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A Continuous-Time Random-Walk Description of Monodisperse, Hard-Sphere Colloids below the Ordering Transition

Jeremy Lechman and Flint Pierce

Nanoscale and Reactive Processes Department
Engineering Sciences Center
Sandia National Laboratories

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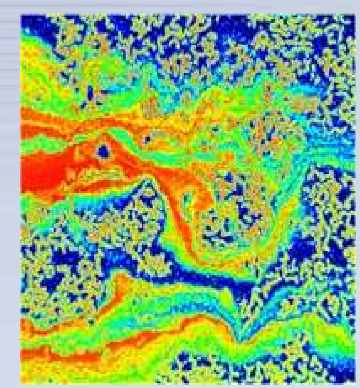
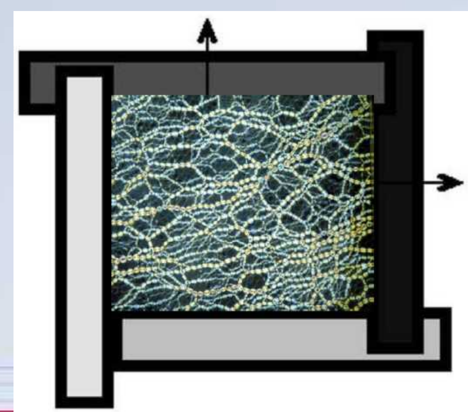
Background and Introduction

- **Need better prediction and control of**
  - Ion transport in composite electrodes (microstructure scale)
  - Durability of composite electrodes

- **Heterogeneous material**
  - Inhomogeneous, discontinuous microstructure and material properties
    - Composites
    - Discrete particles in polymer matrix or suspending fluid



Static µstruct



dynamic µstruct

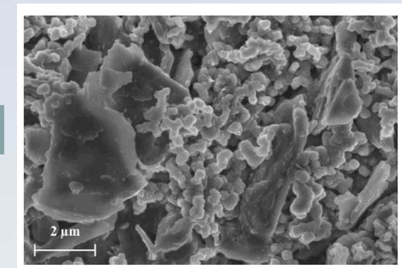


Fig. 4 SEM-image of the nano-silicon/graphite composite electrode after 75 cycles in the capacity-limited mode.

Langevin Equation with Interations

- **Brownian Dynamics**
  - Markov assumption

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

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

  - $\mathbf{F}^B$ assumed Gaussian distributed and self similar
  - Colloid inertia is often neglected
- **Can we find kernel that transforms (non-local) spatial interactions into (non-local time) convolution integral with memory kernel?**
  - This is a constitutive relation we can measure

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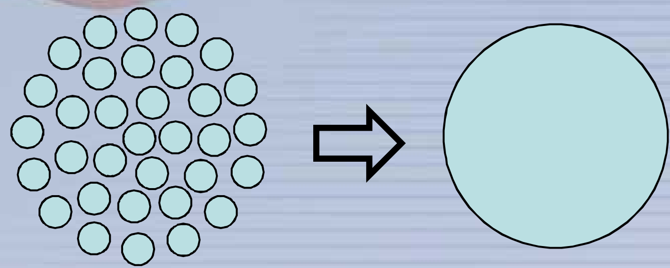
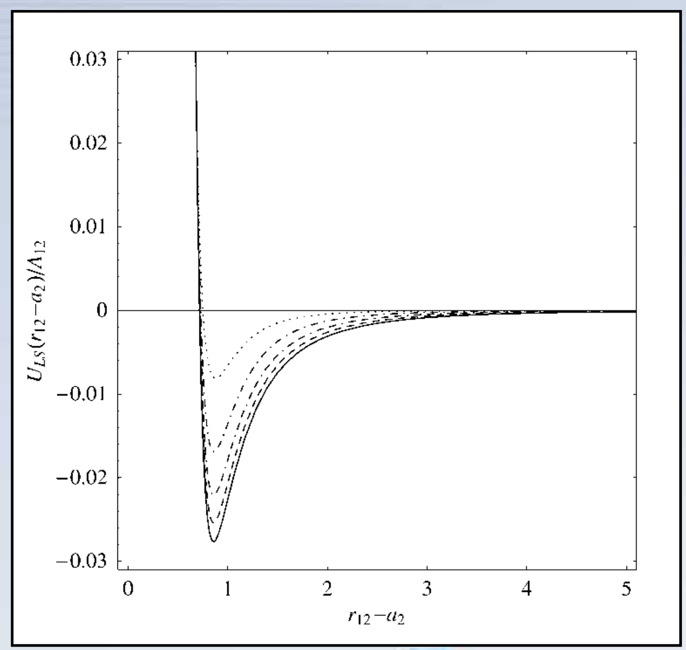
Details: Colloid interactions



- 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)

Details: Hydrodynamic Interactions

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

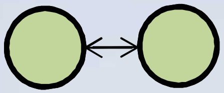
$$R = (I - \mathcal{R})^{-1} R_{1B} + R_{lub}$$

    - Fast Lubrication Dynamics
      - *O(N)*

$$R = R_0 + R_\delta$$

Isotropic Constant
(mean-field mobility)

