \left(\frac{r}{r_1}\right)^{2.0} + \left(\frac{r}{r_2}\right)^{2.6} + \left(\frac{r}{r_3}\right)^{1.5} + \left(\frac{r}{r_4}\right)^{1.0},$

$r_4 < r_3 < r_2 < r_1$

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Nonlocal Space and Time

- **More generally, consider a separable CTRW**
  - Joint jump distribution, $\Psi(\mathbf{y}, \mathbf{x}, t) = g(t)\,\gamma(\mathbf{y}, \mathbf{x})$
    - Jump length distribution, $\gamma(\mathbf{y},\mathbf{x})$ contains spatial correlations
    - Waiting time distribution, g(t) contains temporal correlations

$$\frac{\partial \rho}{\partial t} = \int_0^t \kappa(t-t')\int (\rho(\mathbf{y},t)-\rho(\mathbf{x},t))\,\gamma(\mathbf{y},\mathbf{x})\,d\mathbf{y}\,dt'$$

$$\frac{\partial \rho}{\partial t} = \int_0^t \delta(t-t')\int (\rho(y,t)-\rho(x,t))\,\frac{\partial^2}{\partial y^2}\delta(x-y)\,dy\,dt'$$

- **Do the underlying dynamics give rise to this macro behavior?**

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Nonlocal Diffusion – "Anomalous" Diffusion

- **Recall classical "Fickian" Diffusion**

Fick's first law $\mathbf{j} = -D\nabla\rho$, or $\mathbf{j} = -\frac{\nu}{2}(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)$

Fick's second law $\frac{\partial\rho}{\partial t} = \nabla\cdot\mathbf{j}$

- **Non-Fickian**

$$\mathbf{j}(\mathbf{x},t) = -\frac{1}{2}\int \mathbf{z}\otimes\int_0^1 (\rho(\mathbf{x}-(1-\lambda)\mathbf{z},t) - \rho(\mathbf{x}+\lambda\mathbf{z},t))\gamma(\mathbf{x}-(1-\lambda)\mathbf{z},\mathbf{x}+\lambda\mathbf{z})\,d\lambda\,d\mathbf{z}$$

$$\frac{\partial\rho}{\partial t} = \nabla\cdot\mathbf{j} = \int(\rho(\mathbf{y},t) - \rho(\mathbf{x},t))\underbrace{\gamma(\mathbf{y},\mathbf{x})}_{\text{Constitutive relation}}d\mathbf{y}$$

The "Generalized Langevin Equation" – Nonlocal-Time SDE

- **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**

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

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

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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

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

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

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

- **We can use this to derive the memory kernel**

Memory Kernel

- **Recall, for spheres in dilute limit**

$$\tilde{\mathbf{v}}_i(s) = \frac{\mathbf{v}_0 + \tilde{\mathbf{F}}_i^R(s)}{(s + \tilde{\gamma}(s))}$$

