Problem set 6 – Soft Matter

Problem 21

Viscosity measurements can be used to determine the volume fraction, density or size of colloidal particles, and the molecular weight and degree of swelling of polymers by making use of the Einstein relation for suspension viscosity.

a) Describe how one could determine the effective density of a colloidal material from measuring its viscosity?

b) Is this method also accurate for polydisperse colloids (i.e., where the colloidal particles have different sizes)?

c) How would a polymer brush (with thickness h) on the surface of the colloidal particles influence the calculated density?

Problem 22

Similar viscosity measurements can be used to determine the molecular weight of polymers. In this case, the Mark-Houwink-Sakurada relationship is used.

a) Start from the Einstein expression for intrinsic viscosity (slide 13), and assume that the polymers are effective spheres with a radius R_h (h for hydrodynamic radius) and a volume $V_h = 4\pi R_h^3/3$. Derive the Mark-Houwink-Sakurada relationship.

b) Do the Mark-Houwink-Saturada parameters K_M and a depend on temperature?

c) For rigid rods, such as Tobacco mosaic virus, the Mark-Houwink-Saturada parameter $a = 2$. Also for very strongly charged polyelectrolytes in low salt concentration $a = 2$ (they behave like rigid rods), so $[\eta] = K_M\, M_w^2$. What do you conclude from this about the hydrodynamic radius of a strongly charged polyelectrolyte of length L?

d) What is the Mark-Houwink-Saturada parameter a for solid spherical particles, such as latex colloids?

Problem 23

The Maxwell model is the simplest model of the linear viscoelastic response of soft materials. It is a combination of an elastic spring and a viscous dashpot.

a) Sketch a graph for the extension length Δx as a function of time for a single spring, a single dashpot and a Maxwell element that contains both a spring and a dashpot, if at time $t = t_1$ a constant force is suddenly exerted, which is removed abruptly at time $t = t_2$.

b) Compare the expression for stress of an elastic solid (slide 7) and force in the elastic spring of a Maxwell material (slide 17). How is the constant k_e related to the modulus G? Do the same for the constant k_v and the viscosity η by comparing the force in the viscous dashpot and the stress of a Newtonian liquid (slide 7)?

c) Derive the equation for creep of a Maxwell material (slide 18). Start from the expression of the force in the spring and dashpot (slide 17). In a creep experiment, the applied force F is kept constant. Rewrite $x_e = F/k_e$ and $dx_v/dt = F/k_v$, and find the expression for $\gamma = x_t/L0$.

Problem 24

Many soft materials show nonlinear viscoelastic behavior: they have strain or shear-rate dependent moduli or viscosities, or time-dependence. Let us consider here the viscoelastic *liquids* that have a terminal viscous behaviour (i.e., they flow at long timescales), and their behaviour in an experiment where the shear rate ($\dot{\gamma}$) is gradually increased. For each of the materials below, draw the following two diagrams: (1) the viscosity η as a function of the shear rate $\dot{\gamma}$, and (2) the shear stress σ as a function of shear rate $\dot{\gamma}$.

a) A concentrated polymer solution that shows strong shear thinning behaviour at high shear rates.

b) A suspension of colloidal particles that shows shear thickening behaviour (e.g., like corn starch).

c) A dense emulsion of polymer-stabilized oil droplets in water (e.g., mayonaise) that exhibits a yield stress, followed by medium shear thinning.

d) The sample under b) can become thixotropic upon the addition of salt, meaning that they exhibit a time-dependent shear thinning effect, and return to a tick viscous state at rest over time. Explain what could be the microscopic origin of this effect.