Soft Matter Problem set 6 – Mechanical properties of soft matter Answers

Problem 21

a) Weigh a quantity m and suspend it in a volume V. The mass concentration $C = m/V$. Measure the viscosity of this suspension using, for instance, a capillary viscometer. Calculate the reduced viscosity as $\eta_{\text{red}} = \frac{\eta_s - \eta_0}{\eta_0 C} = 2.5/\rho$ with ρ the effective density.

b) Interestingly, this expression is also valid for polydisperse colloids.

c) The volume fraction ϕ is the Einstein equation for suspension rheology is an effective volume fraction based on the radius of the sphere around which the fluid (medium) flows. This include any polymer brush of thickness h on the surface. The effective density is therefore a weighted average of the density of the core (with radius Rcore) and the polymer brush.

$$\rho_{\text{av}} = \frac{4\pi R_{\text{core}}^3 \rho_{\text{core}}/3 + 4\pi R_{\text{core}}^2 h \rho_{\text{brush}}}{4\pi (R_{\text{core}} + h)^3/3}$$

Problem 22

a)

$$[\eta] = \frac{2.5\phi}{C} = \frac{2.5(n_p \cdot V_h/V_{\text{tot}})}{C} = \frac{2.5(n_p \cdot V_h/V_{\text{tot}})}{(n_p M_w/V_{\text{tot}})/N_{\text{A}}} = \frac{2.5 N_{\text{A}} V_h}{M_w}$$

Then, we use $V_h = 4\pi R_h^3/3$ and $R \sim N^\nu \sum M_w^\nu$

$$[\eta] = \frac{10\pi N_{\text{A}} R_h^3}{3M_w} = K_M \frac{M_w^{3\nu}}{M_w} = K_M M_w^a$$

with $a = 3\nu - 1$.

b) K_M is independent of temperature (see a), but a is dependent on temperature as it depends on the degree of swelling of the polymers (solvent quality), which depends on temperature.

c)

$$[\eta] = \frac{2.5 N_{\text{A}} V_h}{M_w} \sim M_w^2$$

Therefore, $V_h \sim M_w^3$ and $R_h \sim M_w \sim N$. So the hydrodynamic radius must be directly proportional to the contour length L.

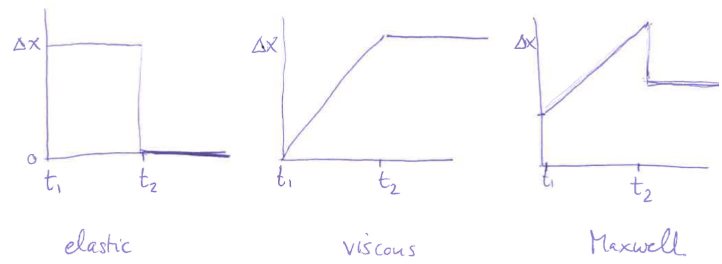
d) $R_h = R$ and $V_h = 4\pi R^3/3 = M/\rho$.

$$[\eta] = \frac{2.5 N_{\text{A}} V_h}{M_w} \sim \frac{M/\rho}{M} \sim \frac{1}{\rho}$$

Therefore, $a = 0$.

Problem 23

a)



b) Elastic solid: $\sigma = G\gamma = G\frac{x_e}{y}$ with y the dimension of the material in the relevant direction (shear or elongation). Since $\sigma = \frac{F}{A}$, $F = GAx_e/y$.

Maxwell material in stress relaxation: $F = k_e x_e$, therefore: $G = k_e y/A$. Check dimensions: k_e is a spring constant (N/m), y a dimension (m) and A and area (m^2), so G has the units of N/m^2 = Pa, which is a modulus.

Similar for a viscous liquid: $\sigma = \eta\dot{\gamma} = \eta\frac{1}{y}\frac{dx_v}{dt}$ with y the dimension of the material in the relevant direction (shear or elongation). Since $\sigma = \frac{F}{A}$, $F = \eta A(dx_v/dt)/y$.

Maxwell material in stress relaxation: $F = k_v dx_v/dt$, therefore: $\eta = k_v y/A$. Check dimensions: k_v has units N s/m, y a dimension (m) and A and area (m^2), so G has the units of $N{\cdot}s/m^2$ = Pa s, which is a viscosity.

c)

$$x_e = \frac{F}{k_e} \qquad \frac{dx_v}{dt} = \frac{F}{k_v} \qquad 1 \cdot dx_v = \frac{F}{k_v}dt$$

The first equation is the elastic response to the applied force, which is not time-dependent. The second is the viscous element's response. We integrate to get:

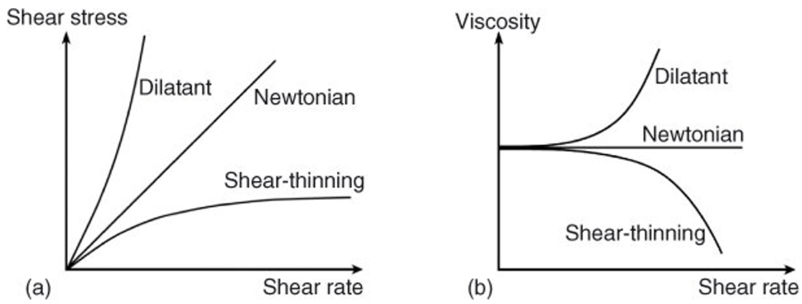
$$x_v = \frac{Ft}{k_v} + C$$

With boundary condition $x_v = 0$ at $t = 0$, hence, $C = 0$. The total extension:

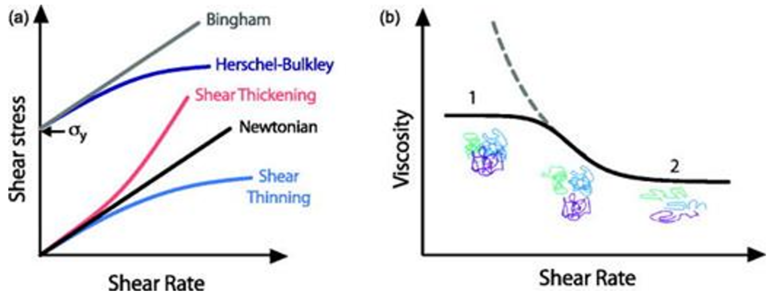
$$x_t = x_e + x_v = \frac{F}{k_e} + \frac{Ft}{k_v} \qquad \gamma = \frac{x_t}{L_0} = \frac{F}{k_e L_0}\left(1 + \frac{k_e t}{k_v}\right) = \gamma_0\,(1 + t/\tau)$$

Problem 24

a and b) Shear thinning and shear thickening (dilatant = shear thickening):



c) Yield stress materials (Bingham and Herschel-Bulkley are two different models for yield stress materials; σ_y is the yield stress)



d) A thixotropic material (like ketchup) typicially has a viscosity that decreases with shaking (high $\dot{\gamma}$), and that increases again slowly over time at rest. This may be caused by reversible (weak/secondary minimum) aggregation of the particles, which can be broken by moderate shaking. Adding salt to colloidal particles that are stabilized by surface charges can decrease the electrostatic repulsion between the particles and lowering the stabilizing energy barrier to create a secondary minimum. At rest, such particles form clusters. Upon (mild) shaking, these clusters can be broken, leading to shear thinning. When the shaking is stopped, the clusters will form again, but this takes time, as the particles have to collide through Brownian motion. Therefore, the viscosity increases slowly over time (thixotropic effect).