Polymer Physics Quiz 11 2020 April 10, 2020

Diffusive wave spectroscopy (DWS) is a method to measure the high frequency viscoelastic properties of a fluid. It has similarities to dynamic light scattering (DLS).



- a) The figure above is the graphical abstract for *From well-entangled to partially-entangled wormlike micelles* W. Zou, G. Tan, H. Jiang, K. Vogtt, M. Weaver, P. Koenig, G. Beaucage and R. G. Larson *Soft Matter* **15** 642-655 (2019). Consider just the *G*' & *G*" versus ω plot. Explain the regimes that are observed and the two crossover frequencies. The different color curves correspond to different salt concentrations in the inset plot of zero shear viscosity, η_0 . η_0 increases with salt since the chains grow in length until they branch at the peak value. Branches in micelles are mobile so that they reduce the viscosity. Why is DWS important to this plot?
- b) DWS is a technique that utilizes probe nano-particles to quantify the viscosity. For the Zou paper "solutions of sulfate latex particles (8.2 wt%, analytical grade with a bead size of 600 nm were used as molecular probes with final bead concentration at 0.5 wt%. The transport mean-free path l* (= 552 mm) was determined from the control sample with the same-size beads in water."

Explain why Zou added polystyrene beads to the WLM system. Explain what is l^* ? (Do not just say it is "the transport mean free path".)

c) Mason, Gang, and Weitz, *Diffusing-wave-spectroscopy measurements of viscoelasticity* of complex fluids, J. Opt. Soc. Am. A14 139-149 (1997), write the equation of motion for a probe particle with the following equation where $\zeta(t-t^2)$ is a memory function.

$$m\dot{v}(t) = f_R(t) - \int_0^t \mathrm{d}t' \zeta(t-t')v(t').$$

v(t) is the velocity, *m* is the mass of a particle and $f_{\rm R}(t)$ is a random pulse function that reflects thermal motion of the probe particle. What is a memory function? Explain how it works in this equation.

d) Mason notes that the time dependent stress, $\tau(t)$, is related to the time dependent rate of strain, $\gamma'(t)$ by the time dependent relaxation modulus $G_r(t-t')$, which is another memory function.

$$\tau(t) = \int_0^t dt' G_r(t - t') \dot{\gamma}(t')$$

and the Laplace transform of the relaxation modulus is directly related to the Laplace transform of the memory function from part c which can be measured in the DWS experiment,

$$\tilde{G}_r(s) = \frac{\zeta(s)}{6\pi a}.$$
(8)

What is the origin of 6 πa in equation 8?

e) In DLS we measure a time correlation function, $g^1(q,t)$ that depends on the scattering vector "q". Give the dependence of $g^1(q,t)$ on q and explain the origin of this dependence.

What is the dependence of the correlation function in DWS on q? Explain your answer.

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a) Explain the regimes that are observed and the two crossover frequencies. Why is DWS important to this plot?

The plot shows the full viscoelastic spectrum from Newtonian flow to the left, the first crossover at the viscoelastic relaxation time, the rubbery plateau and the second crossover for Rouse flow within the tube at highest frequency. As the salt content increases the chains grow so the different curves are effectively for different molecular weight chains. The short chains do not show a rubbery plateau. All of the chains show similar high frequency behavior. The DWS enables observation of the high frequency part of the curve.

b) Explain why Zou added polystyrene beads to the WLM system.

Explain what is l^* ?

DWS requires a probe particle, PS latex beads in this case, which generate the optical signal. The probe particles need to be of sufficient concentration so that multiple scattering occurs. Light scatters from one particle and is then scattered by many other particles until it is detected. The minimum distance the light must travel so that the source of the light is not know is l^* . After this length there is no angular dependence to the scattered light. Motion of the probe particles is governed by their size and the viscoelastic spectrum of the fluid.

c) What is a memory function? Explain how it works in this equation.

$$m\dot{v}(t) = f_R(t) - \int_0^t \mathrm{d}t' \zeta(t-t')v(t').$$

The equation is a force balance on the particles. The input force that makes the particle move is a random thermal motion $f_R(t)$ that is caused by solvent and micelle particles impacting the PS latex spheres. This generates instantaneous acceleration, mv'(t). This acceleration is random in direction and its magnitude is proportional to kT. The random thermal force is dissipated by the drag force, the friction factor, ζ , times the velocity of the particles. This tends to bring the particle back to zero velocity. The friction factor acts as a memory function with a fading memory behavior. Velocities that happened in the past at time t', add to the current drag force at time t weighted by a decaying friction factor memory function. Things from long ago are forgotten. This means that in the absence of thermal input the system will reach a static state eventually. The memory function is a function of the time difference between now, t, and sometime in the past, t'. The lead factor is Stokes law, $6\pi\eta_0 R_{\rm H}$. It might be an exponential decay like $6\pi\eta_0 R_{\rm H} \exp(-t/\tau)$.

d) What is the origin of 6 πa in equation 8?

This comes from Stokes Law.

e) Give the dependence of $g^1(q,t)$ on q and explain the origin of this dependence. What is the dependence of the correlation function in DWS on q? Explain your answer.

$$g^{1}(q; \tau) = \exp(-\Gamma \tau)$$

 $\Gamma = q^{2}D_{t}$
 $\mathbf{D} = \mathbf{k}_{\mathrm{B}}\mathbf{T}/6\pi\eta\mathbf{a}$

This dependence originates from Brownian Motion where $\langle x^2 \rangle = 2Dt$ Which can be rewritten, $t = \langle x^2 \rangle / (2D)$ or $1/(2Dq^2)$ if we assume $x \sim 1/q$. So $-\tau/t = -\tau (2Dq^2)$.