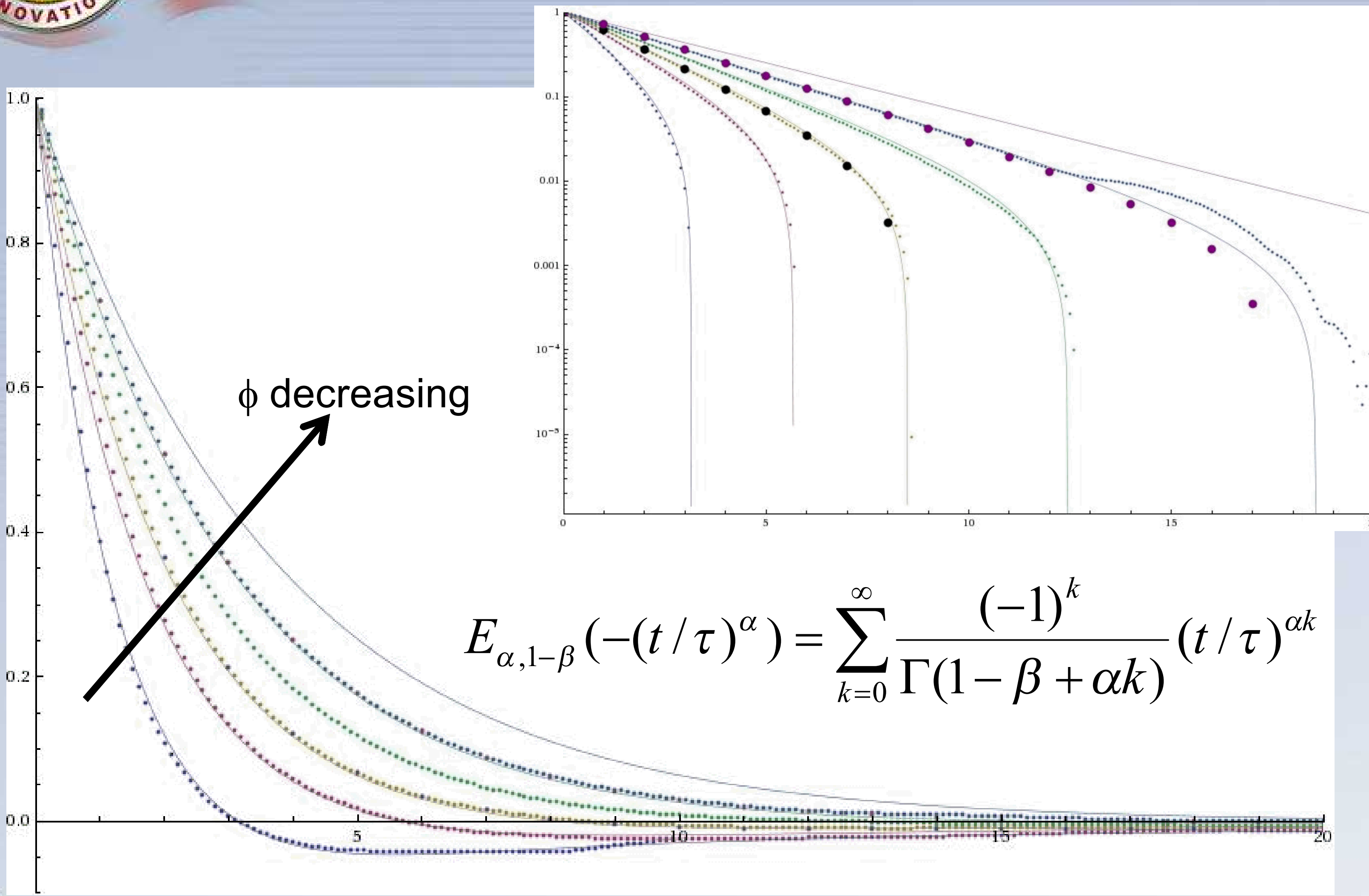
$$\mathbf{v}_i(t) = \mathbf{v}_0 h(t) + \int_0^t h(t-t')\mathbf{F}_i^R(t')dt'$$

- **Impulsive response v*(t)* ~ *h(t)***

$$\tilde{h}(s) = [s + \tilde{\gamma}(s)]^{-1} = \left[s + (\lambda_1 + \lambda_2)s^{1/2} + \lambda_1\lambda_2\right] \qquad \lambda_{1,2} = \sqrt{\tau_{1,2}}$$

$$\tilde{\gamma}(s) = (\lambda_1 + \lambda_2)s^{1/2} + \lambda_1\lambda_2 \rightarrow \gamma(t) = -\frac{\lambda_1 + \lambda_2}{2\sqrt{\pi}} t^{-3/2} + \lambda_1\lambda_2\delta(t)$$

Fits of Mittag-Leffler to VACF (various ϕ)



$$E_{\alpha,1-\beta}(-(t/\tau)^{\alpha}) = \sum_{k=0}^{\infty} \frac{(-1)^k}{\Gamma(1-\beta+\alpha k)} (t/\tau)^{\alpha k}$$

