One- and Two-Particle Microrheology

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Outline

1. Lecture Structure
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   - Generalization to Nonspherical Particles
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   - Two-Particle Langevin Equation
   - Response Functions
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Sphere Through a Fluid

Given:

Navier-Stokes Equation:

\[
\rho \frac{\partial \vec{v}}{\partial t} = -\nabla p + \eta \nabla^2 \vec{v} - \rho \vec{v} \cdot \nabla \vec{v} + \vec{f}
\]

\[
\vdash
\nabla p \approx \eta \nabla^2 \vec{v}
\]
Sphere Through a Fluid

**Given:**

Navier-Stokes Equation:

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\frac{\partial \vec{v}}{\partial t} = -\nabla p + \eta \nabla^2 \vec{v} - \rho \vec{v} \cdot \nabla \vec{v} + \vec{f}
\]

\[
\nabla p \approx \eta \nabla^2 \vec{v}
\]

**BCs:**

\[
\begin{align*}
\nu_r &= 0 & \text{at } r = \text{infty} \\
\nu_\theta &= 0 & \text{at } r = \infty \\
\nu_r &= -V \cos \theta & \text{at } r = R \\
\nu_\theta &= V \sin \theta & \text{at } r = R
\end{align*}
\]
Sphere Through a Fluid

Solution:

\[
\begin{align*}
\nu_r &= \frac{V}{2} \left[ 3 \left( \frac{R}{r} \right) - \left( \frac{R}{r} \right)^3 \right] \cos \theta \\
\nu_\theta &= -\frac{V}{4} \left[ 3 \left( \frac{R}{r} \right) + \left( \frac{R}{r} \right)^3 \right] \sin \theta
\end{align*}
\]
Flow Past a Sphere

Given:

Can either reset BCs and solve again or
Flow Past a Sphere

**Given:**

Can either reset BCs and solve again or superimpose uniform flow (in spherical coordinates) on to our solution of a sphere moving through a fluid.

**Solution:**

\[ v_r = -V \left[ 1 - \frac{3}{2} \left( \frac{R}{r} \right) + \frac{1}{2} \left( \frac{R}{r} \right)^3 \right] \cos \theta \]

\[ v_\theta = V \left[ 1 - \frac{3}{4} \left( \frac{R}{r} \right) + \frac{1}{4} \left( \frac{R}{r} \right)^3 \right] \sin \theta \]
Drag

**Technique:**

Having found the velocity, one can get the pressure from the Navier-Stokes Eq. The force of the fluid on the sphere is then the integral of the pressure over the total surface area.
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Having found the velocity, one can get the pressure from the Navier-Stokes Eq. The force of the fluid on the sphere is then the integral of the pressure over the total surface area.

**Solution:**

\[ \vec{F} = 6\pi \eta R \vec{V} \]

\[ = \xi \vec{V} \]

\( \xi \) is call the friction coefficient.
“Falling Ball” Rheology

Give $\vec{F}$, $R$ and measuring $\vec{V}$ one can determine $\eta$. 
NonSpherical Objects

Orientation

Now the drag depends on the orientation suggesting
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\[ F_i = 6\pi \eta R_{ij} V_j \]
Now the drag depends on the orientation suggesting

\[ F_i = 6\pi \eta R_{ij} V_j \]

**Orientation**

For a rigid body, \( \hat{R} \) depends solely on the size and shape of the object. For a sphere, \( R_{ij} = R \delta_{ij} \).
Grouping Translation Tensor and Viscosity

\[ \hat{\xi} \equiv 6\pi \eta \hat{R} \]

Why was this a good idea?
Friction

Grouping Translation Tensor and Viscosity

\[ \hat{\xi} \equiv 6\pi \eta \hat{R} \]

Why was this a good idea?
No-slip at spherical surface:

\[ \vec{F} = 6\pi \eta R \vec{V} \]
Friction

Grouping Translation Tensor and Viscosity

\[ \hat{\xi} \equiv 6\pi \eta \hat{R} \]

Why was this a good idea?

Perfect-slip at spherical surface:

\[ \vec{F} = 4\pi \eta R \vec{V} \]
Friction

Grouping Translation Tensor and Viscosity

\[ \hat{\xi} \equiv 6\pi \eta \hat{R} \]

Why was this a good idea?

General-slip at spherical surface:

\[ \vec{F} = 6\pi \eta R \left( \frac{\beta R + 2\eta}{\beta R + 3\eta} \right) \vec{V} \]
Grouping Translation Tensor and Viscosity

\[ \hat{\xi} \equiv 6\pi \eta \hat{R} \]

Why was this a good idea?
Spherical Liquid Droplet:

\[ \vec{F} = 6\pi \eta R \left( \frac{\epsilon/R + 2\eta_o + 3\eta_i}{\epsilon/R + 3\eta_o + 3\eta_i} \right) \vec{V} \]
Grouping Translation Tensor and Viscosity

\[ \hat{\xi} \equiv 6\pi \eta \hat{R} \]

Why was this a good idea?

