Scattering Function for Polymer Blends

Calculation of the pair correlations in a dense melt of strongly interacting chains is simplified by the notion that each chain experiences an average field resulting from contacts with many other chains and hence all chains remain nearly ideal. The pair correlation function can thus be evaluated by calculating the system response to a weakly perturbing field, assuming ideal chain statistics. DeGennes applied this “random phase approximation” method to calculate scattering functions for melts of selectively labeled polymer chains (J. Physique 31, 235 (1970)). It is analogous to the self-consistent field approach used by Edwards for describing polymer solutions. Here we follow the Edwards’ formalism as applied by Olvera de la Cruz, Freed, and others to calculate the scattering function of a mixture of A and B chains. Here we examine the case of an incompressible melt.

System: \( n_A \) chains of A, each with \( N_A \) segments \( n_B \) chains of B, each with \( N_B \) segments  
segment size \( b_A = b_B = b \)

The partition function of the mixture is written as:

\[
Z = \int D[\{r_i^\alpha(s)\}] \ P[\{r_i^\alpha(s)\}] \ \delta(c_A(r) + c_B(r) - \bar{c})
\]

where the delta function imposes the incompressibility condition and \( P[\{r_i^\alpha(s)\}] \) is the probability distribution for a given configuration \( \{r_i^\alpha(s)\} \):

\[
P[\{r_i^\alpha(s)\}] = \exp \left\{ -\sum_{i=A,B} \frac{3}{2b} \sum_{\alpha_i=1}^{n_i} \int_0^{L_i} ds \left( \frac{\partial r_i^\alpha(s)}{\partial s} \right)^2 - \frac{U[\{r_i^\alpha(s)\}]}{kT} \right\}
\]

where \( L_i = N_i b \) is the contour length of the chain, and the parameter \( s \) varies continuously from 0 to \( L_i \). The potential term \( U[\{r_i^\alpha(s)\}] \) is defined as the sum of \( ij \) contact interactions of strength \( \varepsilon_{ij} \):
The local density of the $i$th component is the sum of contributions from all $n_i$ chains:

$$c_i(r) = \sum_{\alpha=1}^{n_i} \int_0^{L_i} \frac{ds_\alpha}{b} \delta\left( r - r_i^\alpha(s_\alpha) \right)$$

Taking the F.T. of this expression:

$$c_{ik} = \frac{1}{V} \sum_{\alpha=1}^{n_i} \int_0^{L_i} \frac{ds_\alpha}{b} \exp\left[ ik \cdot r_i^\alpha(s_\alpha) \right]$$

Substituting into the definition for the potential gives:

$$U[\{r_i^\alpha(s)\}] = \sum_{i,j}^{A,B} \frac{1}{2} \epsilon_{ij} \int_{-\infty}^{\infty} drc_i(r)c_j(r)$$

$$U[\{c_{ik}\}] = \sum_{i,j}^{A,B} \frac{V}{2} \epsilon_{ij} \sum_{k \neq 0} c_{ik}c_{jk}$$
To obtain the partition function in terms of the local density fluctuations $\rho_{ik}$ we multiply $Z$ by 1 in the form:

$$1 = \int_{-\infty}^{\infty} dx \, \delta(x)$$

$$1 = \prod_{i=A,B} \int_{-\infty}^{\infty} \prod_{k} dc_{ik} \, \delta \left( c_{ik} - \frac{1}{V} \sum_{\alpha=1}^{n_{i}} \int_{0}^{L_{i}} ds_{\alpha} \frac{1}{b} \exp \left[ ik \cdot r_{i}^{\alpha}(s_{\alpha}) \right] \right)$$

$$= \prod_{i=A,B} \int_{-\infty}^{\infty} \prod_{k} dc_{ik} \int_{-\infty}^{\infty} d\lambda_{ik} \frac{\exp(i\lambda_{ik} c_{ik})}{2\pi}$$

$$\times \exp \left( -i\lambda_{ik} \frac{1}{V} \sum_{\alpha=1}^{n_{i}} \int_{0}^{L_{i}} ds_{\alpha} \frac{1}{b} \exp \left[ ik \cdot r_{i}^{\alpha}(s_{\alpha}) \right] \right)$$

where we have used the equality:

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(i\lambda x) \, d\lambda$$

The partition function becomes:
The second exponential in this expression is then expanded in powers of the effective field $i\lambda_{i\kappa}$:

$$
\exp\left(-i\lambda_{i\kappa}\frac{1}{V}\sum_{\alpha=1}^{L_i} \int_0^{L_i} \frac{ds_\alpha}{b} \exp\left[i\mathbf{k} \cdot \mathbf{r}_{i\alpha}(s_\alpha)\right]\right)
$$

$$
= 1 - i \int_0^{L_i} \frac{ds}{b} \lambda\left(\mathbf{r}_{i\alpha}(s)\right) - \frac{1}{2} \int_0^{L_i} \frac{ds}{b} \lambda\left(\mathbf{r}_{i\alpha}(s)\right) \int_0^{L_i} \frac{ds'}{b} \lambda\left(\mathbf{r}_{i\alpha}(s')\right) + ...
$$

Substituting into $Z$ gives:
\[ Z = \int \left( \prod_{k} dc_{Ak} dc_{Bk} \right) \prod_{i=A,B} \int_{-\infty}^{\infty} d\lambda_{ik} \frac{1}{2\pi} \prod_{\alpha=1}^{n_i} \exp(-i\lambda_{i0}N_i) \times \exp \left( -\frac{N_i^2}{2} \sum_{k \neq 0} |\lambda_{ik}|^2 P_i(k) \right) \exp \left( i \sum_{k} \lambda_{ik} c_{ik} \right) \exp \left( -U[\{c_{ik}\}] \right) \delta \left( c_A(r) + c_B(r) - \bar{c} \right) \]

where \( P_i(k) \) is the unperturbed single-chain Debye scattering function:

\[ P_i(x) = \frac{2}{x^2} \left[ x + \exp(-x) - 1 \right] \]

where \( x = k^2 N_i b^2 / 6 \)

Employing the incompressibility condition, the total scattering function \( S(k) = S_{AA}(k) = S_{BB}(k) = -S_{AB}(k) \) is given by:

\[ S(k) = < c_{Ak} c_{Ak}^* > = -V \frac{\partial Z_k}{\partial \varepsilon_{AA}} \]

Using the definitions: \( \phi_i = \frac{c_{i0}}{\bar{c}} \)

the incompressibility condition becomes: \( \phi_A + \phi_B = 1 \)
and the final form of the scattering function is:

\[
\frac{1}{S(k)} = \frac{1}{\phi_A N_A P_A(k)} + \frac{1}{\phi_B N_B P_B(k)} - 2\chi_{AB}
\]

where \(\chi_{AB}\) is identified with the Flory interaction parameter:

\[
\chi_{AB} = \frac{c}{kT} \left[ \epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2} \right]
\]

At \(k=0\), \(S(k)\) is given by:

\[
\frac{1}{S(0)} = \frac{1}{\phi_A N_A} + \frac{1}{\phi_B N_B} - 2\chi_{AB}
\]

which is equivalent to \(d^2(\Delta F_{site}/kT)/d\phi^2\), where \(\Delta F_{site}\) is the F-H free energy of mixing per site. This equation indicates that the scattering intensity diverges at \(k = 0\) upon approaching the spinodal.

Data from C.C. Han, B.J. Bauer, et al. Polymer 29, 1988, 2002

Scattering from PS/PVME blend with RPA fits