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

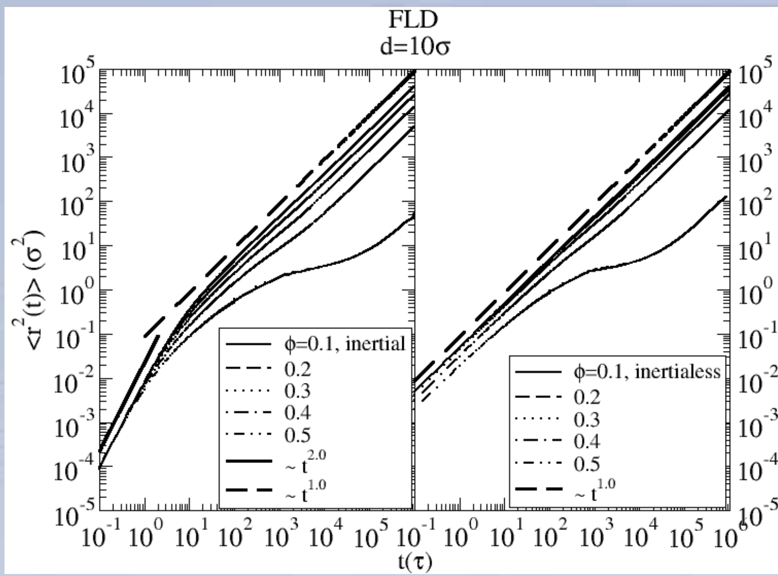


δ

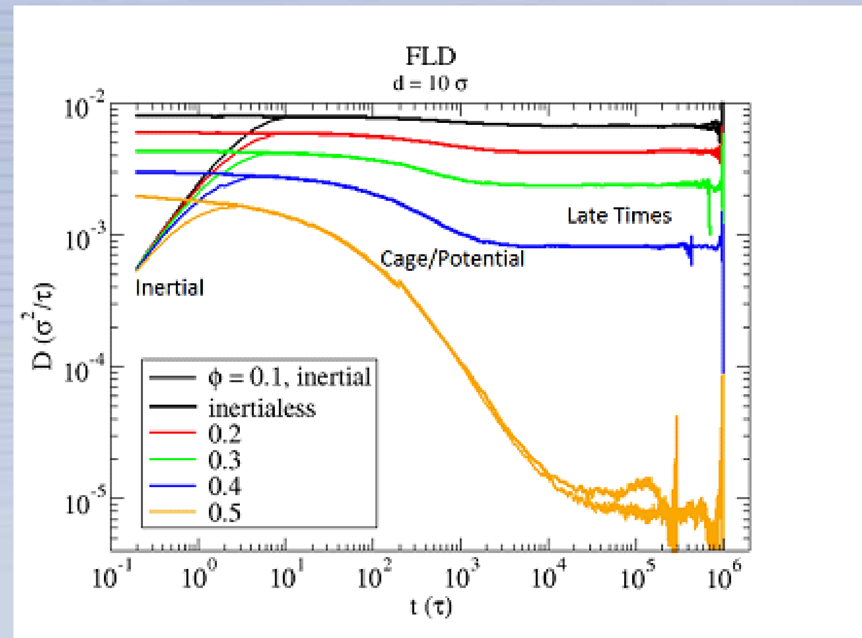
δ^{-1} or $\delta^{-1} + \log(\delta^{-1})$

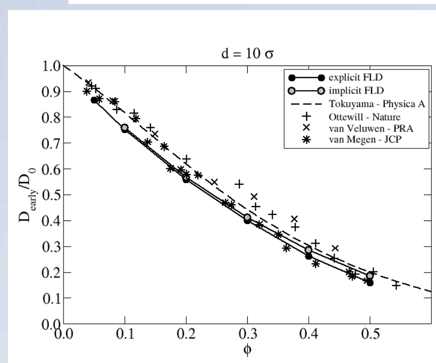
Kumar and Higdon, Phys Rev E, 82, 051401 (2010)
Ball and Melrose, Physica A, 247, 444-472 (1997)

