

# PH30028: Soft Condensed Matter Physics

## Outline solutions to problems

### (1) Relaxation time in atomic fluids

#### Brownian motion:

$$\text{displacement } x_B = \left( \langle x^2 \rangle \right)^{1/2} = (2Dt)^{1/2} = \left( \frac{k_B T}{3\pi\eta R} t \right)^{1/2} = 30 \mu\text{m} \left( \frac{t}{\text{min}} \right)^{1/2}$$

and thus in 1 min: 30  $\mu\text{m}$  and in one hour: 229  $\mu\text{m}$

#### Sedimentation:

$$\text{displacement: } x_{sed} = v_{sed} t = \frac{2R^2 \Delta \rho g}{9\eta} t = 41 \text{ nm} \frac{t}{\text{min}}$$

and thus in 1 min: 41 nm and in 1 hour 2.5  $\mu\text{m}$

### (2) Equipartitioning

$$\text{Equipartitioning: } \frac{3}{2} k_B T = \frac{1}{2} m \langle v^2 \rangle$$

and thus

$$v_{rms} = \langle v^2 \rangle^{1/2} = \sqrt{\frac{3k_B T}{m}}$$

and relaxation time

$$\tau_R \sim \frac{R}{v_{rms}}$$

Example:

$$m = 18u \approx 3 \times 10^{-26} \text{ kg}, \quad R \approx 0.2 \text{ nm} \quad (\text{eg. H}_2\text{O}) \quad \text{and } T = 300 \text{ K}$$

$$\therefore v_{rms} \approx 650 \text{ m s}^{-1} \quad \text{and} \quad \tau_R \approx 3 \times 10^{-13} \text{ s}$$

### (3) Gravitational length

- (a) Distribution of particle number:  $n(h) = n_B e^{-mgh/k_B T} = n_B e^{-h/L_g}$   
where the 'gravitational length'

$$L_g = \frac{k_B T}{mg} = \frac{3k_B T}{4\pi R^3 \Delta \rho g} = 2 \times 10^{-24} \text{ m}^3 \text{ R}^{-3}$$

and thus  $L_g = 1.6 \text{ cm}$  for  $R = 50 \text{ nm}$  and  $L_g = 2 \mu\text{m}$  for  $R = 1 \mu\text{m}$ .

- (b) Total number  $N = n_a A H$  (with  $n_a$  the average density) and

$$N = A \int_0^H n_B e^{-h/L_g} dh = A L_g n_B [1 - e^{-H/L_g}]$$

$$\Rightarrow n_a A H = A L_g n_B [1 - e^{-H/L_g}]$$

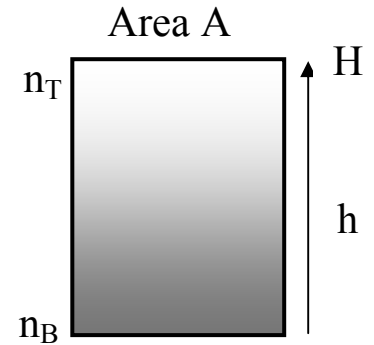
$$\Rightarrow n_B = n_a \frac{H}{L_g} \frac{1}{1 - e^{-H/L_g}}$$

$$\Rightarrow n_T = n_B e^{-H/L_g} = n_a \frac{H}{L_g} \frac{1}{e^{H/L_g} - 1}$$

$$\Rightarrow n_B = 2.7 n_a \text{ and } n_T = 0.23 n_a \text{ for } R = 50 \text{ nm and}$$

$$n_B = 20 \times 10^3 n_0 \text{ and } n_T \approx 0 \text{ for } R = 1 \mu\text{m}$$

Note  $L_g \approx R \approx 1 \mu\text{m}$  means that at thermal equilibrium in a tube of this suspension there will be hardly any particles a few particle diameters above the bottom of the tube. Almost all particles will thus be sedimented.



- (c) In order to establish the concentration gradient, some particles initially at the top of the sample will have to settle to the bottom, Thus some estimate (probably an underestimate) of the time required is the time taken by a particle to sediment a distance H. The time t can be calculated from the sedimentation velocity by

$$t = \frac{H}{v_{sed}} = \frac{9\eta H}{2R^2 \Delta \rho g} = 3.6 \times 10^{-7} \text{ m}^2 \text{ s R}^{-2}$$

thus  $t = 4.6 \text{ years}$  for  $R = 50 \text{ nm}$  and  $t = 4.2 \text{ days}$  for  $R = 1 \mu\text{m}$ .