Because the particle’s interaction with the fluid requires definition

\[ \vec{F} \equiv \hat{\xi} \vec{V} \]

\[ \hat{\xi} = 6\pi k\eta \hat{R} \]

where \( k \) is any correction term to Stokes drag.
Elipsoids

Elipsoid (Return to translation tensor for a moment)

\[
\hat{R} = \begin{pmatrix}
R_{1,1} & R_{1,2} & R_{1,3} \\
R_{2,1} & R_{2,2} & R_{2,3} \\
R_{3,1} & R_{3,2} & R_{3,3}
\end{pmatrix}
\]

Can always rotate to principle moments (think moment of inertia tensor)
Elipsoids

Elipsoid (Return to translation tensor for a moment)

\[
\hat{R} = \begin{pmatrix}
R_1 & 0 & 0 \\
0 & R_2 & 0 \\
0 & 0 & R_3 \\
\end{pmatrix}
\]

\(R_i\) are the principle translation coefficients.
Elipsoids

Elipsoid (Return to translation tensor for a moment)

\[
R_1 = \frac{8}{3} \frac{a^2 - b^2}{(2a^2 - b^2) S - 2a}
\]

\[
R_2 = R_3 = \frac{16}{3} \frac{a^2 - b^2}{(2a^2 - 3b^2) S - 2a}
\]
Elipsoids

Elipsoid (Return to translation tensor for a moment)

\[
R_1 = \frac{8 \left( a^2 - b^2 \right)}{3 \left( 2a^2 - b^2 \right) S - 2a}
\]

\[
R_2 = R_3 = \frac{16 a^2 - b^2}{3 \left( 2a^2 - 3b^2 \right) S - 2a}
\]

Prolate

For \( a > b \):

\[
S = 2 \left( a^2 - b^2 \right)^{-1/2} \ln \left[ \frac{a + \left( a^2 - b^2 \right)^{1/2}}{b} \right]
\]

\( a \gg b \to \) rod.
Elipsoids

Elipsoid (Return to translation tensor for a moment)

\[
R_1 = \frac{8}{3} \frac{a^2 - b^2}{(2a^2 - b^2)S - 2a}
\]

\[
R_2 = R_3 = \frac{16}{3} \frac{a^2 - b^2}{(2a^2 - 3b^2)S - 2a}
\]

Oblate

For \( a < b \):

\[
S = 2 \left( a^2 - b^2 \right)^{-1/2} \tan^{-1} \left[ \frac{a + (a^2 - b^2)^{1/2}}{a} \right]
\]

\( b \gg a \rightarrow \text{disk.} \)
Mean Friction

Mean Translation Coefficient

\[
\frac{1}{\langle R \rangle} = \frac{1}{3} \left( \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} \right)
\]

which amounts to an equivalent radius.

Mean Friction Coefficient

\[
\frac{1}{\langle \xi \rangle} = \frac{1}{3} \left( \frac{1}{\xi_1} + \frac{1}{\xi_2} + \frac{1}{\xi_3} \right)
\]

where 1, 2, 3 are the principle axes.
The ratio of the mean translation coefficient to a sphere of the same volume is called the Perin Factor:

\[ F = \frac{\langle R \rangle}{R_{\text{sph}}} = \frac{\langle \xi \rangle}{\xi_{\text{sph}}} \]
Mobility

\[ \vec{V} \equiv \hat{\mu} \vec{F} \]

\( \hat{\mu} \)'s relation to \( \hat{\xi} \):
**Mobility**

\[ \vec{V} \equiv \hat{\mu} \vec{F} \]

\( \hat{\mu} \)’s relation to \( \hat{\xi} \):

\[ \hat{\mu} \equiv \hat{\xi}^{-1} \]
Mean Mobility

Mean Friction Coefficient

\[
\frac{1}{\langle \xi \rangle} = \frac{1}{3} \left( \frac{1}{\xi_1} + \frac{1}{\xi_2} + \frac{1}{\xi_3} \right)
\]

and \( \mu = 1/\xi \) therefore . . .
Mean Mobility

\[ \frac{1}{\langle \xi \rangle} = \frac{1}{3} \left( \frac{1}{\xi_1} + \frac{1}{\xi_2} + \frac{1}{\xi_3} \right) \]

and \( \mu = 1/\xi \) therefore . . .

Mean Mobility Coefficient

\[ \langle \mu \rangle = \frac{1}{3} (\mu_1 + \mu_2 + \mu_3) \]
Consider the velocity of perturbed fluid due to the sphere’s movement:

\[
\begin{align*}
\nu_r &= \frac{V}{2} \left[ 3 \left( \frac{R}{r} \right) - \left( \frac{R}{r} \right)^3 \right] \cos \theta \\
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Vector Notation

\[ \mathbf{v} = v_r \mathbf{e}_r + v_\theta \mathbf{e}_\theta \]
Consider the velocity of perturbed fluid due to the sphere’s movement:

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**Vector Notation**

\[ \vec{v} = \frac{V}{2} \left[ 3 \left( \frac{R}{r} \right) - \left( \frac{R}{r} \right)^3 \right] \cos \theta \vec{e}_r - \frac{V}{4} \left[ 3 \left( \frac{R}{r} \right) + \left( \frac{R}{r} \right)^3 \right] \sin \theta \vec{e}_\theta \]
Oseen-Burgers Tensor

Vector Notation

\[ \vec{V} = \frac{V}{2} \left[ 3 \left( \frac{R}{r} \right) - \left( \frac{R}{r} \right)^3 \right] \cos \theta \vec{e}_r - \frac{V}{4} \left[ 3 \left( \frac{R}{r} \right) + \left( \frac{R}{r} \right)^3 \right] \sin \theta \vec{e}_\theta \]

\[ = \frac{3V}{4} \left( \frac{R}{r} \right) \left[ 2\vec{e}_r \cos \theta - \vec{e}_\theta \sin \theta \right] - \frac{V}{4} \left( \frac{R}{r} \right)^3 \left[ 2\vec{e}_r \cos \theta + \vec{e}_\theta \sin \theta \right] \]

\[ \approx \frac{3V}{4} \left( \frac{R}{r} \right) \left[ 2\vec{e}_r \cos \theta - \vec{e}_\theta \sin \theta \right] - \mathcal{O}(r^{-3}) \]
Since \( \vec{e}_z = \vec{e}_r \cos \theta - \vec{e}_\theta \sin \theta \), the velocity to 1\textsuperscript{st} order is

\[
\vec{v} = \frac{3V}{4} \left( \frac{R}{r} \right) [2\vec{e}_r \cos \theta - \vec{e}_\theta \sin \theta]
\]

\[
= \frac{3V}{4} \left( \frac{R}{r} \right) [\vec{e}_z + \vec{e}_r \cos \theta]
\]
Vector Notation