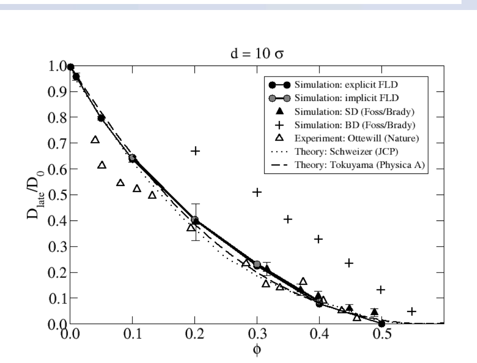
Simulation Results and Validation



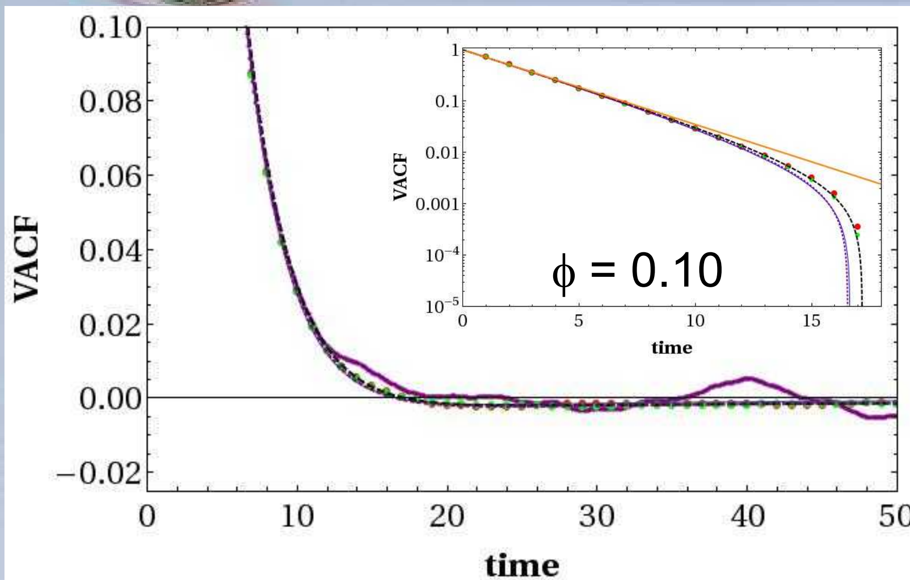
MSD

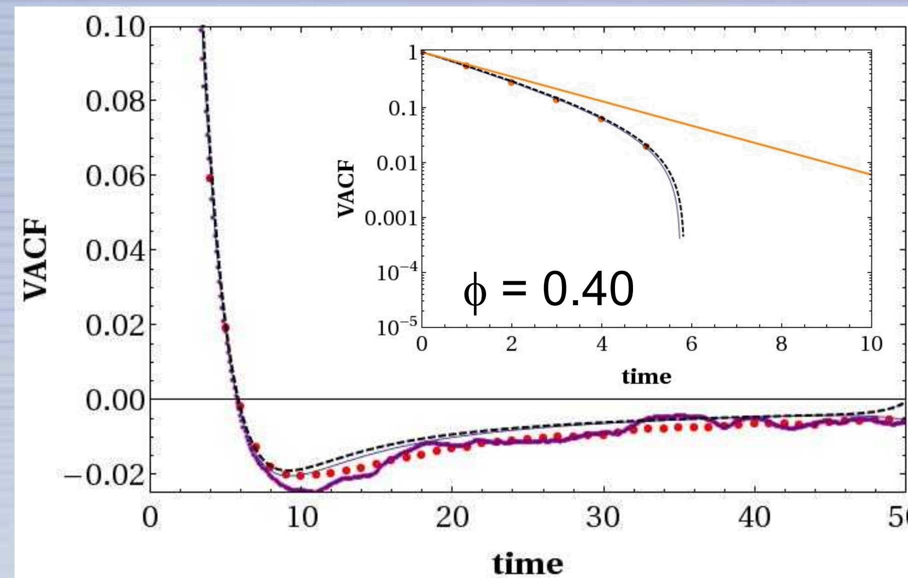






Memory Kernel from the VACF





- **Fit VACF with**

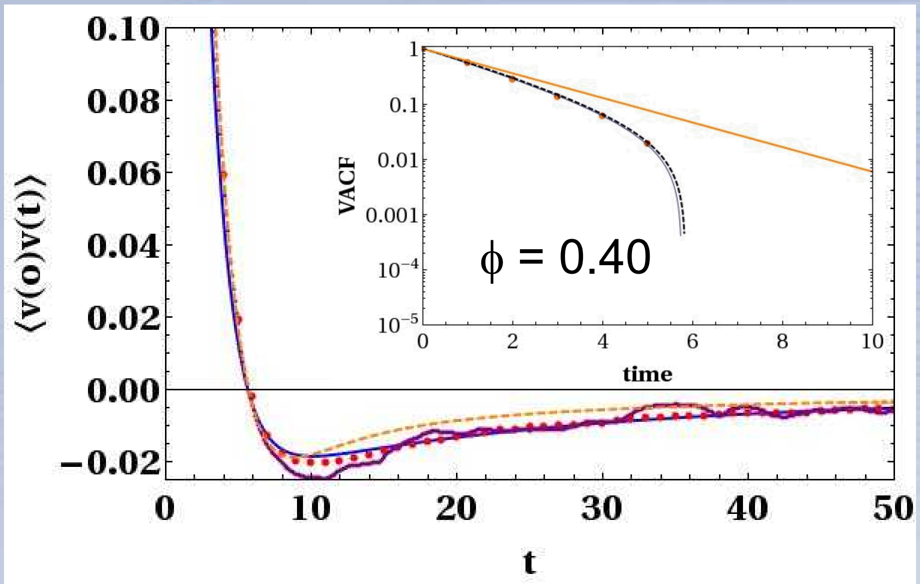
$$f(t/\tau_B;\tau_{coll},\theta) \propto \sum_{n=0}^{\infty} \frac{(-1)^n (t/\tau_{coll})^{2(n+1)-\theta n-2}}{n!} \sum_{k=0}^{\infty} \frac{(k+n)!(-1)^k}{k!\Gamma(1+2n+k-\theta n)} (t/\tau_B)^k$$

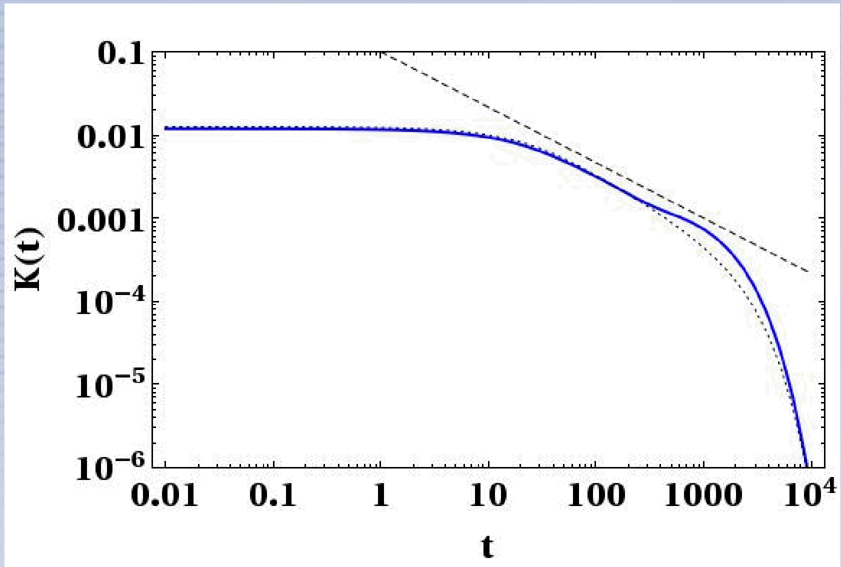
- **Which is a solution to**

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

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

Alternative Form of VACF





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

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

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

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Equivalent Macroscopic, Deterministic Eqn