Note the Boltzmann distribution as used above is only valid if the particles do NOT interact with each other. Otherwise

$n(h) \sim n_0 e^{-U/k_B T}$  where  $U$  is the gravitational p.e. + interparticle interaction.

#### (4) Peclet number

In one dimension  $\langle x^2(t) \rangle = 2Dt = 2(k_B T / \xi)t$ . Hence time to diffuse

$$\text{distance } R: \tau_R = \frac{R^2 \xi}{2k_B T}$$

$$\text{Time to sediment a distance } R \text{ is: } \tau_{sed} = \frac{R}{v_{sed}} = \frac{R\xi}{m_B g}$$

$$\therefore Pe = \frac{\tau_R}{\tau_{sed}} = \frac{R^2 \xi}{2k_B T} \frac{m_B g}{R\xi} = \frac{m_B g R}{2k_B T} \sim \frac{\text{gravitational PE to raise distance } R}{\text{thermal kinetic energy}}$$

#### (5) Diffusion equation:

$$n(x, t) = C \times \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}$$

$$\begin{aligned} \frac{\partial n}{\partial t} &= -C \times \frac{1}{\sqrt{4\pi Dt} 2t} e^{-x^2/4Dt} + C \times \frac{x^2}{\sqrt{4\pi Dt} 4Dt^2} e^{-x^2/4Dt} \\ &= -C \times \frac{1}{\sqrt{4\pi Dt} 2t} e^{-x^2/4Dt} \left( 1 - \frac{x^2}{2Dt} \right). \end{aligned}$$

$$\frac{\partial n}{\partial x} = C \times \frac{-2x}{\sqrt{4\pi Dt} 4Dt} e^{-x^2/4Dt}$$

$$\begin{aligned} \frac{\partial^2 n}{\partial x^2} &= C \times \frac{-2}{\sqrt{4\pi Dt} 4Dt} e^{-x^2/4Dt} + C \times \frac{4x^2}{\sqrt{4\pi Dt} (4Dt)^2} e^{-x^2/4Dt} \\ &= -C \times \frac{1}{\sqrt{4\pi Dt} 2Dt} e^{-x^2/4Dt} \left( 1 - \frac{x^2}{2Dt} \right) = \frac{1}{D} \frac{\partial n}{\partial t} \end{aligned}$$

Total number of particles:

$$N_{total} = \int_{-\infty}^{\infty} n(x, t) dV = A \int_{-\infty}^{\infty} n(x, t) dx = A \int_{-\infty}^{\infty} C \times \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} dx = AC$$

$$\therefore C = \frac{N_{total}}{A}$$

## (6) Mean square displacement

The diffusion equation is

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}$$

Multiply by  $x^2$  and integrate:

$$\int_{-\infty}^{\infty} x^2 \frac{\partial n}{\partial t} dx = D \int_{-\infty}^{\infty} x^2 \frac{\partial^2 n}{\partial x^2} dx$$

Now, noting that

$$\langle x^2(t) \rangle = \frac{1}{N} \int_{-\infty}^{\infty} x^2 n(x, t) dx$$

we can write the LHS as

$$\int_{-\infty}^{\infty} x^2 \frac{\partial n}{\partial t} dx = \frac{\partial}{\partial t} \int_{-\infty}^{\infty} x^2 n dx = N \frac{\partial}{\partial t} \langle x^2(t) \rangle$$

The right hand side can be integrated by parts and, using the fact that as  $n \rightarrow 0$ ,  $\partial n / \partial x \rightarrow 0$  as  $|x| \rightarrow \infty$

$$D \int_{-\infty}^{\infty} x^2 \frac{\partial^2 n}{\partial x^2} dx = D \left[ x^2 \frac{\partial n}{\partial x} \right]_{-\infty}^{\infty} - 2D \int_{-\infty}^{\infty} x \frac{\partial n}{\partial x} dx = 0 - 2D \left[ xn \right]_{-\infty}^{\infty} + 2D \int_{-\infty}^{\infty} n dx = 2DN$$

