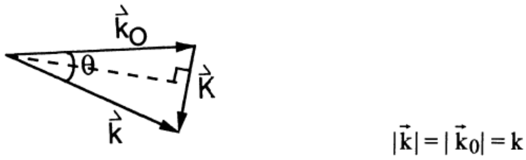
Problem set 3 – Liquids

Problem 13

a) Show that magnitude of the scattering vector is given by $K \equiv \mid \vec{K} \mid = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$ using the figure below.



b) Calculate the scattering angle corresponding to a K-value of 0.015 nm^{-1} for light scattering ($\lambda = 532$ nm) and X-Ray scattering ($\lambda = 0.15$ nm).

c) The scattered intensity is proportional to the form factor $P(K)$ times the structure factor $S(K)$, i.e. $I(K) \propto P(K)S(K)$. Briefly explain how the structure factor can be extracted from the total scattered intensity in an experiment.

d) Sketch how the radial distribution functions and structure factors for a hard sphere system change as the number density ρ is increased.

Problem 14

The Ornstein-Zernike equation can be written as

$$h_{12} = c_{12} + \rho \int d\tau_3 c_{13} h_{32}.$$

a) Explain the meaning of each symbol, also taking into account the subscripts. Give physical interpretations of h and c. What is meant by the term 'closure relation'?

b) Explain the basis for the Ornstein-Zernike equation in terms of direct and indirect interactions using a sketch.

c) The Fourier transform of the Ornstein-Zernike equation reads

$$\hat{h}(K) = \hat{c}(K) + \rho\hat{c}(K)\hat{h}(K).$$

Show that this can be rearranged to

$$1 + \rho\hat{h}(K) = \frac{1}{1 - \rho\hat{c}(K)},$$

and explain the experimental significance of the left-hand side of this equation.

Problem 15

The compressibility equation is given by

$$1 + 4\pi\rho \int_0^\infty h(r) r^2 \mathrm{d}r = \rho k_B T \kappa_T, \qquad \text{Eq. 1}$$

where $\rho = \frac{N}{V}$ is the number density, $h(r) \equiv g(r) - 1$ the total correlation function and $\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T$ the isothermal compressibility.

a) Sketch the total correlation function $h(r)$ for a *very dilute* fluid of hard spheres. The hard spheres have a diameter σ.

b) The structure factor for an isotropic fluid is given by

$$S(K) = 1 + \rho \int h(r) e^{i\vec{K}\cdot\vec{r}} \mathrm{d}\vec{r}.$$

Show that the isothermal compressibility κ_T can be measured from a scattering experiment by extrapolating the structure factor to $K \to 0$, in other words, show that $S(K \to 0) = \rho k_B T \kappa_T$.

c) For isotropic systems the structure factor can also be written in spherical coordinates:

$$S(K) = 1 + \frac{4\pi\rho}{K} \int_0^\infty h(r) \sin(Kr) r \mathrm{d}r.$$

Derive the following analytic expression for $S(K)$ for a *very dilute* gas of hard spheres.

$$S(K) = 1 + \frac{4\pi\rho}{K^2}\left(\sigma\cos(K\sigma) - \frac{\sin(K\sigma)}{K}\right).$$

Hints: use your result from part a) and integration by parts.

d) Find the limit of $S(K)$ as $\sigma \to 0$, and then calculate the equation of state (the pressure) using the result from part b), i.e. via the compressibility κ_T. Comment on your answers.

Problem 16

In the dilute limit ($\rho \to 0$), the radial distribution function $g(r)$ is related to the pair potential $\phi(r)$ via

$$g(r) = \exp\left(-\beta\phi(r)\right).$$

Sketch the pair potentials and corresponding radial distribution functions for the following systems at low number density ρ:

a) perfect gas,

b) hard sphere gas (diameter σ),

c) attractive hard sphere gas (diameter σ).

Problem 17

The internal energy E is related to the canonical partition function Q via

$$E = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}, \qquad \text{with} \qquad Q = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} Z_N.$$

Here Z_N is the configuration integral Z_N.

a) Use the above equations to show that

$$E = \frac{3}{2}N k_B T + kT^2 \left(\frac{\partial \ln Z_N}{\partial T}\right)_{N,V} \qquad (= E_{kin} + \langle U \rangle).$$

b) From part a), we see that $\langle U \rangle = kT^2 \left(\frac{\partial \ln Z_N}{\partial T}\right)_{N,V}$. Combine this with $Z_N = \int \cdots \int e^{-\beta U(\tau_1,\ldots,\tau_N)} d\tau_1 \cdots d\tau_N$ to show that

$$\langle U \rangle = \frac{\int d\tau_1 \cdots \int d\tau_N U e^{-\beta U(\ldots)}}{Z_N}.$$

c) Next, using pairwise additivity, $U = \sum_{i>j} \phi_{ij}$, derive the following expression for the mean potential energy in terms of the pair potential $\phi(r)$ and the radial distribution function $g(r)$:

$$\langle U \rangle = 2\pi \rho N \int_0^\infty r^2 \phi(r) g(r) dr.$$

d) Finally, using that in the dilute limit $g(r) = \exp(-\beta\phi(r)$, calculate the average potential energy for the square well potential,

$$\phi(r) = \begin{cases} \infty & r < \sigma, \\ -\epsilon & \sigma \le r \le \lambda\sigma, \\ 0 & r > \lambda\sigma. \end{cases}$$

Comment on the result you obtain for the case that $\lambda = 1$.