Since \( \vec{e}_z = \vec{e}_r \cos \theta - \vec{e}_\theta \sin \theta \), the velocity to 1st order is

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\vec{v} = \frac{3V}{4} \left( \frac{R}{r} \right) [2\vec{e}_r \cos \theta - \vec{e}_\theta \sin \theta]
\]

\[
= \frac{3V}{4} \left( \frac{R}{r} \right) \left[ \vec{e}_z + \vec{e}_r \cos \theta \right]
\]

That’s pretty.
Oseen-Burgers Tensor

Hydrodynamic Interaction

In terms of the drag force, \( \vec{F} = 6\pi \eta RV \vec{e}_z \)
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\vec{v} = \frac{3V}{4} \left( \frac{R}{r} \right) [\vec{e}_z + \vec{e}_r \cos \theta]
\]

\[
= \frac{3}{4} \frac{\vec{F}}{6\pi \eta R \vec{e}_z} \left( \frac{R}{r} \right) [\vec{e}_z + \vec{e}_r \cos \theta]
\]

\[
= \frac{1}{8\pi \eta r} \left[ \frac{\vec{e}_z + \vec{e}_r \cos \theta}{\vec{e}_z} \right] \vec{F}
\]

\[
= \frac{1}{8\pi \eta r} \left[ \hat{l} + \vec{e}_r \vec{e}_r \right] \vec{F}
\]
In terms of the drag force, \( \vec{F} = 6\pi \eta RV \vec{e}_z \).
Hydrodynamic Interaction

In terms of the drag force, \( \vec{F} = 6\pi \eta RV \hat{e}_z \)

\[
\vec{v} = \hat{\Omega} \vec{F}
\]

where the Oseen-Burgers Tensor

\[
\hat{\Omega} = \frac{1}{8\pi \eta r} \left[ \hat{l} + \hat{e}_r \hat{e}_r \right]
\]

describes the perturbation of fluid due to motion of a sphere.
Oseen-Burgers Tensor

Hydrodynamic Interaction

In terms of the drag force, $\vec{F} = 6\pi \eta RV \vec{e}_z$

$$\vec{v} = \hat{\Omega} \vec{F}$$

where the Oseen-Burgers Tensor

$$\hat{\Omega} = \frac{1}{8\pi \eta r} \left[ \hat{I} + \vec{e}_r \vec{e}_r \right]$$

describes the perturbation of fluid due to motion of a sphere. Notice that it decays as $r^{-1}$ with $O(r^{-3})$. 
Compliance (Often Called Response Function)

\[ \vec{r} \equiv \hat{\alpha} \vec{F} \]
Compliance

Compliance (Often Called Response Function)

\[ \vec{r} \equiv \hat{\alpha} \vec{F} \]

So then:

\[ \hat{\alpha} \equiv \hat{\mu} \times t \]

This may seem silly but it turns out to be most useful.
Compliance (Often Called Response Function)

$$\vec{r} \equiv \hat{\alpha} \vec{F}$$

So then:

$$\hat{\alpha} \overset{?}{=} \hat{\mu} \times t$$

This may seem silly but it turns out to be most useful. We’ll come back to this in a moment after we generalize the Stokes Equation.
Extending “Falling Ball” Rheology to Finite Frequencies

Idea

The “falling ball” rheology is very passive and can be thought of as the zero-frequency limit of more active experiments.
Extending “Falling Ball” Rheology to Finite Frequencies

**Idea**

The “falling ball” rheology is very passive and can be thought of as the zero-frequency limit of more active experiments

\[
\eta = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega}
\]

\(G''\) is the loss modulus: \(G''(\omega) = \omega \eta(\omega)\).

**Reconsidering Compliance Tensor**

Now the compliance doesn’t seem so silly, does it?
Extending “Falling Ball” Rheology to Finite Frequencies

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The “falling ball” rheology is very passive and can be thought of as the zero-frequency limit of more active experiments

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\(G''\) is the loss modulus: \(G''(\omega) = \omega \eta(\omega)\).

Reconsidering Compliance Tensor

Now the compliance doesn’t seem so silly, does it?

\[
\alpha = \frac{\mu}{\omega} = \frac{1}{\hat{\xi} \omega} = \frac{1}{6\pi \omega \eta(\omega) R}
\]

\[
= \frac{1}{6\pi R G''}
\]
Complication 1) Lose and Storage

Consider the relation between the compliance and the shear modulus for a viscous fluid:

$$\alpha = \frac{1}{6\pi RG''}$$

It stands to reason (and was previously discussed by Dr. Harden) then that for a viscoelastic fluid with $G^*(\omega) = G' + iG''$, the compliance is also complex: $\alpha^*(\omega) = \alpha' + i\alpha''$
Complication 1) Lose and Storage

Consider the relation between the compliance and the shear modulus for a viscous fluid:

\[ \alpha = \frac{1}{6\pi RG''} \]