- **Consider CTRW of the form**

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

  - 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)*

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

Macroscopic, Deterministic Equation for NonMarkovian Stochastic Dynamics

- **Nonlocal-time model**

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

  - **Solution**

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

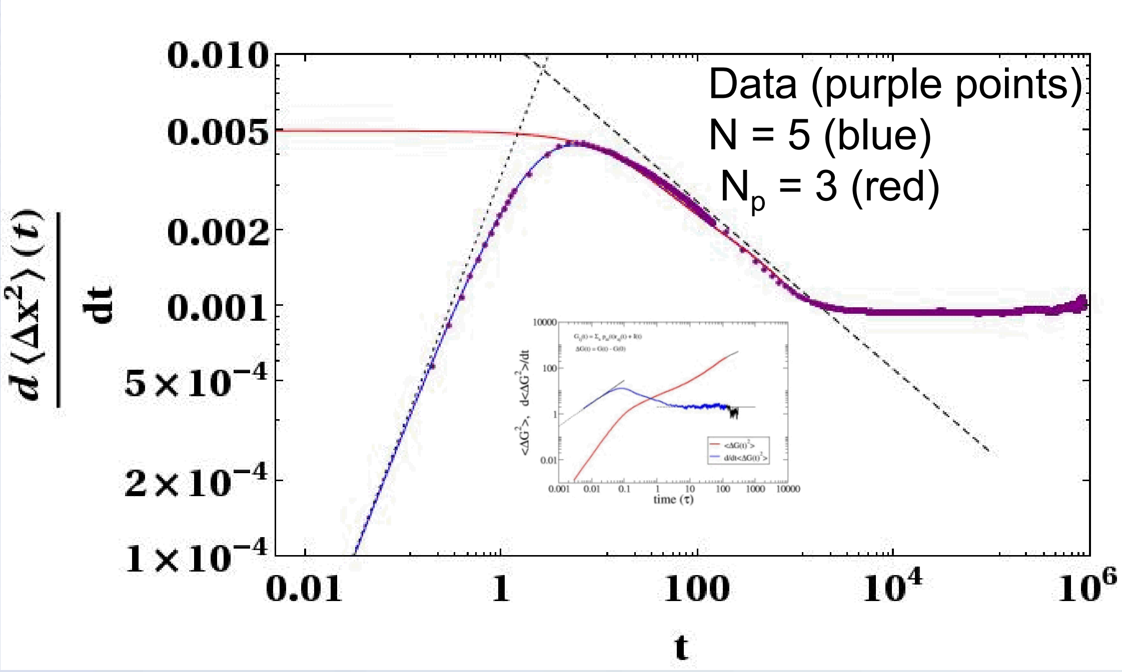
  - **Choose g(t)**

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

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

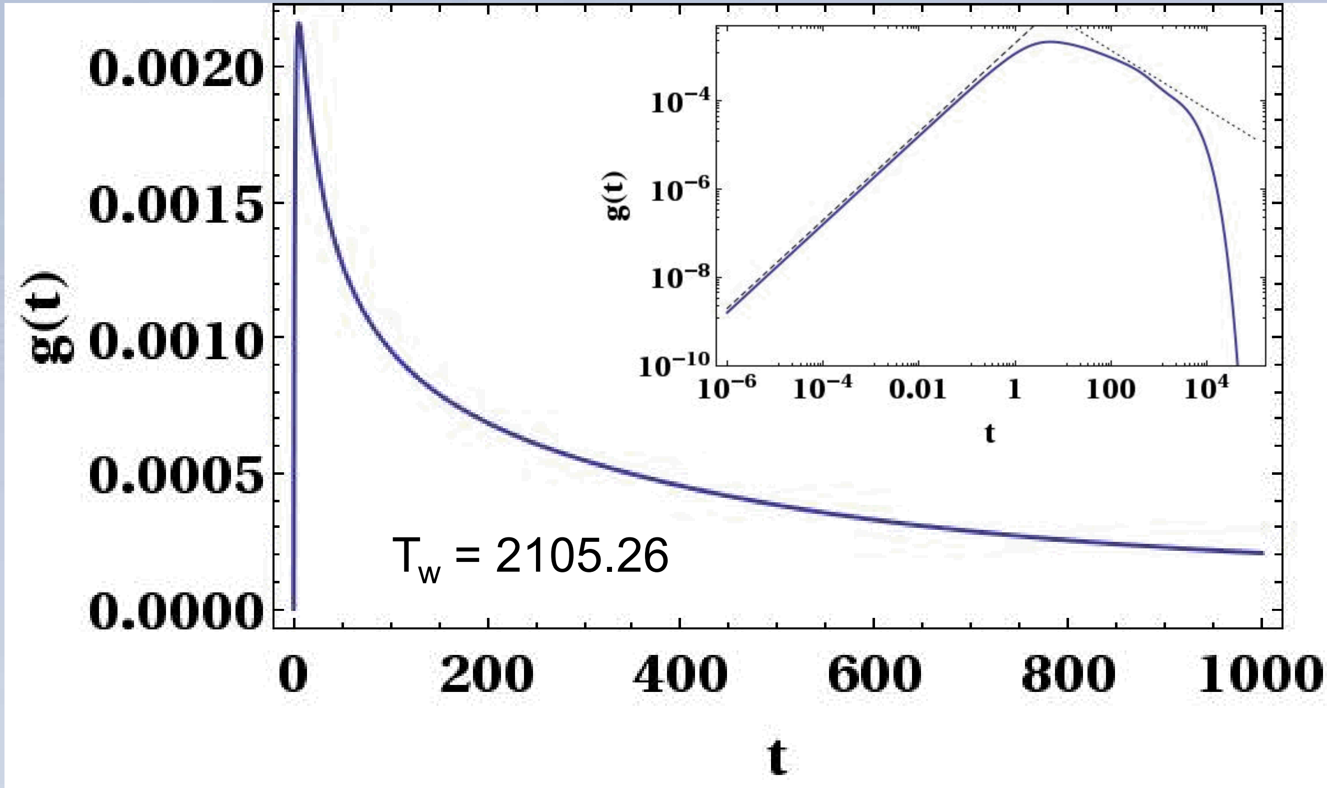
  - **Note:**

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



Waiting Time Distribution

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

