Fluctuation Rheology Using a Polymer.

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Outline

1. Rheology measurement by looking at the fluctuations

2. Using polymer, why and how?

3. Summary

Fluctuation-dissipation theorem

A particle doing 1D Brownian motion, where $\hat{\eta}(t)$ is the thermal random force.

$$x(t) = \int_{-\infty}^{t} dt' \alpha(t-t')\hat{\eta}(t') \quad \text{or} \quad x(\omega) = \alpha(\omega)\hat{\eta}(\omega)$$

Callen, Welton, Kubo (1950s'):

$$\langle \hat{\eta}(\omega)\hat{\eta}(-\omega)\rangle = \frac{2k_BT}{\omega}\mathrm{Im}\left(\alpha^{-1}(\omega)\right)\underbrace{\left[\frac{\hbar\omega}{2k_BT}\coth\frac{\hbar\omega}{2k_BT}\right]}_{\approx 1 \text{ for small } \omega}$$

or

$$\langle x(\omega)x(-\omega)\rangle = \frac{2k_BT}{\omega}\alpha''(\omega)$$

Fluctuation Rheology (Gittes et. al. 97)

- Measure $\langle x(0)x(t)\rangle$. FT to get $\langle x(\omega)x(-\omega)\rangle$.
- Use FDT to get $\alpha''(\omega) = (\omega/2k_BT)\langle x(\omega)x(-\omega)\rangle$
- The real part can be obtained by Kramers & Kronig's formula

$$\alpha'(\omega) = \frac{2}{\pi} P \int_0^\infty d\xi \frac{\xi\ \alpha''(\xi)}{\xi^2 - \omega^2}$$

- For a spherical particle

$$\alpha(\omega) = \frac{1}{6\pi a G^*(\omega)} \quad \text{provided}$$

$$\sigma(t) = \int_{-\infty}^{t} G(t-t')\nabla\mathbf{v}(t')dt' \quad \text{where} \quad G^*(\omega) \equiv i\omega \int_0^\infty d\tau e^{-i\omega\tau} G(\tau)$$

Problems

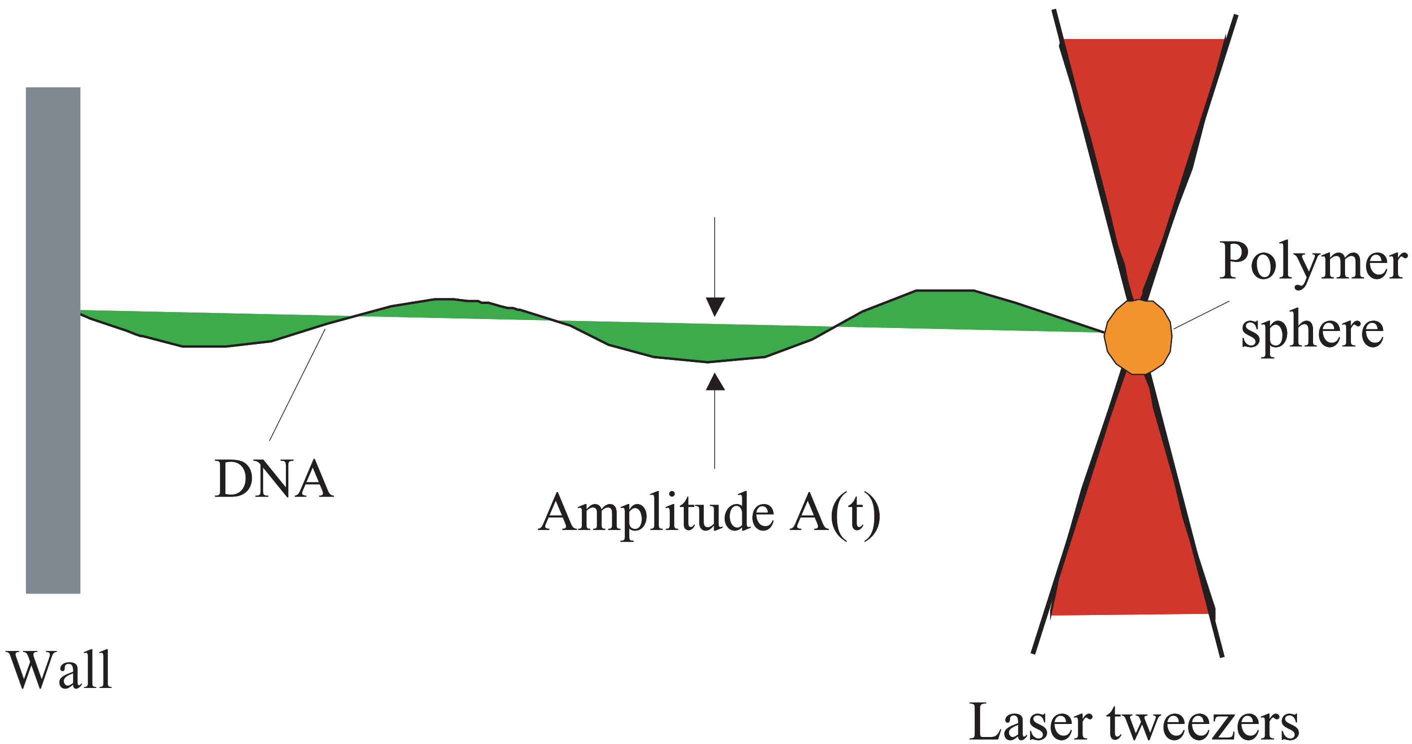
Rheological property depends on the length scale. Small sphere can only probe the Microrheology. How to do Macrorheology?

