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# Physics with neutrons 2

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Exercise sheet 7  
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## EXERCISE 7.1

On the homepage you find two scattering data sets from a 2D monoatomic cubic Bravais lattice (artificially created with a 2D Fast-Fourier transform). The atoms have a certain probability to be displaced, i.e. the data is diffuse neutron scattering. In the following we want to use the Reverse Monte Carlo (RMC) method to find out if there is a random displacement of atomic positions or a certain tendency or is completely uncorrelated in the two data sets. Therefore, we follow the steps of the RMC algorithm (we neglect units for the algorithm):

- Import the data with the software of your choice and plot it on a logarithmic scale.
- Create a  $100 \times 100$  grid with 169 atoms in a cubic lattice with a distance of 8 and scattering length  $b = 1$ .
- Calculate  $F_{calc}(Q)$  from the arrangement with a 2D Fast Fourier transform and  $\chi_{old}^2 = \sum_{j=1}^{10000} (F_{calc}(Q_j) - F_{data}(Q_j))^2$ , where the sum is over all experimental data points.
- Apply the RMC algorithm:
  1. Move one randomly selected atom in a random direction by a random, but short (1 – 3 positions in the grid) distance.
  2. Recalculate  $F_{calc}(Q)$  and  $\chi_{new}^2 = \sum_{j=1}^{10000} (F_{calc}(Q_j) - F_{data}(Q_j))^2$ .
  3. Compare  $\chi_{new}^2$  and  $\chi_{old}^2$  and decide if the fit has improved. If so, accept the step and start again with the new arrangement. If not, accept the step anyway with a probability of the order of  $\exp(-(\chi_{new}^2 - \chi_{old}^2)/2)$  or otherwise reject the step.
  4. Repeat these steps until the fit is satisfactory.  
*Hint: A lot of steps might be necessary and it is not easy to reach convergence.*

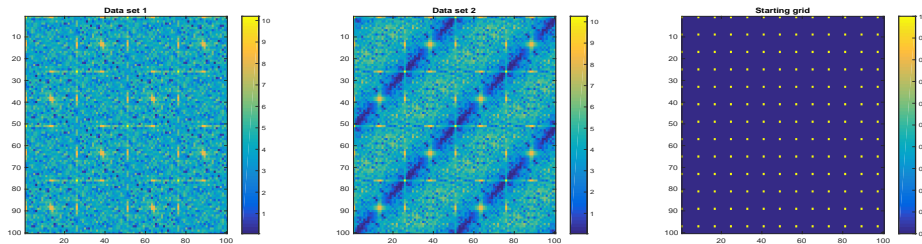


Figure 1: (l) Data set 1, (m) Data set 2, (r) Starting grid for the fitting.

**Solution.** A Matlab code was discussed in the Exercise. □

**EXERCISE 7.2**

The microscopic diffusion of  $H_2O$  has been determined under high pressures. In order to avoid freezing of the liquid the sample has been heated to  $T = 400K$  (see phase diagram of water 2). Figure 3 shows FWHM (meV) plotted as function of  $Q^2(\text{\AA}^{-1})$  values for  $P = 0.6GPa$  and  $P = 2.9GPa$ .

1. Determine the diffusion constant  $D$  at  $P = 0.6GPa$  and  $P = 2.9GPa$ .
2. The diffusion constants at ambient pressure are  $D = 1.2 \cdot 10^{-9}m^2/s$  and  $D = 2.3 \cdot 10^{-9}m^2/s$  at  $T = 273K$  and  $T = 298K$ , respectively. The following equations relate the diffusion constant with the viscosity.

$$D = \frac{k_b T}{6\pi\eta r_{se}}, \quad \text{Stokes-Einstein,} \quad (1)$$

$$D = D_0 \exp\left(\frac{-E_A}{k_B T}\right), \quad \text{Arrhenius law,} \quad (2)$$

$$\eta \sim \exp(g_\nu T_m/T), \quad (3)$$

(see e.g. Poirier, "Introduction to the Physics of the Earth's Interior", Cambridge University Press (2000)), where  $D$  is the diffusion constant,  $\eta$  is the viscosity,  $r_{se}$  is the particle's free radius,  $E_A$  is the activation energy,  $T_m$  is the melting temperature and  $g_\nu$  is a constant. The density of water at  $P = 2.6GPa$  and  $T = 400K$  is  $\rho = 1.38g/cm^3$ .