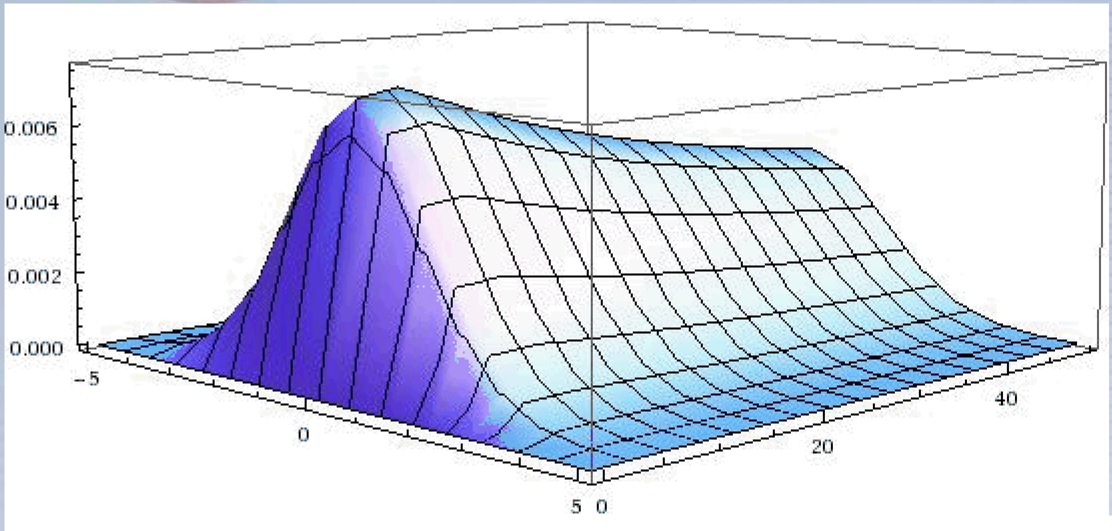


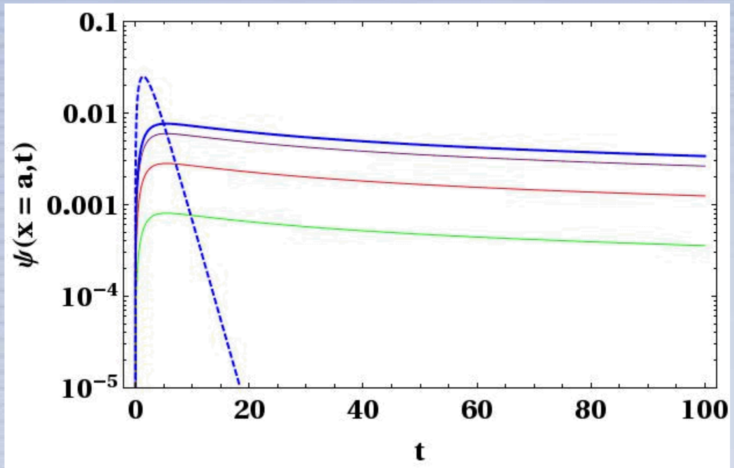
$$g(t) = A_N \sum_{i=0}^{N} c_i e^{-\lambda_i t}$$

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

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

Full Jump Distributions

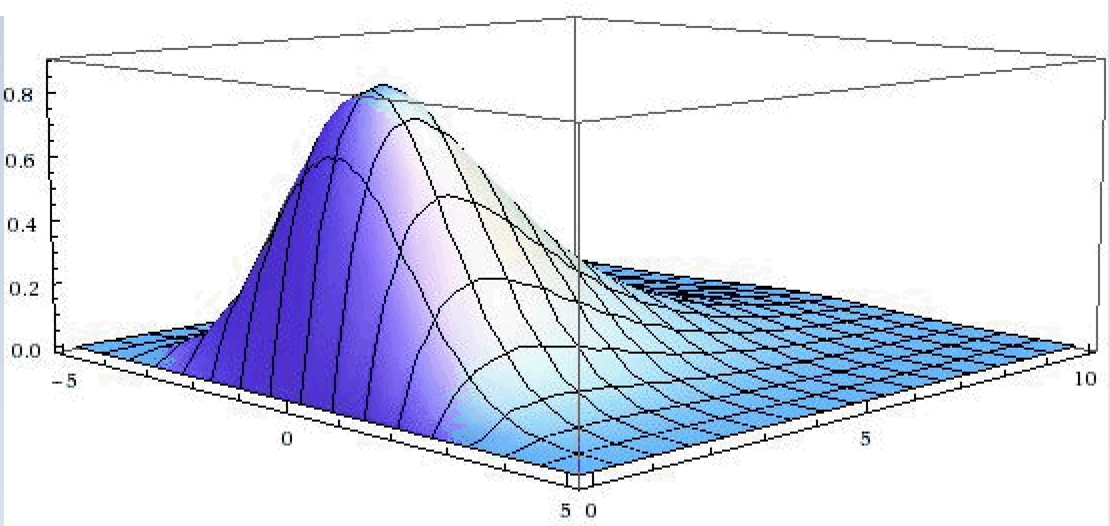




- **Recall**

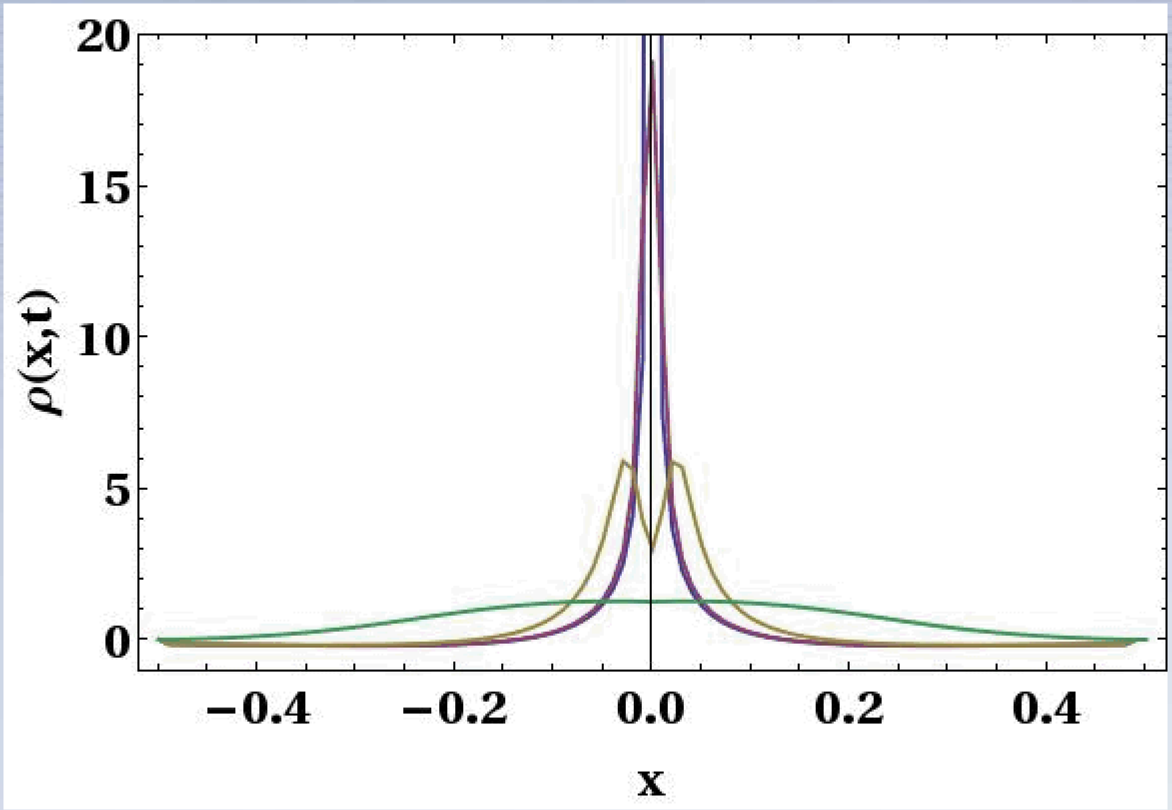
$$\psi(k,s) = g(s)\phi(k)$$

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



Green's Function for CTRW

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



Conclusions

- **Solution on interaction Langevin Equation leads to GLE**
  - Memory Kernel
- **With Memory Kernel we can determine waiting time distribution for CTRW**
  - Assuming Gaussian Jumps
  - Leads to Generalized diffusion equation
- **Connection to Experiments forth coming**