2 spheres, or ....

Using a Polymer to do Macrorheology

- Use the conformation degree of freedom to do fluctuation rheology.
- The test polymer can be very long. One can use the long wavelength mode to get the macrorheology.
- Can probe many wavelengths at the same experiment.

A possible experimental setup.



Length scale dependent viscoelasticity

Linear response regime.

- The stress $\sigma(\mathbf{r}, t)$ is proportional to the strain rate $\nabla\mathbf{v}(\mathbf{r}', t')$.

$$\sigma(\mathbf{r}, t) = \int \int_{-\infty}^{t} g(\mathbf{r} - \mathbf{r}', t - t')\nabla\mathbf{v}(\mathbf{r}', t')dt'd\mathbf{r}'$$

- The complex modulus can be defined as

$$G^*(\mathbf{k}, \omega) \equiv i\omega \int d\mathbf{r} \int_0^\infty d\tau e^{-i\omega\tau} e^{-i\mathbf{k}\cdot\mathbf{r}} g(\mathbf{r}, \tau)$$

- The macroscopic viscoelasticity is just $G^*(0, \omega)$ or written as $G^*(\omega)$.

Polymer Dynamic Equation

The Newton's 2nd law

$$\underbrace{\rho(\partial_t \mathbf{v} + \mathbf{v}\cdot\nabla\mathbf{v})}_{\text{inertia terms}} = -\nabla P - \frac{\delta F}{\delta \mathbf{r}} + \underbrace{\nabla\cdot\sigma}_{\text{viscoelastic force}} + \underbrace{\hat{\eta}}_{\text{random noise}}$$

- The polymer elastic force

$$-\frac{\delta F}{\delta \mathbf{r}} = \int ds\ \delta^3(\mathbf{r} - \mathbf{R}(s,t))\,(\epsilon\mathbf{R}(s,t))$$

where $\epsilon \equiv (3k_B T/b)\partial_s^2$

- Solve the flow field by FT on space and time.

$$\mathbf{v}(\mathbf{k},\omega) \simeq \mathcal{G}(\mathbf{k},\omega)\cdot\int \theta(\mathbf{k},s)\,(\epsilon\mathbf{R}(s,\omega) + \hat{\eta}(s,\omega))\ ds$$

where $\mathcal{G}(\mathbf{k},\omega) = \dfrac{i\omega(\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}})}{\rho(i\omega)^2 + G^*(\mathbf{k},\omega)k^2}$, $\theta(\mathbf{k},s) = e^{-i\mathbf{k}\cdot\mathbf{R}_0(s)}$