$$\therefore N \frac{\partial}{\partial t} \langle x^2(t) \rangle = 2DN$$

$$\therefore \langle x^2(t) \rangle = 2Dt$$

## (7) Relaxation time in colloidal suspensions

Based on  $\langle \underline{r}^2 \rangle = 6Dt$ , we estimate that  $R^2 \sim 6D\tau_R$  or  $\tau_R \sim R^2 / D$ . Taking into account the Stokes-Einstein relation  $D = k_B T / (6\pi\eta R)$ , we arrive at

$$\tau_R \sim \frac{R^2 6\pi\eta R}{k_B T}$$

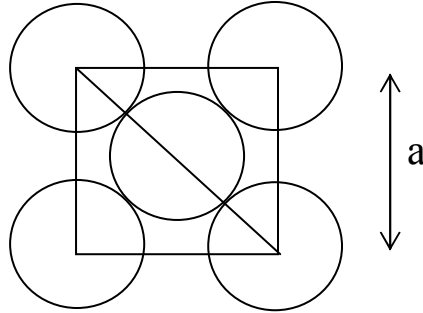
which indicates a very fast increase in  $\tau_R$  as  $R$  increases.

For  $R \approx 1\mu m$  we get

$$\tau_R \approx \frac{(10^{-6} m)^2 \cdot 6\pi \cdot 10^{-3} \text{ Nm}^{-2} s \cdot 10^{-6} m}{1.38 \times 10^{-23} \text{ JK}^{-1} 300 \text{ K}} \approx 5 s$$

This is seriously long, especially compared to  $\tau_R$  in atomic fluids.

## (8) Colloidal Crystals



### Upper limit:

Particles per unit cell: 8 in corners ( $8 \times 1/8$ ) + 6 in faces ( $6 \times 1/2 = 3$ )

So total of 4 particles with volume  $V_{part} = 4 \times \frac{4\pi}{3} R^3$

Length of a unit cell:  $a = 4R\sqrt{1/2} = 2\sqrt{2}R$

Thus volume of a unit cell:  $V_{cell} = a^3 = 16\sqrt{2}R^3$

Hence volume fraction:  $\phi = \frac{V_{part}}{V_{cell}} = \frac{4 \times \frac{4}{3} \pi R^3}{16\sqrt{2}R^3} = \frac{\pi}{3\sqrt{2}} = 0.740$

### Lower limit

‘swollen’ fcc cell (length  $a$ ):

$$0.545 = \phi = \frac{V_{part}}{V_{cell}} = \frac{4 \times \frac{4}{3} \pi R^3}{a^3} = \frac{16\pi R^3}{3a^3}$$

$$\Rightarrow a = \left( \frac{16\pi R^3}{3\phi} \right)^{1/3} = \left( \frac{16\pi}{3\phi} \right)^{1/3} R = 3.13R$$

## (9) Lagrange’s expression for radius of gyration

$$\begin{aligned}
 R_g^2 &= \frac{1}{N} \sum_{j=1}^N (\underline{R}_j - \underline{R}_G)^2 = \frac{1}{N} \sum_{j=1}^N \left( \underline{R}_j - \frac{1}{N} \sum_{k=1}^N \underline{R}_k \right)^2 \\
 &= \frac{1}{N} \sum_{j=1}^N \underline{R}_j^2 - \frac{2}{N^2} \sum_{j=1}^N \sum_{k=1}^N \underline{R}_j \cdot \underline{R}_k + \frac{1}{N} \sum_{j=1}^N 1 \frac{1}{N^2} \sum_{k=1}^N \sum_{l=1}^N \underline{R}_k \cdot \underline{R}_l
 \end{aligned}$$

Now, using the hint and changing dummy indices gives

$$R_g^2 = \frac{1}{N} \sum_{j=1}^N \underline{R}_j^2 - \frac{1}{N^2} \sum_{j=1}^N \sum_{k=1}^N \underline{R}_j \cdot \underline{R}_k$$