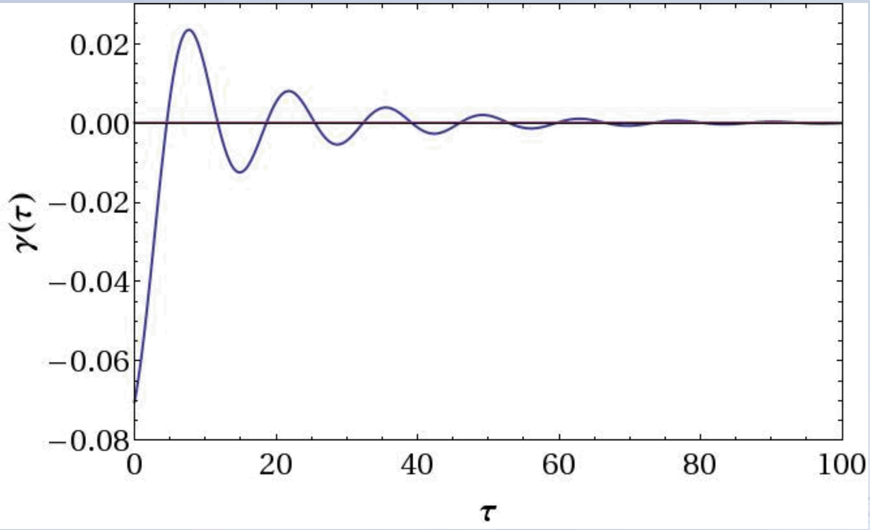
Summary and Outlook

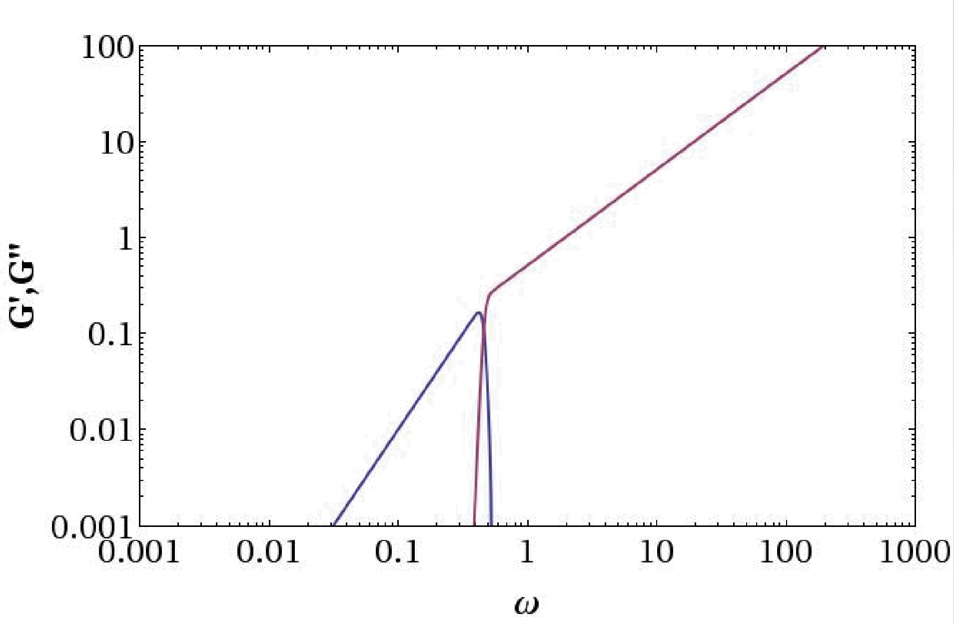
- **Recall Mason and Weitz**

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

$$\langle \mathbf{v}_i(0)\tilde{\mathbf{v}}_i(s)\rangle = \frac{\langle \mathbf{v}_i(0)\mathbf{v}_i(0)\rangle + \langle \mathbf{v}_i(0)\tilde{\mathbf{F}}_i^R(s)\rangle}{ms+\tilde{\gamma}(s)}$$

$$\tilde{\gamma}(s) = \frac{3k_BT}{\langle \mathbf{v}_i(0)\tilde{\mathbf{v}}_i(s)\rangle} - ms$$



