Background for RPA:

$$\text{Distance} = \left(\frac{1}{\text{spring constant}}\right) Force$$

1) $\varepsilon = J\sigma = \alpha\sigma$

α is the susceptibility

$$\varphi_k = \alpha_k \Psi_k$$

2) Change in free energy, dG, is proportional to the field (force) and to the response, change in distance,

$$dG_k = \Psi_k d\varphi_k$$
$$= a_k \varphi_k d\varphi_k$$

so

$$G_k = \frac{a_k \varphi_k^2}{2}$$

3) For a thermally equilibrated system the average free energy is kT,

$$\langle G_k \rangle = \frac{a_k \langle \varphi_k^2 \rangle}{2} \equiv kT$$

Mean composition is related to a mean field. If we use only these average fluctuations then we are considering only an average or mean field.

4) $\langle \varphi_k^2 \rangle = \dfrac{2kT}{a_k} = 2\alpha_k kT$

This is important since the scattering from a single phase is proportional to this expression where k => q.

5) $S(q = k) = \dfrac{\langle \varphi_k^2 \rangle}{V_c} = \dfrac{2\alpha_k kT}{V_c} = \mathrm{KI(q)}$

where K is the inverse of the contrast factor. Scattering only considers a mean field in this context.

6) The Boltzman distribution for thermally equilibrated states (number density of fluctuations at a wave vector k of size φ_k) is given by,

$$P(\varphi_k) = P_0 \exp \frac{\langle G_k \rangle}{kT} = P_0 \exp \frac{a_k \varphi_k^2}{2kT}$$

Two Component, Athermal System:

1) Consider a simplified 2 component system where the field only affects component A, and the component B can not be seen, i.e. it has no scattering contrast for instance. We write (1) above in terms of component A,

$$\varphi_{k,A} = \alpha_k^0 \Psi_k$$

where α_k^0 is **the collective response coefficient** for A units under athermal conditions (0) in a mixture with B units. This corresponds to the scattering from a polymer blend for example. We what to solve for this function of k or q.

2) We understand that the system is incompressible and that there is conservation of mass so that a fluctuation in A leads to an equal and opposite fluctuation in B,

$$\varphi_{k,A} = -\varphi_{k,B} = \varphi_k$$

3) The field only effects A units, yet there must be a response to fluctuations in A by the B units according to (2). Then we can consider an effective field that acts on B units. This field is called the **internal field**.

$$\varphi_{k,B} = -\varphi_k = \alpha_k^{BB} \underline{\Psi}_k$$

where α_k^{BB} is the response coefficient for isolated B units, i.e. the scattering from isolated B units. For polymers this is the Debye function for a single B chain.

4) Similarly we can write the flux of A units in terms of the response coefficient for isolated A chains (these isolated coefficients are usually know and correspond to dilute conditions of a single component.

$$\varphi_{k,A} = \varphi_k = \alpha_k^{AA} \left(\Psi_k + \underline{\Psi}_k \right)$$

5) We need an expression for the **internal field** in terms of known functions. This can be obtained since expression 3) and 4) are related to each other, summing the two expressions we get 0,

$$\varphi_k = \alpha_k^{AA} \left(\Psi_k + \underline{\Psi}_k \right) = -\alpha_k^{BB} \left(\underline{\Psi}_k \right)$$

$$\underline{\Psi}_k = -\Psi_k \frac{\alpha_k^{AA}}{\alpha_k^{AA} + \alpha_k^{BB}}$$

6) Then we can substitute this expression for the internal field into expression 3),

$$\varphi_k = -\alpha_k^{BB} \underline{\Psi}_k = \Psi_k \frac{\alpha_k^{AA} \alpha_k^{BB}}{\alpha_k^{AA} + \alpha_k^{BB}}$$

7) And equate expression 6) and 1) to solve for the collective response coefficient (scattering from a blend of two polymers for instance).

$$\varphi_k = \Psi_k \frac{\alpha_k^{AA}\alpha_k^{BB}}{\alpha_k^{AA} + \alpha_k^{BB}} = \alpha_k^0 \Psi_k$$

$$\alpha_k^0 = \frac{\alpha_k^{AA}\alpha_k^{BB}}{\alpha_k^{AA} + \alpha_k^{BB}}$$

or

$$\frac{1}{\alpha_k^0} = \frac{1}{\alpha_k^{AA}} + \frac{1}{\alpha_k^{BB}}$$

that is similar to the Zimm equatin in that the inverse of the scattering is related to the inverse of the Debye function. By comparison with the Zimm function an expression to determine the interaction parameter is directly obtained.

Two Component, Thermal System:

1) Consider units with an enthalpic interaction per average units A and B of $\chi' = 2\chi kT/V_c$. This enthalpic interaction serves to dampen, if χ is negative, or enhance, if χ is positive, the externally applied field by a factor, $\varphi\chi'$.

$$\varphi_{k,A} = \alpha_k^0 \left(\Psi_k + \varphi_k \chi'\right)$$

2) We solve for φ,

$$\varphi_k = \frac{\alpha_k^0 \Psi_k}{1 - \alpha_k^0 \chi'}$$

3) By comparison with expression 1) for the athermal system we have for the thermal collective response coefficient,

$$\frac{1}{\alpha_k} = \frac{1}{\alpha_k^0} - \chi' = \frac{1}{\alpha_k^{AA}} + \frac{1}{\alpha^{BB}} - \frac{2kT\chi}{V_c}$$

This can be used to obtain the interaction parameter from scattering in a polymer blend.