Again using the hint and playing with dummy indices

$$\begin{aligned}
 R_g^2 &= \frac{1}{N^2} \sum_{j=1}^N \sum_{k=1}^N \underline{R}_j^2 - \frac{1}{N^2} \sum_{j=1}^N \sum_{k=1}^N \underline{R}_j \cdot \underline{R}_k \\
 &= \frac{1}{2N^2} \sum_{j=1}^N \sum_{k=1}^N \underline{R}_j^2 + \frac{1}{2N^2} \sum_{j=1}^N \sum_{k=1}^N \underline{R}_k^2 - \frac{1}{N^2} \sum_{j=1}^N \sum_{k=1}^N \underline{R}_j \cdot \underline{R}_k \\
 &= \frac{1}{2N^2} \sum_{j=1}^N \sum_{k=1}^N (\underline{R}_j - \underline{R}_K)^2
 \end{aligned}$$

## (10) Mean length

For a freely jointed chain, we have from lectures that  $\langle \underline{R}^2 \rangle = Nb^2$ .

Now  $N=10^5$  and  $b=4.322\text{\AA}$

Hence,  $\sqrt{\langle \underline{R}^2 \rangle} = \sqrt{10^5 \times 4.322^2} = 1366\text{\AA}$ .

For a fixed bond angle, from notes:

$$\langle \underline{R}^2 \rangle = Nb^2(1+\cos\theta)/(1-\cos\theta)$$

$$\theta=180-108.0^\circ, \cos\theta=0.31$$

Hence,  $\langle \underline{R}^2 \rangle = 01.9Nb^2, \Rightarrow \sqrt{\langle \underline{R}^2 \rangle} = 1.88 \times 10^3\text{\AA}$

## (11) Real data

(a)

$M (10^6 \text{ g mol}^{-1})$	4.04	1.56	1.20	1.06	0.626	0.394
$\langle R_g^2 \rangle (\text{nm}^2)$	3260	1210	928	770	484	305
$B = (\langle R_g^2 \rangle / M)^{1/2}$	0.0284	0.0279	0.0278	0.0270	0.0278	0.0278

with the average value  $B=0.0278\pm0.0004$  and thus

$$\langle R_g^2 \rangle^{1/2} \approx 0.028 M^{1/2} \text{ nm g}^{1/2} \text{ mol}^{-1/2}$$

(b)

$$\langle R_g^2 \rangle^{1/2} \approx 0.028 N^{1/2} M_M^{1/2} \text{ nm g}^{1/2} \text{ mol}^{-1/2} = 0.28 N^{1/2} \text{ nm}$$

$$\therefore \langle R^2 \rangle = 6 \langle R_g^2 \rangle = 0.5 N \text{ nm}^2$$

$$\therefore \langle R^2 \rangle = C N b_0^2 = 0.5 N \text{ nm}^2$$

$$\therefore C = \frac{0.5 \text{ nm}^2}{b_0^2} \approx 9.5 \quad \text{for } b_0 = 0.23 \text{ nm}$$

For the freely rotating chain, this leads to

$$C = \frac{1 + \cos \theta}{1 - \cos \theta} \Rightarrow \cos \theta = \frac{C - 1}{C + 1} = 0.81$$

$$\therefore \theta \approx 36^\circ$$

These are fairly typical values of bond angle and persistence length ( $b' = C b_0 = 9.5 b_0$ )

(c) From part (a) we get

$$\langle R_g^2 \rangle^{1/2} = 0.028 (10^7 \text{ g mol}^{-1})^{1/2} \text{ nm g}^{-1/2} \text{ mol}^{1/2} \approx 89 \text{ nm}$$

(d)

The volume occupied by the monomers of one coil is

$$V_M = \frac{M}{N_A \rho} = \frac{10^7 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1} 10^6 \text{ g m}^3} = 1.6 \times 10^{-23} \text{ m}^3$$

and the volume of the coil is given by

$$V_{coil} = \frac{4\pi}{3} \langle R^2 \rangle = 2.9 \times 10^{-21} \text{ m}^3$$

Thus the monomers occupy only about  $V_M / V_{coil} = 0.5\%$  of the volume taken up by the coil. 99.5% of the material inside the coil is solvent!

To reach the overlap concentration  $c^*$ , we need  $1/V_{coil}$  molecules and this a monomer volume  $V_M / V_{coil}$  and monomer mass per volume

$\rho V_M / V_{coil} = 5.5 \text{ mg ml}^{-1}$ . We can also get this value using the equation in the notes:

$$c^* = \frac{3M}{4\pi N_A \langle R_g^2 \rangle^{3/2}} = \frac{3 \times 10^7 \text{ g mol}^{-1}}{4\pi \times 6.02 \times 10^{23} \text{ mol}^{-1} (89 \text{ nm})} = 5.5 \text{ mg ml}^{-1}$$

Upon an increase (decrease) in temperature, the solvent becomes a good (poor) solvent and the coil swells (collapses), i.e.  $\langle R_g^2 \rangle$  increases (decreases) , and  $c^*$  thus decreases (increases).