Acknowledgements

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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Micro-rheology to Macro-rheology

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

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

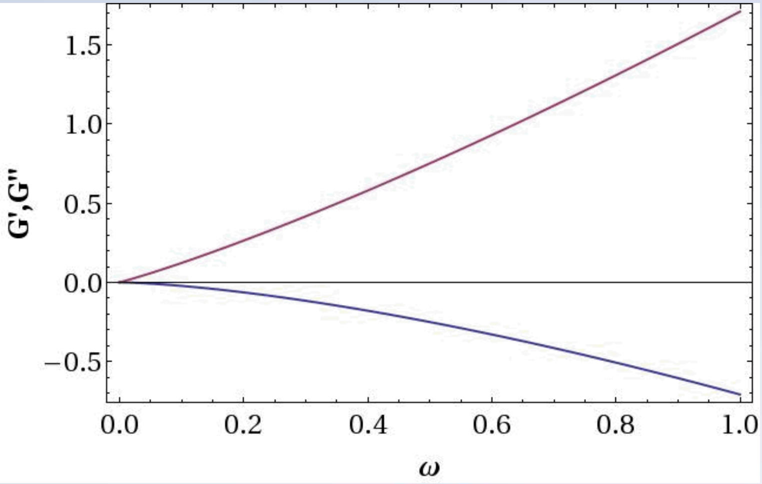
- **Relaxation Modulus for Transient BD**

$$\tilde{G}_r(s) \approx \frac{\tilde{\xi}(s)}{6\pi a} = \frac{1}{6\pi a}\left[(\lambda_1 + \lambda_2)s^{1/2} + \lambda_1\lambda_2\right]$$

- **Viscoelastic (complex) modulus**

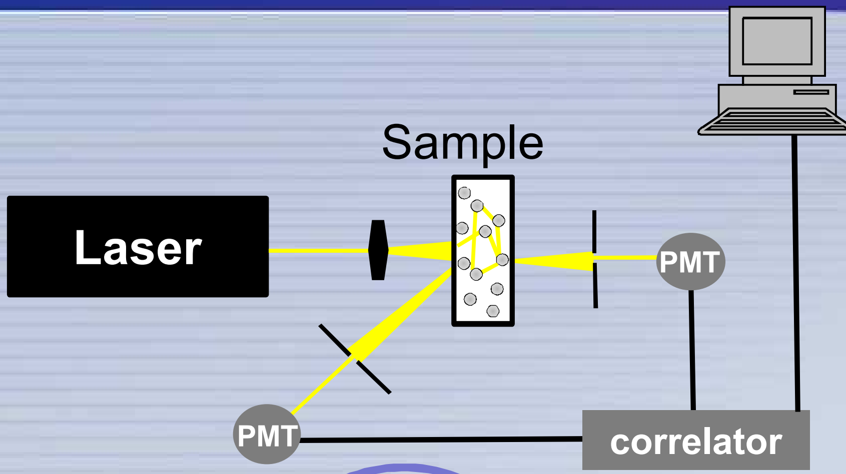
$$\tilde{G}(s) = s\tilde{G}_r(s); \quad s \to i\omega$$

$$G^*(\omega) \sim \frac{\lambda_1 + \lambda_2}{2\sqrt{\pi}}(i\omega)^{3/2} + \lambda_1\lambda_2(i\omega)$$

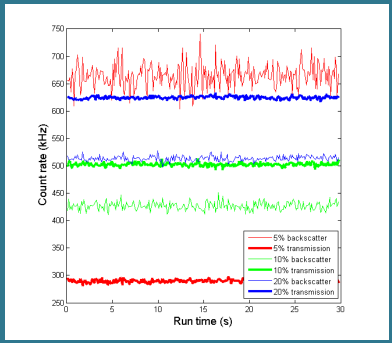


Validation: Diffusing-Wave Spectroscopy

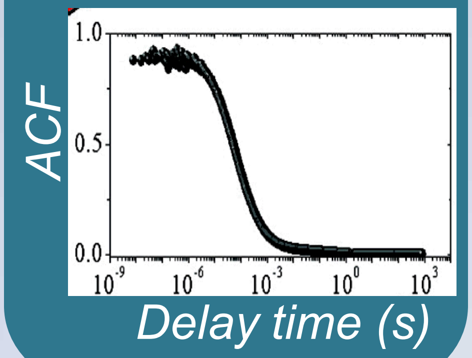
- **Diffusivity of turbid suspensions**
- **Connect stochastic colloidal dynamics to rheology**



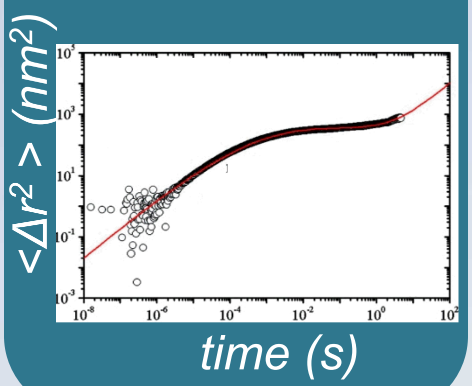
Measure:
intensity fluctuations vs. time



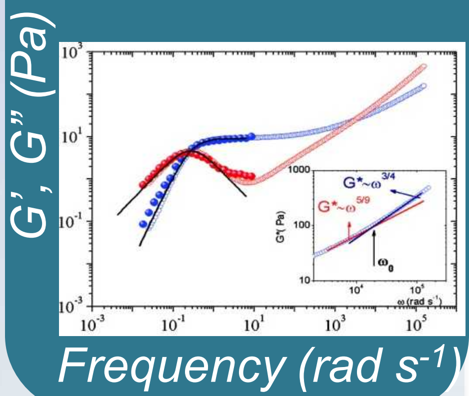
Autocorrelation :
Transmission-> f(τ, l*)
Backscatter-> f(τ)