It stands to reason (and was previously discussed by Dr. Harden) then that for a viscoelastic fluid with \( G^*(\omega) = G' + iG'' \), the compliance is also complex:

\[ \alpha^*(\omega) = \alpha' + i\alpha'' \]

\[ \alpha^*(\omega) = \frac{1}{6\pi RG^*(\omega)} \]
History Dependence

Complication 2) Memory

\[ F(t) = \int_{t-\infty}^{t} \xi^*(\tau) V(\tau) d\tau = (\xi^* \ast V)(t) \]

\[ V(t) = \int_{t-\infty}^{t} \mu^*(\tau) F(\tau) d\tau = (\mu^* \ast F)(t) \]

\[ r(t) = r(0) - \int_{t-\infty}^{t} \alpha^*(\tau) F(\tau) d\tau = (\alpha^* \ast F)(t) \]
History Dependence

Complication 2) Memory

Friction Coefficient

\[ F(t) = \int_{-\infty}^{t} \xi^*(t - \tau) V(\tau) d\tau \]
\[ = (\xi^* * V)(t) \]
Complication 2) Memory

- Friction Coefficient

\[ F(t) = \int_{-\infty}^{t} \xi^*(t-\tau) V(\tau) \, d\tau \]
\[ = (\xi^* * V)(t) \]

- Mobility

\[ V(t) = \int_{-\infty}^{t} \mu^*(t-\tau) F(\tau) \, d\tau \]
\[ = (\mu^* * F)(t) \]
**History Dependence**

### Complication 2) Memory

- **Friction Coefficient**

\[
F (t) = \int_{-\infty}^{t} \xi^*(t - \tau) V(\tau) \, d\tau = \left( \xi^* \ast V \right)(t)
\]

- **Mobility**

\[
V(t) = \int_{-\infty}^{t} \mu^*(t - \tau) F(\tau) \, d\tau = \left( \mu^* \ast F \right)(t)
\]

- **Compliance**

\[
r(t) - r(0) = \int_{-\infty}^{t} \alpha^*(t - \tau) F(\tau) \, d\tau = \left( \alpha^* \ast F \right)(t)
\]
Convolution

Because we’ll use it so often . . .
Because we’ll use it so often . . .

\[(f \ast g)(t) = \int_{-\infty}^{\infty} f(t - \tau) g(\tau) \, d\tau\]
Lecture Structure
“Falling Ball” Rheology
Response Tensors
Generalized Stokes Equation
Viscoelastic Materials
Inhomogeneities
Two-Particle Microrheology

Complex Response Functions
Generalized Response Functions
Frequency Domains
Generalized Einstein Equation
General Transform

Laplace Transform

Definition

\[ \tilde{f}(s) = \int_0^\infty e^{-st} f(t) \, dt \]
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### Definition

\[ \tilde{f}(s) = \int_0^{\infty} e^{-st} f(t) \, dt \]

### Convolution

\[ (f * g)(t) = \tilde{f}(s) \tilde{g}(s) \]

### Linearity

\[ f(t) + ig(t) = \tilde{f}(s) + i\tilde{g}(s) \]

### Derivative

\[ \tilde{f}'(t) = sf(s) + f(0) \]
Fourier Transform

Definition

\[ \tilde{f}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-it\omega} f(t) \, dt \]
Fourier Transform

**Definition**

\[
\overline{f}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-it\omega} f(t) \, dt
\]

**Convolution**

\[
(f \ast g)(t) = \overline{f}(\omega) \overline{g}(\omega)
\]

**Linearity**

\[
\overline{f(t) + ig(t)} = \overline{f}(\omega) + i\overline{g}(\omega)
\]

**Derivative**

\[
\overline{f'(t)} = i\omega\overline{f}(\omega)
\]
Response Functions in Each Domain

### Lag-Time, Fourier and Laplace Domains

#### Friction Coefficient

\[ F(t) = [\xi^* \ast V](t) \]
\[ F(\omega) = \tilde{\xi}^*(\omega) \tilde{V}(\omega) \]
\[ F(s) = \xi^*(s) V(s) \]

#### Mobility

\[ V(t) = [\mu^* \ast F](t) \]
\[ V(\omega) = \tilde{\mu}^*(\omega) F(\omega) \]
\[ V(s) = \mu^*(s) F(s) \]

#### Compliance

\[ \Delta r(\omega) = [\alpha^* \ast F](t) \]
\[ \Delta r(\omega) = \tilde{\alpha}^*(\omega) F(\omega) \]
\[ \Delta r(s) = \alpha^*(s) F(s) \]
Response Functions in Each Domain

Lag-Time, Fourier and Laplace Domains

- **Friction Coefficient**
  \[
  F(t) = |\xi* \ast V|(t) \\
  \mathcal{F}(\omega) = \xi^*(\omega) \mathcal{V}(\omega) \\
  F(s) = \xi^*(s) \mathcal{V}(s)
  \]

- **Mobility**
  \[
  V(t) = |\mu^* \ast F|(t) \\
  \mathcal{V}(\omega) = \mu^*(\omega) \mathcal{F}(\omega) \\
  V(s) = \mu^*(s) \mathcal{F}(s)
  \]

- **Compliance**
  \[
  \Delta_r(\omega) = |\alpha^* \ast F|(t) \\
  \Delta\mathcal{r}(\omega) = \alpha^*(\omega) \mathcal{F}(\omega) \\
  \Delta r(s) = \alpha^*(s) \mathcal{F}(s)
  \]

Nice

By working in the Laplace (or frequency) domain we recover relationships that look like the Stokes Equation.
Viscoelastic materials have memory so their random walk can be more complicated:

\[ m \ddot{V} = F_{\text{rnd}} - \int_0^t \xi(t - \tau) V(\tau) \, d\tau \]
Viscoelastic materials have memory so their random walk can be more complicated:

\[ m \dot{V} = F_{\text{rnd}} - \int_{0}^{t} \xi (t - \tau) V(\tau) d\tau \]

Need to know entire history in time if you want to know it’s current behaviour.
Viscoelastic materials have memory so their random walk can be more complicated:

\[ m \dot{V} = F_{\text{rnd}} - \int_0^t \xi (t - \tau) V(\tau) \, d\tau \]

Need to know entire history in time if you want to know its current behaviour.