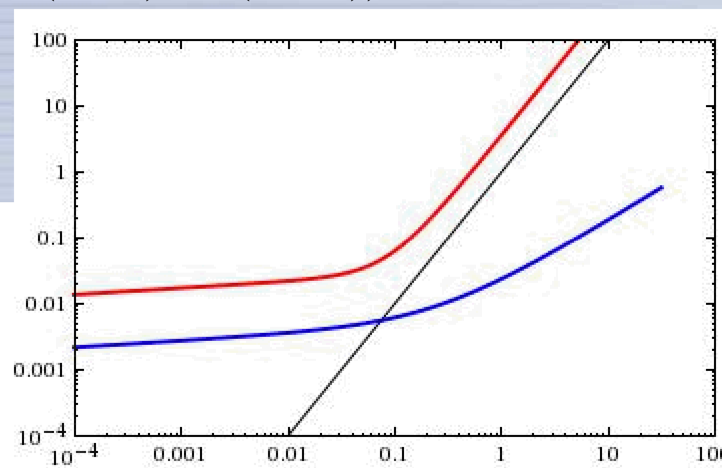


Micro-rheology

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

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

$$\langle \tilde{v}(s)v(0)\rangle = \frac{1}{s+s^{\theta-1}+c}$$



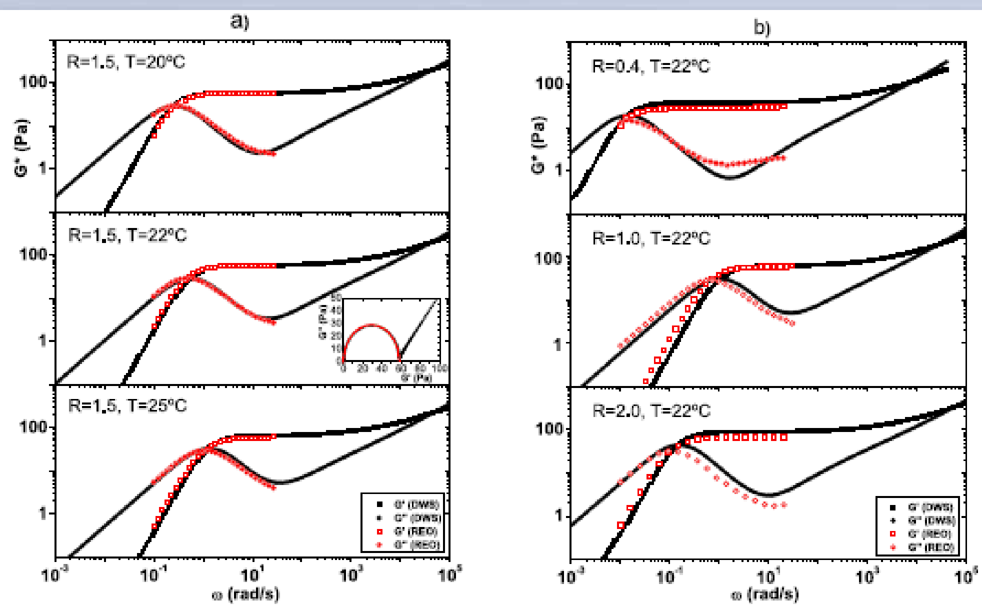


Fig. 4. The elastic, G', and the viscous, G'', components of the complex modulus for the CTAB/NaSal/water system at different temperatures and fixed $W = 1.5$ (a). Inset: Cole-Cole plot from DWS microrheology (line: best fit for Maxwell model). b) At different W values and fixed $T = 22\,^{\circ}$C.

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$$0.00133333\left(-0.0555556\,e^{-0.0555556\,t}-0.0164609\,e^{-0.0164609\,t}-0.00205761\,e^{-0.00205761\,t}\right)+0.0033\,e^{-0.666667\,t}$$