Dispersion relation

- $$\overbrace{\partial_t \mathbf{R}(s,t)}^{\text{polymer velocity}} = \int d\mathbf{r}\,\delta^3(\mathbf{r}-\mathbf{R}(s,t))\mathbf{v}(\mathbf{r},t) \simeq \int \frac{d\mathbf{k}}{(2\pi)^3}\theta(\mathbf{k},s)\mathbf{v}(-\mathbf{k},t)$$

$$i\omega \mathbf{R}(s,\omega) \simeq \int \underbrace{\int \frac{d\mathbf{k}}{(2\pi)^3} \overbrace{\langle \theta(\mathbf{k},s)\theta(-\mathbf{k},s')\rangle}^{S(\mathbf{k},s-s')} \mathcal{G}(-\mathbf{k},\omega)}_{\mathbf{H}(s-s',\ \omega)} \left[\epsilon \mathbf{R}(s',\omega) + \hat{\eta}(s',\omega)\right] \; ds'$$

- FT on $s \to q$ (the normal coordinate), the dispersion relation is

$$\left[i\omega + H_x(q,\omega)\epsilon(q)\right] R_x(q,\omega) = H_x(q,\omega)\hat{\eta}(q,\omega)$$

- FDT: $$\langle |R_x(q,\omega)|^2\rangle = \frac{2k_BT}{\omega}\mathrm{Im}\left[\frac{H_x(q,\omega)}{i\omega + H_x(q,\omega)\epsilon(q)}\right]$$

Structure function $S(\mathbf{k}, q)$

- The structure function $S(\mathbf{k}, q)$ is defined by

$$S(\mathbf{k}, q) = \int ds' \langle e^{-i\mathbf{k}\cdot\left(\mathbf{R}_0(s+s')-\mathbf{R}_0(s)\right)}\rangle e^{-iqs'}$$

- For Gaussian chain under applied tension force F,

$$S(\mathbf{k}, q) = \frac{12k^2/b}{k^4 + 4(k_z F/k_B T + 3q/b)^2}$$

- The applied tension can change $S(\mathbf{k}, q)$ (and possibly $\epsilon(q)$).

Mobility H_x

$$
\begin{aligned}
H_x(q,\omega) &= \underbrace{\frac{i\omega}{G^*(\omega)}\int\frac{d\mathbf{k}}{(2\pi)^3}\overbrace{\left(S(\mathbf{k},q)\frac{(1-\hat{k}_x^2)}{k^2}\right)}^{\text{universal at large } k}\overbrace{\left(\frac{G^*(\omega)}{G^*(\mathbf{k},\omega)}-1\right)}^{\text{vanishes at low } k}}_{Rouse} \\
&+ \underbrace{\frac{i\omega}{G^*(\omega)}\int\frac{d\mathbf{k}}{(2\pi)^3}S(\mathbf{k},q)\frac{(1-\hat{k}_x^2)}{k^2}}_{Zimm \quad \propto\, q^{-1/2}} \\
&+ \underbrace{\frac{i\rho\omega^3}{(G^*(\omega))^2}\int\frac{d\mathbf{k}}{(2\pi)^3}S(\mathbf{k},q)\frac{(1-\hat{k}_x^2)}{k^4}}_{\text{Inertia correction } \propto\, q^{-3/2}} \\
&= \frac{i\omega}{G^*(\omega)}(h^R+h^Z(q))+\delta H(q,\omega)
\end{aligned}
$$

Recipes

- Drop the inertia effect first.

- One can choose different q, or change the tension, so that $\epsilon(q)$ and $h(q)$ are different. Three measurements (at each ω) will give $G'(\omega)$, $G''(\omega)$, and h^R.

$$\langle |R_x(q,\omega)|^2 \rangle = \frac{2k_BT}{\omega} \frac{(h^R + h^Z(q))G''(\omega)}{\left[h^R\epsilon(q) + h^Z(q)\epsilon(q) + G'(\omega)\right]^2 + G''^2(\omega)}$$

- Inertia correction can be included by the iteration process.

Summary

Advantages of fluctuation rheology using a polymer

- Can do macrorheology.
- Elastic coupling provides more data than the two spheres method. One can avoid the analytical continuation completely.
- The applied tension provides a new controlled parameter.
- In principle one can measure the anisotropic properties by changing the orientations of the probing polymer.

Disadvantages

- Have to calibrate $\epsilon(q)$ and $S(\mathbf{k}, q)$.
- Still can't measure the system with the slow modes.