In the Laplace Domain, the random walk of the Langevin Equation is much simpler.
Langevin Equation in Laplace Domain

\[ m\dot{V} = F_{\text{rnd}} - \int_{0}^{t} \xi(t - \tau) V(\tau) d\tau \]

\[ m\ddot{V} = \tilde{F}_{\text{rnd}} - (\xi * \tilde{V})(t) \]

\[ ms\tilde{V} - mV(0) = \tilde{F}_{\text{rnd}} - \tilde{\xi}\tilde{V} \]

\[ \tilde{V}(s) = \frac{mV(0) + \tilde{F}_{\text{rnd}}(s)}{ms + \tilde{\xi}(s)} \]
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Generalized Einstein Equation

Langevin Equation in Laplace Domain

Recall, the velocity autocorrelation was the connection to the diffusion coefficient so multiply by \( V(0) \) and average:
Langevin Equation in Laplace Domain

Recall, the velocity autocorrelation was the connection to the diffusion coefficient so multiply by $V(0)$ and average:

$$\left\langle V(0) \tilde{V}(s) \right\rangle = \left\langle V(0) \frac{mV(0) + \tilde{F}_{\text{rnd}}(s)}{ms + \tilde{\xi}(s)} \right\rangle$$
Recall, the velocity autocorrelation was the connection to the diffusion coefficient so multiply by $V(0)$ and average:

$$\langle V(0) \tilde{V}(s) \rangle = \frac{m \langle V^2(0) \rangle + \langle V(0) \tilde{F}_{\text{rnd}}(s) \rangle}{ms + \tilde{\xi}(s)}$$
Langevin Equation in Laplace Domain

Recall, the velocity autocorrelation was the connection to the diffusion coefficient so multiply by \( V(0) \) and average:

\[
\left\langle V(0) \tilde{V}(s) \right\rangle = \frac{m \left\langle V^2(0) \right\rangle + \left\langle V(0) \tilde{F}_{\text{rnd}}(s) \right\rangle}{ms + \tilde{\xi}(s)}
\]

1) Average of Random Noise

\[
\left\langle V(0) \tilde{F}_{\text{rnd}}(s) \right\rangle = 0
\]
Recall, the velocity autocorrelation was the connection to the diffusion coefficient so multiply by $V(0)$ and average:

$$\langle V(0) \tilde{V}(s) \rangle = \frac{m \langle V^2(0) \rangle + 0}{ms + \tilde{\xi}(s)}$$
Generalized Einstein Equation

Langevin Equation in Laplace Domain

Recall, the velocity autocorrelation was the connection to the diffusion coefficient so multiply by $V(0)$ and average:

$$\langle V(0)\tilde{V}(s)\rangle = \frac{m\langle V^2(0)\rangle + 0}{ms + \tilde{\xi}(s)}$$

2) Equipartition Theorem

$$\frac{1}{2}m\langle V^2(0)\rangle = \frac{1}{2}k_B T$$
Langevin Equation in Laplace Domain

Recall, the velocity autocorrelation was the connection to the diffusion coefficient so multiply by $V(0)$ and average:

$$\langle V(0) \tilde{V}(s) \rangle = \frac{k_B T}{ms + \tilde{\xi}(s)}$$
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3) Negligible Inertia

$$\tilde{\xi} \gg ms$$
3) Negligible Inertia

\[ \tilde{\xi} \gg ms \]

Langevin Equation in Laplace Domain

Recall, the velocity autocorrelation was the connection to the diffusion coefficient so multiply by \( V(0) \) and average:

\[
\left\langle V(0) \tilde{V}(s) \right\rangle = \frac{k_B T}{0 + \tilde{\xi}(s)}
\]
Lecture Structure
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Langevin Equation in Laplace Domain
Recall, the velocity autocorrelation was the connection to the diffusion coefficient so multiply by $V(0)$ and average:

$$\langle V(0) \tilde{V}(s) \rangle = \frac{k_B T}{\tilde{\xi}(s)}$$
Generalized Einstein Equation

Langevin Equation in Laplace Domain

Recall, the velocity autocorrelation was the connection to the diffusion coefficient so multiply by \( V(0) \) and average:

\[
\langle V(0) \hat{V}(s) \rangle = \frac{k_B T}{\hat{\xi}(s)}
\]

Replace Viscous with Viscoelastic

We’ve been doing it all lecture

\[ \xi \rightarrow \xi^* \]
Recall, the velocity autocorrelation was the connection to the diffusion coefficient so multiply by $V(0)$ and average:

$$\left\langle V(0) \tilde{V}(s) \right\rangle = \frac{k_B T}{\tilde{\xi}^*(s)}$$
Identity

In Laplace Domain, it is true that the velocity autocorrelation and the mean square displacement are equivalent by the identity:

\[
\langle V(0) \tilde{V}(s) \rangle \equiv \frac{s^2}{2} \langle \Delta \tilde{r}^2(s) \rangle
\]

Notice, I wrote \( \langle \Delta \tilde{r}^2(s) \rangle \equiv \langle \Delta r^2 \rangle(s) \) just because it’s prettier that way.
Generalized Einstein Equation

Hard Earned Results

\[ \tilde{\xi}^* (s) = \frac{2k_B T}{s^2 \langle \Delta \tilde{r}^2 (s) \rangle} \]
Generalized Einstein Equation