What can you conclude? Is the Stokes-Einstein relation valid?

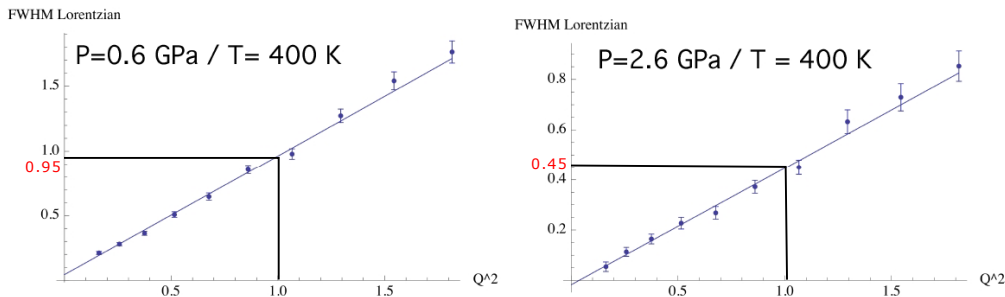
**Solution.** 1. We have quasielastic scattering

$$S_{inc}(Q, \omega) = \frac{1}{\pi\hbar} \frac{DQ^2}{\omega^2 + (DQ^2)^2},$$

e.g. it is a Lorentzian. Hence, we have

$$\Gamma^{fwhm} = 2\hbar DQ^2 \Rightarrow D = \frac{\Gamma^{fwhm}}{2\hbar Q^2}$$

and the FWHM of the energy as a function of  $Q^2$  is linear. From Figure 3 we can extract the slope



and calculate

$$\Rightarrow D_1(0.6GPa, 400k) = \frac{dQ^2}{2\hbar \cdot d\Gamma^{fwhm}} = \frac{0.95meV}{2\hbar \cdot 1 \cdot 10^{-20}m^{-2}} = 7 \cdot 10^{-9} \frac{m^2}{s}$$

$$\Rightarrow D_2(2.6GPa, 400k) = \frac{1meV}{2\hbar \cdot 0.45 \cdot 10^{-20}m^{-2}} = 3.5 \cdot 10^{-9} \frac{m^2}{s}$$

2. From Eq. (3) with  $T_m$  the melting temperature and constant  $g_\nu$  follows

- $\eta$  is constant along the melting line,

- for  $P_1 = 2.6GPa$  at  $400K$  we have  $D_2 = 3.5 \cdot 10^{-9} \frac{m^2}{s}$

- for ambient pressure the diffusion constants are given

$$273K : D_0 = 1.2 \cdot 10^{-9} \frac{m^2}{s}$$

$$298K : D'_0 = 2.3 \cdot 10^{-9} \frac{m^2}{s}$$

It follows that the points of  $D_0$  and  $D_2$  sit on (or close to) the melting line. In the Einstein-Stokes model with only free parameter  $r_{se}$  for constant  $\eta$  we get

$$D_{ES} \sim T,$$

$$\Rightarrow D_2/D_0 = \frac{400}{273} = 1.46$$

$$\text{observed: } D_2 = 3.5 \cdot 10^{-9} \frac{m^2}{s},$$

$$D_0 = 1.2 \cdot 10^{-9} \frac{m^2}{s}.$$

Therefore, Einstein-Stokes is not valid!

The only free parameter in Einstein-Stokes is the radius  $r_{SE}$ . Assume  $r_{SE}$  scales with the density  $r_{SE}^{-1/3} \sim \rho$ . Then  $D$  would increase by  $(1.38/1)^{-1/3} = 1.11$ , which is still not enough. Therefore something has to happen to  $r_{SE}$ , e.g. the free radius decreases more rapidly along the melting line than  $\rho$ . Neutron scattering reveals structural changes in the short range order of water along the melting line (*PRL* 96, 067801, (2006)).

