

Zimm Equation and RPA Function:

1) For low angle scattering ($qR_g \ll 1$) we observe constant scattering intensity related to the contrast between the polymer and the solvent since the Debye function for polymer coils reaches a constant value at very low scattering vector q . Scattering occurs due to binary interference so we consider the concentration at two points. The scattering media has an average concentration $\langle \phi \rangle$ and we consider only deviations from this average concentration. We call this deviation ϕ , and the scattered intensity is then proportional to ϕ^2 in order to account for binary interference, i.e. the probability of contrast at two random points in the solution.

2) Consider scattering from a dilute solution of polymer in solvent. For a one phase system such as a polymer in solution the deviation in concentration is caused by thermal fluctuations of the concentration that are dampened by the increase in reduced osmotic pressure π with increasing concentration. The fluctuations are constantly changing in space and time. Then we consider the scattered intensity as proportional to the integral of the derivative or the average change in ϕ^2 , $2\phi \langle d\phi/d(\pi/kT) \rangle$

$$S(q \Rightarrow 0) = 2kT\phi \left\langle \frac{d\phi}{d\pi} \right\rangle \quad (1)$$

3) We have a simple expression for $d\pi/d\phi$ from the Flory-Huggins equation,

$$\frac{\pi}{kT} = \frac{\phi}{N} + \frac{(1-2\chi)}{2} \phi^2 \quad (2)$$

so,

$$\frac{\phi}{S(q \Rightarrow 0)} = \left(\frac{1}{N} + (1-2\chi)\phi \right) \quad (3)$$

4) Zimm used the approximation that equation (1) could be generalized to all q by simply multiplying the contrast factor of equation (1) by the Debye scattering function,

$$S_D(Q) = \frac{2}{Q^2} (Q - 1 + \exp(-Q)) \quad \text{where } Q = q^2 R_g^2 \quad (4)$$

We previously found that equation (4) can be reduced to Guinier's law at low- q ,

$$S_D(q \Rightarrow 0) = \exp\left(\frac{-q^2 R_g^2}{3}\right) \quad \text{and} \quad \frac{1}{S_D(q \Rightarrow 0)} = \exp\left(\frac{q^2 R_g^2}{3}\right) \cong \left(1 + \frac{q^2 R_g^2}{3}\right) \quad (5)$$

Zimm arrived at the following equation,

$$\frac{\phi}{S(qR_g \ll 1)} = \left(\frac{1}{N} + (1-2\chi)\phi \right) \left(1 + \frac{q^2 R_g^2}{3} \right) \quad (6).$$

Equation (6) is based on the assumption that the chain scattering function (equation (5)) is independent of the thermodynamics causing concentration fluctuations (equation(3)) so that the two components contribute to the scattering intensity independently. This is, of course, absurd since the chain structure is determined by thermodynamics. However, the assumption becomes plausible in the limit of $\phi \Rightarrow 0$ and $q \Rightarrow 0$. For this reason Zimm suggested a plot involving a double extrapolation as shown below.

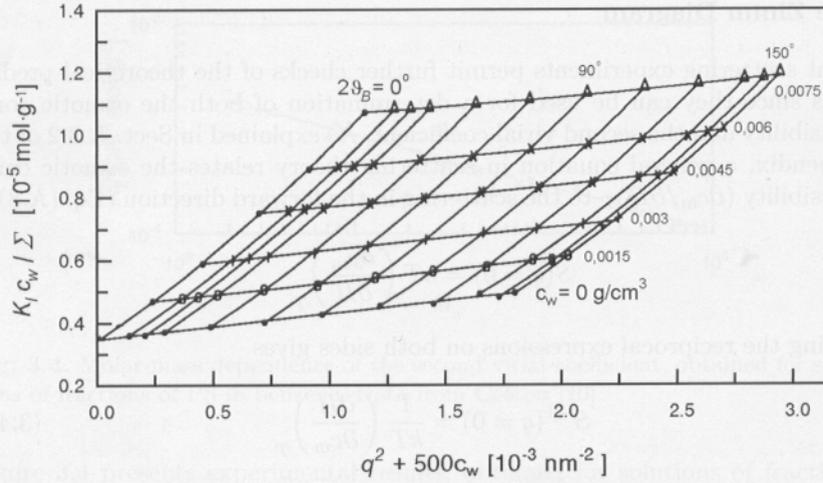


Fig. 3.5. Light scattering experiments on solutions of PS ($M = 2.8 \times 10^5 \text{ g mol}^{-1}$) in toluene at 25 °C. Results are presented in a Zimm plot, enabling an extrapolation to $c_w = 0$ and $q = 0$. Data from Lechner et al. [11]

From Gert Strobl, *The Physics of Polymers 3'rd Edition*. $K_1 = \frac{4\pi^2 n^2 \left(\frac{dn}{dc}\right)^2}{N_0 \lambda^4}$ and Σ is the scattering intensity.

At $c \Rightarrow 0$ (bottom line) the slope is proportional to $\frac{R_g^2}{3N}$, while at $q \Rightarrow 0$ (left curve) the slope is proportional to $(1 - 2\chi)$ or A_2 . The intercept on the y-axis is proportional to $1/N$, the weight average molecular weight for the polymer.

The Zimm plot is widely used to determine the weight average molecular weight, the coil radius of gyration and the second virial coefficient despite the approximation involved because it is only used in extrapolation.

A rigorous and general description of the scattering from polymer blends and solutions at all values of q was arrived at by de Gennes using the random phase approximation (RPA). The RPA is discussed in a separate section, the function for scattered intensity is,

$$\frac{1}{S(q)} = \frac{1}{\phi_1 N_1 S_D(q, R_{g1})} + \frac{1}{\phi_2 N_2 S_D(q, R_{g2})} - 2\chi \quad (7) \text{ (RPA Blend)}$$

where N_i is the weight average molecular weight and the equation is written for a polymer blend. For a polymer solution $N_1 = 1$, $\phi_1 \sim 1$ and $S_D(q, R_{g1}) \sim 1$ so equation (7) can be rewritten,

$$\frac{\phi_2}{S(q)} = \frac{1}{N_2 S_D(q, R_{g2})} + \phi_2(1 - 2\chi) \quad (8) \text{ (RPA Solution)}$$

Equation (8) bears resemblance to equation (6). The difference is that the inverse Debye function modifies only the first virial term in (8) while it modifies both the first and second virial coefficients in equation (6).

The RPA equation can be generalized to include scaling transitions in the polymer coils if more sophisticated scattering functions are used rather than the Debye function such as the unified scattering function which can accommodate scaling changes including good solvent scaling and blob scaling transitions,

$$\frac{1}{S(q)} = \frac{1}{\phi_1 N_1 S_U(q, R_{g1})} + \frac{1}{\phi_2 N_2 S_U(q, R_{g2})} - 2\chi \quad (9) \text{ (RPA for Scaling Changes)}$$

where $S_U(q, R_g, d_f)$ for a chain of arbitrary fractal scaling and in the absence of blobs (simple case) is given by,

$$S_U(q, R_g, d_f, d_{\min}) = \exp\left(\frac{-q^2 R_g^2}{3}\right) + \left(\frac{d_{\min}}{R_g^{d_f}} \Gamma\left(\frac{d_f}{2}\right)\right) q^{*-d_f} \quad (10)$$

where $d_{\min} = d_f$ for a linear chain and $1 \leq d_{\min} < d_f$ for a branched chain (PRE **70**, 031401 (2004)) and $q^* = q / [\text{erf}(qR_g/6^{1/2})]^3$.