Hard Earned Results

\[ \tilde{\xi}^* (s) = \frac{2k_B T}{s^2 \langle \Delta \tilde{r}^2 (s) \rangle} \]

\[ \tilde{\mu}^* (s) = \frac{s^2 \langle \Delta \tilde{r}^2 (s) \rangle}{2k_B T} \]
Generalized Einstein Equation

Hard Earned Results

\[ \tilde{\xi}^* (s) = \frac{2k_B T}{s^2 \langle \Delta \tilde{r}^2 (s) \rangle} \]

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\[ \tilde{\alpha}^* (s) = \frac{s \langle \Delta \tilde{r}^2 (s) \rangle}{3k_B T} \]
Generalized Einstein Equation

Hard Earned Results

\[ \tilde{\xi}^* (s) = \frac{2k_B T}{s^2 \langle \Delta \tilde{r}^2 (s) \rangle} \]

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\[ \tilde{G}^* (s) = \frac{k_B T}{\pi R s \langle \Delta \tilde{r}^2 (s) \rangle} \]
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Complex Response Functions
Generalized Response Functions
Frequency Domains
Generalized Einstein Equation
General Transform

General Treatment

General Response Function

Last time David said:

\[ R(t) = k \beta T \frac{\partial C_0}{\partial t} \]

where \( R \) is a response function (say \( \alpha \)) and \( C_0 \) is the autocorrelation function (say \( \langle \Delta q_2(t) \rangle \)).
General Response Function

Last time David said:

\[ R(t) = \frac{1}{k_B T} \frac{\partial C_0}{\partial t} \]

where \( R \) is a response function (say \( \alpha \)) and \( C_0 \) is the autocorrelation function (say \( \langle \Delta q^2(t) \rangle \)).
General Treatment

General Response Function

$$\mathcal{R}(t) = \frac{1}{k_B T} \frac{\partial C_0}{\partial t}$$

General Laplace

$$\tilde{\mathcal{R}} = \frac{1}{k_B T} \frac{\partial \tilde{C}_0}{\partial t}$$

$$= \frac{s}{k_B T} \tilde{C}_0$$

$$= \frac{s}{k_B T} \langle \Delta \tilde{q}^2(s) \rangle$$

$$= \frac{s}{k_B T} \langle \Delta \tilde{q}^2(s) \rangle$$
General Treatment

General Response Function

\[ R(t) = \frac{1}{k_B T} \frac{\partial C_0}{\partial t} \]

General Fourier

\[ \overline{R} = \frac{1}{k_B T} \overline{\frac{\partial C_0}{\partial t}} = \frac{i\omega}{k_B T} \overline{C_0} \]
The Fourier transform of a cross correlation is

\[ q \star p = \int_{-\infty}^{\infty} q^{CC}(\tau) p(t+\tau) d\tau \]

\[ = (q^{cc}(-t) \star p(t))(t) \]

\[ (q \star p) = \overline{q^{CC}p} \]
The Fourier transform of a cross correlation is

\[ q \star p = \int_{-\infty}^{\infty} q^{CC}(\tau) p(t + \tau) \, d\tau = (q^{cc}(-t) \ast p(t))(t) \]

\[ (q \star p) = \overline{q^{CC}p} \]

Therefore, for autocorrelation we have

\[ (q \star q) = \overline{q^{CC}q} = |\overline{q}|^2 \]

Return to response function . . .
General Treatment

General Response Function

\[ R(t) = \frac{1}{k_B T} \frac{\partial C_0}{\partial t} \]

General Fourier

\[ \overline{R} = \frac{1}{k_B T} \overline{\frac{\partial C_0}{\partial t}} \]

\[ = \frac{i \omega}{k_B T} \overline{C_0} \]

\[ = \frac{i \omega}{k_B T} |\overline{q}|^2 \]

Note: be aware of upcoming statement about this solution.
In the laboratory

Fourier Domain

We found the complex, viscoelastic response functions in Laplace space **but**
In the laboratory

Fourier Domain

We found the complex, viscoelastic response functions in Laplace space \textbf{but} in the experiment one controls the frequency.
In the laboratory

**Fourier Domain**

We found the complex, viscoelastic response functions in Laplace space **but** in the experiment one controls the frequency. Use Fourier

\[
\alpha''(\omega) = \frac{\omega |\Delta \bar{r}^2|}{2k_B T}
\]

Important point:
In the laboratory

**Fourier Domain**

We found the complex, viscoelastic response functions in Laplace space but in the experiment one controls the frequency. Use Fourier

\[
\overline{\alpha''}(\omega) = \frac{\omega |\Delta \bar{r}^2|}{2 k_B T}
\]

Important point: only get loss compliance
In the laboratory

**Kramers-Kronig**

For any complex function, $f = f + ig$, there is an identity

$$g = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{f(w)}{w - \omega} dw$$

i.e. $f$ and $g$ are not independent.
In the laboratory

Kramers-Kronig

For any complex function, \( f = f + ig \), there is an identity

\[
g = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{f(w)}{w - \omega} \, dw
\]

i.e. \( f \) and \( g \) are not independant.

Our case:

\[
\alpha'(\omega) = \frac{2}{\pi} \mathcal{P} \int_0^{\infty} \frac{w \alpha''(w)}{w^2 - \omega^2} \, dw
\]

\[
= \frac{2}{\pi} \int_0^{\infty} \cos(\omega t) \, dt \int_0^{\infty} \alpha''(w) \sin(wt) \, dw
\]
Local Medium

Probe particle is really existing in a bubble. Do the response functions see outside of the local region?