□

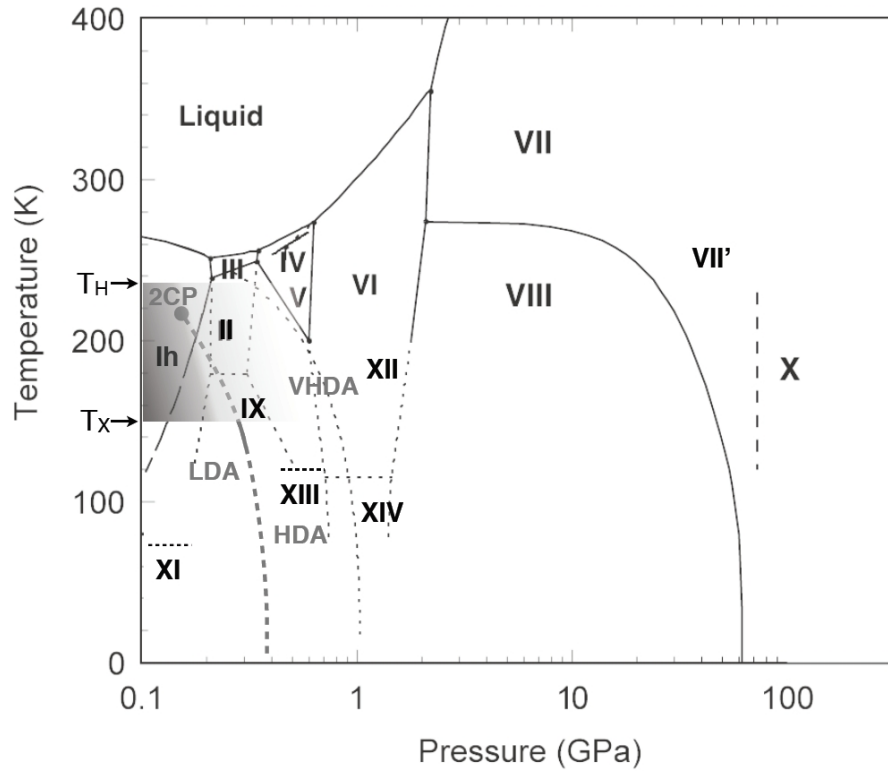


Figure 2: Phase diagram of water. Note the logarithmic scale for the x-axis.

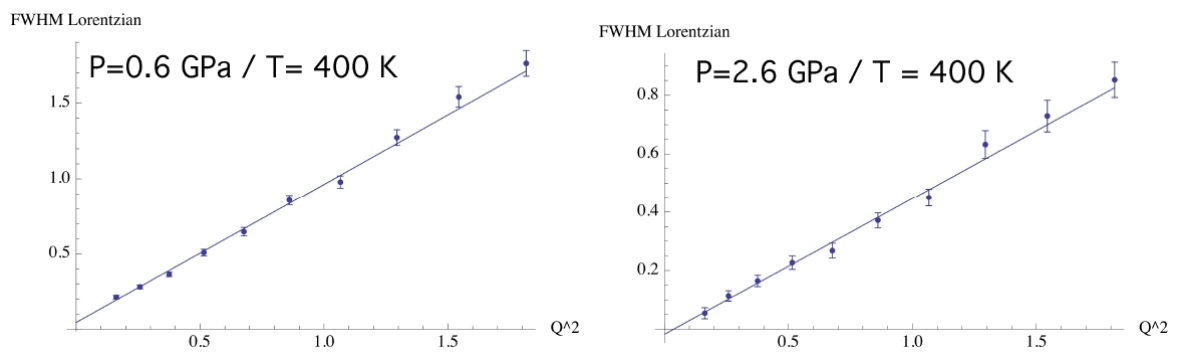


Figure 3: Measured linewidth (FWHM) in  $meV$  versus square of the scattering vector in  $\text{\AA}^{-2}$ .