## (12) Micelles

Using the results of section 8.2, we can calculate the volume of the hydrophobic part and the critical chain length as

$$v = (27.4 + 26.9 \times 10) \times 10^{-3} \text{ nm}^3 = 0.2964 \text{ nm}^3$$

$$l_c = (0.154 + 0.1265 \times 10) \text{ nm} = 1.419 \text{ nm}$$

$$a_0 = 0.65 \text{ nm}^2$$

Hence

$$\frac{v}{a_0} = 0.456 = \frac{R}{3} = \frac{l_c}{3.11}$$

implying spherical micelles of average size  $R = 1.368 \text{ nm}$ .

Finally, since  $Na_0 = 4\pi R^2$  , we can calculate that  $N=36$ .

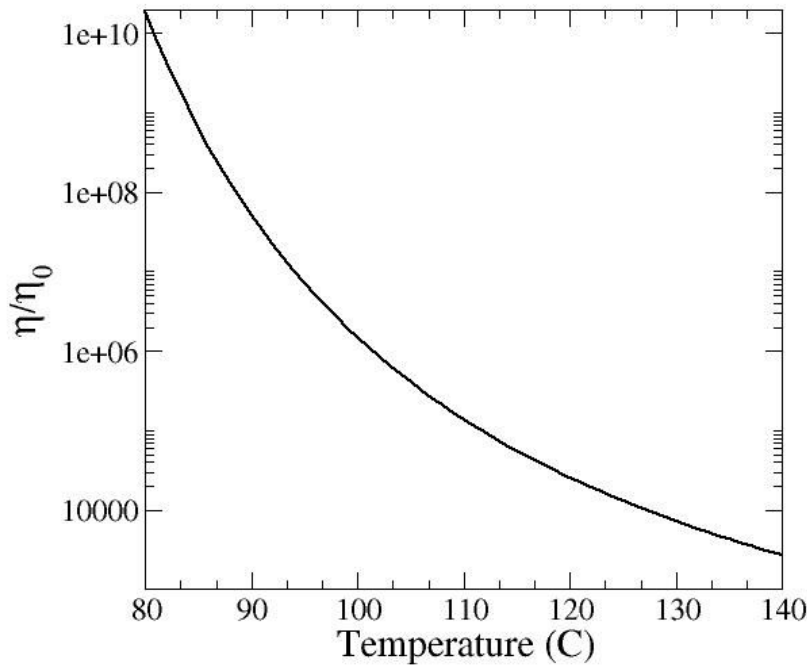
## (13) Viscosity

Using the Vogel-Fulcher law

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right)$$

We obtain the graph





Between  $T=100^{\circ}\text{C}$  and  $T=140^{\circ}\text{C}$ , the viscosity changes by a factor of about 550.

## (14) The glass transition

The glass transition occurs when the system falls out of equilibrium on the experimental timescale  $\tau_{\text{exp}}$ , i.e. when  $\tau_{\text{config}} > \tau_{\text{exp}}$ .

When  $\tau_{\text{exp}}=1000\text{s}$ , the glass transition temperature is  $101.4^{\circ}\text{C}$ . Thus we can calculate

$$\tau_0 = 1000 \exp\left(\frac{-710}{101.4 - 50}\right) = 1.002 \times 10^{-3} \text{s}$$

- (a) Rearranging the Vogel-Fulcher law, we find that the glass transition temperature is given by

$$T_g = T_0 + B \left[ \ln \frac{\tau_{\text{exp}}}{\tau_0} \right]^{-1}$$

implying that  $T_g=88.5^\circ\text{C}$ .

(b) For  $T_g=60^\circ\text{C}$ , the Vogel-Fulcher law yields

$$\tau_{\text{config}} = 1.002 \times 10^{-3} \exp\left(\frac{710}{60 - 50}\right) = 6.8 \times 10^{27} s$$

or  $2 \times 10^{20}$  years.