*We imagine that each probe sphere is surrounded by a pocket of perturbed material with rheological properties different from those of the bulk.*
Homogeneous Media

For a homogeneous media, we went to great lengths to demonstrate

\[ \hat{\Omega} \propto \frac{R}{r} \]
Local Medium

Homogeneous Media

For a homogeneous media, we went to great lengths to demonstrate

\[ \hat{\Omega} \propto \frac{R}{r} \]

Pocket Model

The hydrodynamic interaction still extends with the same scaling \textbf{but} it must displace some viscoelastic matrix at the interface between the bulk and the pocket.
Example

Levine and Lubensky

Assume that the media responds elastically to the perturbations due to the probe motion in viscous fluid:

\[ 0 = \lambda_1 \nabla^2 \vec{u} + (\lambda_1 + \lambda_2) \nabla \cdot \vec{u} \]

where \( \vec{u} \) is the displacement of the media and \( \lambda_i \) are Lamè coefficients (for describing elasticity).
Example

Levine and Lubensky

Assume that the media responds elastically to the perturbations due to the probe motion in viscous fluid:

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where \( \vec{u} \) is the displacement of the media and \( \lambda_i \) are Lamè coefficients (for describing elasticity).

Find:

\[ \hat{\alpha} = \frac{i}{6\pi \eta R} Z(\lambda_{1, \text{in}}, \lambda_{2, \text{in}}, \xi/R) \]
Compliance Only Depends on Pocket Properties

The correction factor $Z(\lambda_{1,\text{in}}, \lambda_{2,\text{in}}, \xi/R)$ fails to capture storage information about bulk.
Compliance Only Depends on Pocket Properties

The correction factor $Z(\lambda_{1,\text{in}}, \lambda_{2,\text{in}}, \xi/R)$ fails to capture storage information about bulk. FYI: if bulk can be treated as incompressible then $Z$ takes the relatively simple form

$$Z = \frac{4\beta^6 \kappa''^2 + 10\beta^3 \kappa' - 9\beta^5 \kappa' \kappa + 2\kappa \kappa'' + 3\beta \left[ 2 + \kappa - 3\kappa^2 \right]}{2 \left[ \kappa'' - 2\beta^5 \kappa' \right]}$$

where $\beta = 1 + \xi/R$, $\kappa = G_{\text{out}}^*/G_{\text{in}}^*$, $\kappa' = \kappa - 1$ and $\kappa'' = 3 + 2\kappa$. 
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Two-Particle Langevin Equation
Response Functions
Microrheology Scheme

Langevin Equation

1-Particle

\[ m \ddot{\vec{V}} = \vec{F}_{\text{rnd}} - \int_{0}^{t} \xi^* (t - \tau) \vec{V} (\tau) \, d\tau \]
Langevin Equation

1-Particle

\[ m \ddot{\mathbf{V}} = \mathbf{F}_{\text{rnd}} - \int_0^t \hat{\xi}^*(t - \tau) \mathbf{V}(\tau) \, d\tau \]

2-Particles

\[ m \ddot{\mathbf{V}}_i = \mathbf{F}_{\text{rnd}} - \int_0^t \hat{\xi}_{ii}^*(t - \tau) \mathbf{V}_i(\tau) \, d\tau - \mathbf{F}_{ij} \]
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Tyler Shendruk
One- and Two-Particle Microrheology
Force on particle $i$ due to particle $j$ - Viscous Fluid
Force on particle $i$ due to particle $j$ - Viscoelastic Fluid
Force on particle $i$ due to particle $j$

**Force from Second Particle**

The second particle ($j$) acts on the first ($i$) because it’s moving through the viscoelastic fluid.
Force on particle $i$ due to particle $j$

Force from Second Particle

The second particle ($j$) acts on the first ($i$) because it’s moving through the viscoelastic fluid. Sphere $j$ has some velocity $V_j$ which causes a drag

$$\vec{F}_j = \int_0^t \hat{\xi}_j^* \vec{V}_j dt$$
Force on particle \( i \) due to particle \( j \)

### Force from Second Particle

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\[
\vec{F}_j = \int_{0}^{t} \hat{\xi}_j^* \vec{V}_j dt
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That force propagates through the media \( i.e. \)
Force on particle $i$ due to particle $j$

**Force from Second Particle**

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That force propagates through the media *i.e.* by the HI tensor:

$$\vec{v} = \hat{\Omega} \vec{F}_j$$
Force on particle \( i \) due to particle \( j \)

**Force from Second Particle**

The second particle \( (j) \) acts on the first \( (i) \) because it’s moving through the viscoelastic fluid. Sphere \( j \) has some velocity \( V_j \) which causes a drag

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\vec{F}_j = \int_0^t \hat{\xi}_j^* \vec{V}_j dt
\]

That force propagates through the media *i.e.* by the HI tensor:

\[
\vec{v} = \hat{\Omega} \vec{F}_j
\]

Resulting in the force \( \vec{F}_{ij} \) on particle \( i \):

\[
\vec{F}_{ij} = \hat{\Omega}^{-1} \vec{v}
= \hat{\Omega}^{-1} \hat{\Omega} \vec{F}_j
= \vec{F}_j
= \int_0^t \hat{\xi}_j^* \vec{V}_j dt
\]
Two-Particle Langevin Equation

\[ m \dot{V}_i = F_{\text{rnd}} - \int_0^t \xi_i^* (t - \tau) V_i(\tau) \, d\tau - F_{ij} \]

\[ = F_{\text{rnd}} - \int_0^t \xi_i^* (t - \tau) V_i(\tau) \, d\tau - \int_0^t \xi_j^* (t - \tau) V_j(\tau) \, d\tau \]

\[ = F_{\text{rnd}} - \int_0^t \xi_{ii}^* (t - \tau) V_i(\tau) \, d\tau - \int_0^t \xi_{ij}^* (t - \tau) V_j(\tau) \, d\tau \]

\[ = F_{\text{rnd}} - (\xi_{ii}^* * V_i)(t) - (\xi_{ij}^* * V_j)(t) \]