Mean square displacement



Rheology



The Classical Langevin Equation Model for Brownian Dynamics of Colloids

- **Translation of Isolated small sphere in Newtonian fluid**
  - Time dependent Stokes drag force on sphere
    - Nonlocal model: 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**

$$\left. \begin{array}{l} \gamma(t-t') = \gamma\delta(t-t') \\ \mathbf{f}(t) = \mathbf{F}^R(t) \end{array} \right\} \quad \boxed{\begin{array}{l} \dfrac{d\mathbf{v}_i(t)}{dt} = -\dfrac{1}{\tau_B}\mathbf{v}_i(t) + \dfrac{1}{m}\mathbf{F}_i^R(t) \\ \left\langle \mathbf{F}_i^R(t) \right\rangle = 0; \left\langle \mathbf{F}_i^R(t)\mathbf{F}_i^R(t') \right\rangle = 2k_B T\gamma\delta(t-t') \end{array}}$$

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

- Interactionless, Markovian, SDE

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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?**

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**

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

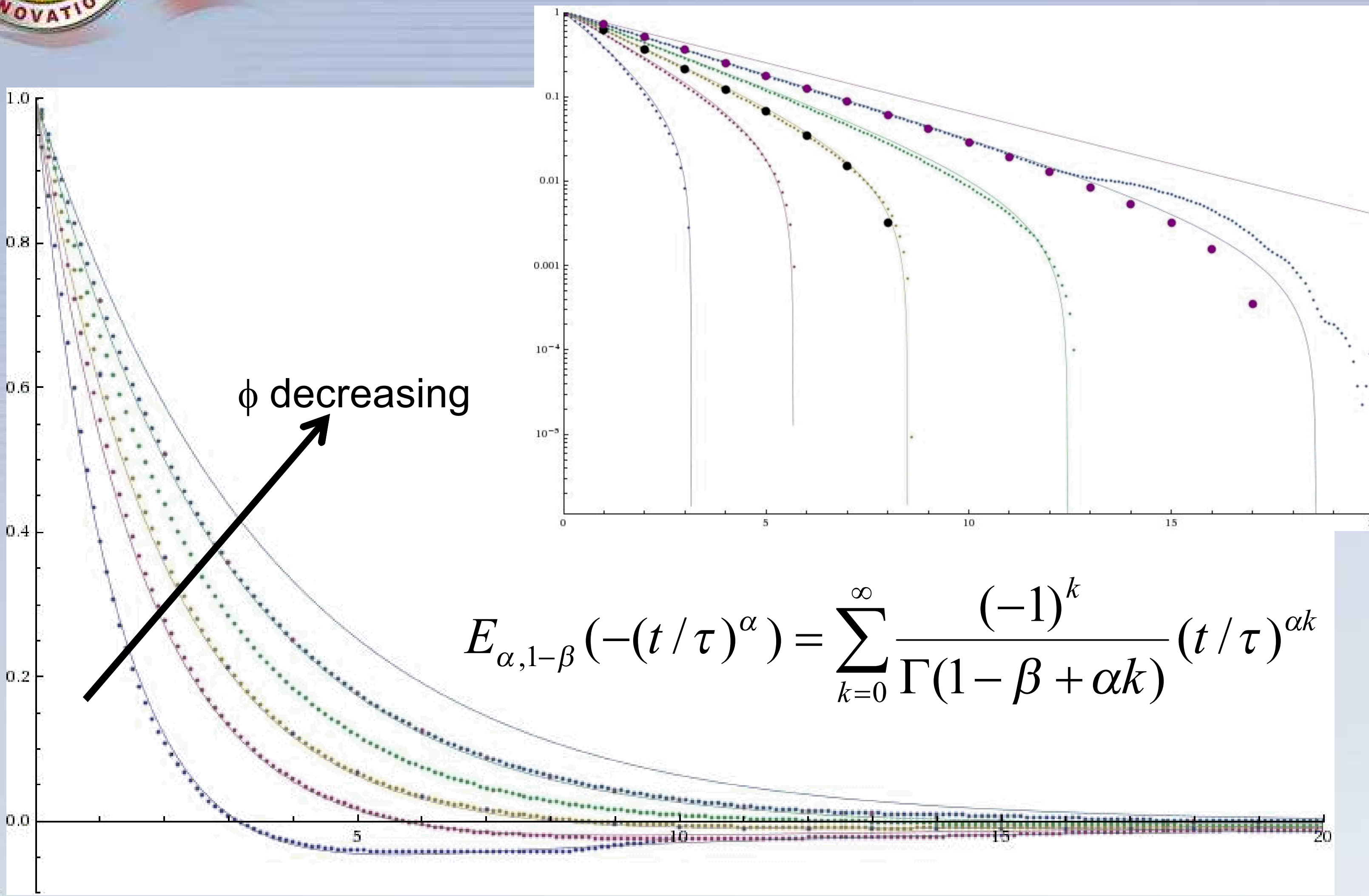
$$\mathbf{v}_i(t) = \mathbf{v}_0 h(t) + \int_0^t h(t-t')\mathbf{F}_i^R(t')dt'$$

- **Impulsive response** $\mathrm{v}(t) \sim h(t)$

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

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

Fits of Mittag-Leffler to VACF (various ϕ)



