

040514 Quiz 7 Polymer Properties

The RPA equation can be derived for an athermal system using the following equations:

$$\begin{aligned} \chi_{k,A} &= \chi_k = \frac{0}{k} \quad \chi_k = -\chi_{k,B} = \frac{AA}{k} \left(\chi_k + \underline{\chi_k} \right) \\ \chi_{k,B} &= \frac{BB}{k} \underline{\chi_k} \end{aligned}$$

- 1)
 - a) Explain what the terms in these equations refer to.
 - b) Write the RPA equation as $\chi_k^0 = f\left(\frac{AA}{k}, \frac{BB}{k}\right)$
- 2) Derive the athermal RPA equation from these equations
- 3)
 - a) Write the thermal RPA equation.
 - b) By replacing χ_k with $\left(\chi_k + \chi_k'\right)$ **where** $\chi_k' = \frac{2 kT}{V_c}$, derive the thermal RPA equation through a modification of part "2".
- 4) Explain how a linear constitutive equation, the Boltzmann distribution and the Gaussian distribution function are used to obtain an expression relating the mean square composition fluctuation and the susceptibility. (Write the linear constitutive equation, the Boltzmann function using an energy obtained from the linear constitutive equation by integrating dG and finally compare with the Gaussian function to obtain the square of the standard deviation or the mean square composition fluctuation.)
- 5) Explain how the mean square composition fluctuation is related to the scattered intensity.

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1) a) $\chi_{k,A}$ and χ_k refer to composition fluctuations of "A" from the average composition $\langle A \rangle$ for the "k" wave vector Fourier component of the fluctuations.

χ_k^0 refers to the susceptibility of the "A" composition fluctuations to an external field in the absence of enthalpic interactions, i.e. $\chi_k^0 = 0$.

χ_k is the "k" wave vector component of the external field, i.e. the part of the field that effects the composition at wave vector "k".

χ_k^{AA} is the susceptibility associated with component "A" as it responds to both the external field and the internal field χ_k . χ_k^{AA} is equated with the isolated scattering function for component "A" divided by kT .

χ_k is the field that is produced internally in response to fluctuations of one of the two components. The internal field effects "A" and "B" components equally and is associated with a condition of constant density, incompressibility.

χ_k^{BB} is the susceptibility associated with component "B" as it responds to the internal field χ_k . χ_k^{BB} is equated with the isolated scattering function for component "B" divided by kT .

b)
$$\frac{1}{\chi_k^0} = \frac{1}{\chi_k^{AA}} + \frac{1}{\chi_k^{BB}}$$

2)
$$\chi_k^{AA} (\chi_k + \chi_k) = -\chi_k^{BB} \chi_k \text{ so } \chi_k = -\chi_k \frac{\chi_k^{AA}}{\chi_k^{AA} + \chi_k^{BB}} \text{ and}$$

$$\chi_k = -\chi_k \frac{\chi_k^{BB}}{\chi_k^{AA} + \chi_k^{BB}} = \chi_k^0 \text{ so } \frac{1}{\chi_k^0} = \frac{1}{\chi_k^{AA}} + \frac{1}{\chi_k^{BB}}$$

3) a)
$$\frac{1}{\chi_k} = \frac{1}{\chi_k^{AA}} + \frac{1}{\chi_k^{BB}} - \frac{2kT}{V_c}$$

b) This can be obtained by $\chi_k = \chi_k^0 (\chi_k + \chi_k)$ then solving for χ_k ,

$$\chi_k = \frac{\chi_k^0 \chi_k}{1 - \chi_k^0 \chi_k}, \chi_k = \chi_k^0 \text{ so } \frac{1}{\chi_k} = \frac{1}{\chi_k^0} - \chi_k^0 = \frac{1}{\chi_k^{AA}} + \frac{1}{\chi_k^{BB}} - \frac{2kT}{V_c}$$

4) Linear constitutive equation: $\chi_k = \chi_k^0 \chi_k \text{ or } \chi_k = \frac{\chi_k^0}{1 - \chi_k^0 \chi_k}$

and $dG_k = \chi_k d\chi_k = \frac{d\chi_k}{2\chi_k^2}$ so $G_k = \frac{1}{2\chi_k^2}$

The Boltzman probability for a fluctuation χ_k is given by:

$$p(\chi_k) = \exp \left(-\frac{G}{kT} \right) = \exp \left(-\frac{1}{2\chi_k^2 kT} \right) = \exp \left(-\frac{1}{2 \left(\frac{2kT}{\chi_k^2} \right)} \right)$$

where the latter equality is just equating the Gaussian distribution function χ_k with the Boltzman expression, so,

$$\langle I_k^2 \rangle = kT$$

- 5) Scattering at a wave vector "k" arises from compositions (electron densities for instance) at two positions separated by $r = 1/k$. The probability of scattering from one of these positions is the composition c , so the probability for scattering at two is this probability squared. This process is repeated (averaged) over all possible "r" vectors in the sample so the scattered intensity is proportional to $\langle I_k^2 \rangle$ and to c^2 from question "4".