Note: I turned the set friction tensors into an array of tensors.
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Laplace Transform

Two-Particle Langevin Equation

\[ ms \tilde{V}_i - mV_i(0) = \tilde{F}_{\text{rnd}} - \tilde{\xi}_{ij} \tilde{V}_j - \tilde{\xi}_{ii} \tilde{V}_i \]
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Two-Particle Langevin Equation

\[ ms \tilde{V}_i - mV_i(0) = \tilde{F}_{\text{rnd}} - \xi^*_{ij} \tilde{V}_j - \xi^*_{ii} \tilde{V}_i \]

We want to consider the distinct’s interparticle part so on top of multiplying by \( V_i(0) \) again, we also multiply by \( \delta(R - r_{ij}) = \delta_{ij} \) before averaging

\[
ms \langle \tilde{V}_i V_i(0) \delta_{ij} \rangle - m \langle V_i^2(0) \delta_{ij} \rangle = \langle \tilde{F}_{\text{rnd}} V_i(0) \delta_{ij} \rangle - \xi^*_{ij} \langle \tilde{V}_j V_i(0) \delta_{ij} \rangle - \xi^*_{ii} \langle \tilde{V}_i V_i(0) \delta_{ij} \rangle
\]
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Laplace Transform

Two-Particle Langevin Equation

\[ m_s \tilde{V}_i - m V_i(0) = \tilde{F}_{\text{rnd}} - \xi_{ij}^* \tilde{V}_j - \xi_{ii}^* \tilde{V}_i \]

We want to consider the distinct’s interparticle part so on top of multiplying by \( V_i(0) \) again, we also multiply by \( \delta(R - r_{ij}) = \delta_{ij} \) before averaging

\[
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\]

\[
0 - k_B T = 0 - \tilde{\xi}_{ij}^* \langle V_i(0) \tilde{V}_j \delta_{ij} \rangle - 0
\]
Correlation and Response Functions

\[ \left\langle V_i(0) \tilde{V}_j \delta_{ij} \right\rangle = \frac{k_B T}{\tilde{\xi}^{*}_{ij}} \]
Response Functions

Correlation and Response Functions

\[ \langle V_i(0)\tilde{V}_j\delta_{ij} \rangle = \frac{k_B T}{\tilde{\xi}^*_{ij}} \]

Say \( \hat{D} = \langle \Delta r_i(0) \Delta \tilde{r}_j(s) \delta_{ij} \rangle \) is the **distinct** displacement tensor, (or the mobility correlation tensor)
Correlation and Response Functions

\[ \langle V_i (0) \tilde{V}_j \delta_{ij} \rangle = \frac{k_B T}{\tilde{\xi}_{ij}} \]

Say \( \hat{D} = \langle \Delta r_i (0) \Delta \tilde{r}_j (s) \delta_{ij} \rangle \) is the **distinct** displacement tensor, (or the mobility correlation tensor)

\[
D_{ij} = \frac{2k_B T}{s^2 \tilde{\xi}_{ij}^*} \\
= \frac{2k_B T}{s^2} \tilde{\mu}_{ij}^* \\
= \frac{3k_B T}{s} \tilde{\alpha}_{ij}^*
\]
Complex Modulus

But what about the complex modulus, $\tilde{G}^* = 6\pi R\tilde{\alpha}_{ij}$?
But what about the complex modulus, $\tilde{G}^* = 6\pi R \tilde{\alpha}_{ij}$? Since $D_{ij}$ is explicitly distinct with a $\delta (R - r_{ij})$, the form

$$D_{ij} = \frac{k_B T}{2\pi s R \tilde{G}_{ij}^*}$$

can not be permissible.
But what about the complex modulus, $\tilde{G}^* = 6\pi R\tilde{\alpha}_{ij}$? Since $D_{ij}$ is explicitly distinct with a $\delta (R - r_{ij})$, the form

$$D_{ij} \neq \frac{k_B T}{2\pi sR \tilde{G}_{ij}^*}$$

can not be permissible.
Complex Modulus

Probe Independence

The $\delta$ suggests $R \rightarrow r_{ij}$
Complex Modulus

Probe Independence

The $\delta$ suggests $R \rightarrow r_{ij}$ which is correct but I don’t know how to demonstrate in a general way.
Complex Modulus

Probe Independence

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Radial Component

Along the line connecting the particles the mobility correlation function is

$$\tilde{D}_{rr} (s) = \frac{k_B T}{2\pi s r_{ij} \tilde{G}^* (s)}$$
Complex Modulus

Probe Independence
The $\delta$ suggests $R \rightarrow r_{ij}$ which is correct but I don’t know how to demonstrate in a general way.

Radial Component
Along the line connecting the particles the mobility correlation function is

$$\tilde{D}_{rr} (s) = \frac{k_B T}{2\pi s r_{ij} \tilde{G}^* (s)}$$

Non-Radial Components
$$D_{\theta\theta} = D (\phi\phi) = \frac{1}{2} D_{rr}$$
Comparison of Near and Far

Far Field

The two particle method demands that the particles are far from each other.
Comparison of Near and Far

Far Field

The two particle method demands that the particles are far from each other. If local environments overlap then measurements obviously won’t represent the bulk properties.
Conclusion
Thank you for your patience.