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

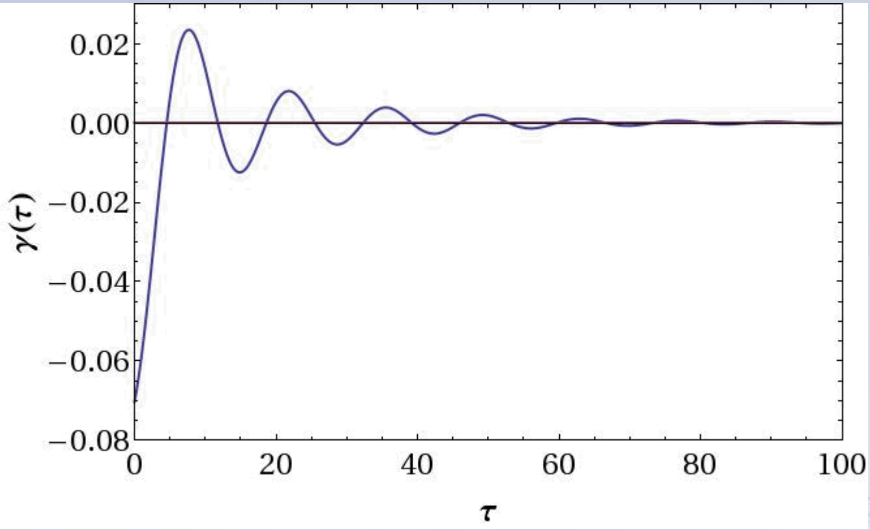
Summary and Outlook

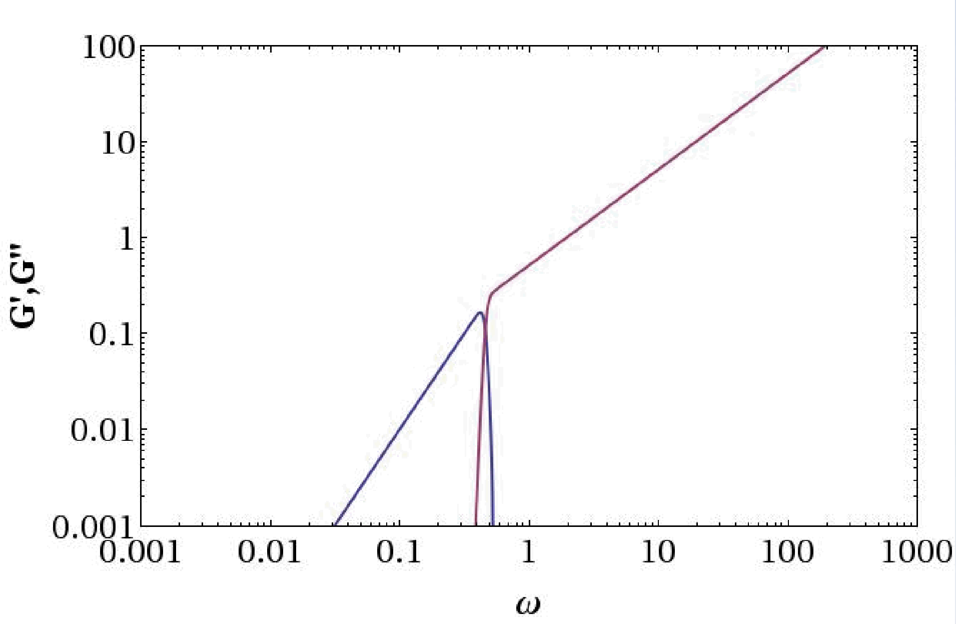
- **Recall Mason and Weitz**

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

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

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



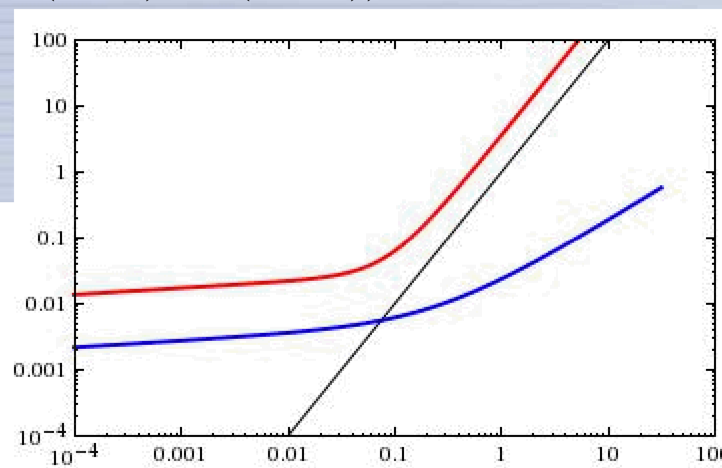


Micro-rheology

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

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

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



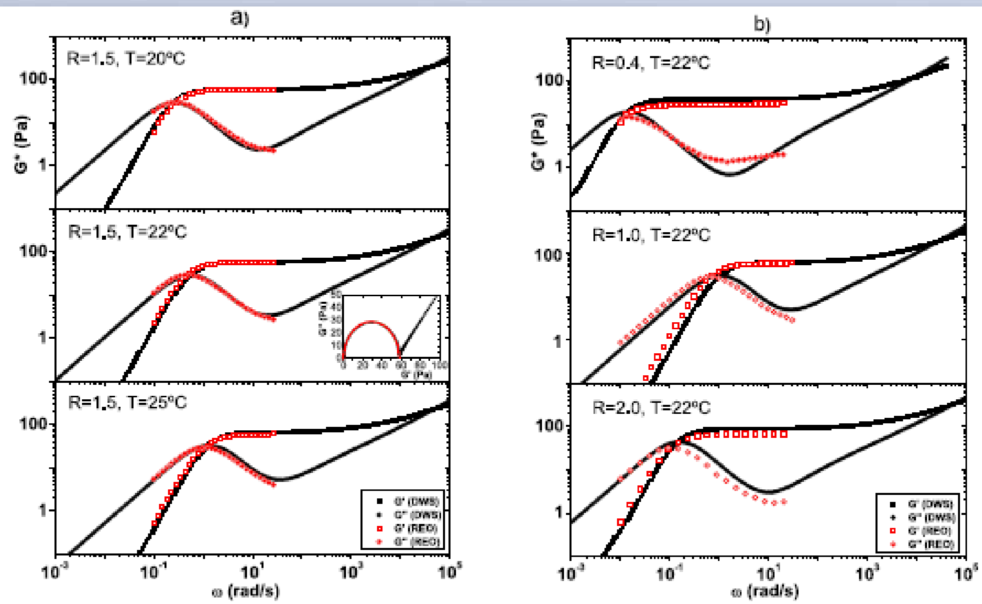


Fig. 4. The elastic, G', and the viscous, G'', components of the complex modulus for the CTAB/NaSal/water system at different temperatures and fixed $W = 1.5$ (a). Inset: Cole-Cole plot from DWS microrheology (line: best fit for Maxwell model). b) At different W values and fixed $T = 22\,^{\circ}$C.