

## Thermal Blob: The Why and What of it.

### What: (Following Strobl p. 52):

The thermic blob (thermal blob) is governed by the blob size  $\xi_t$  (or  $\xi_p$ ) so it is desirable to obtain an expression for  $\xi_t$  in terms of known features of the system, the persistence length,  $l_p$ , the interaction parameter,  $\chi$ , and the like. This can be done in a fairly simple scaling analysis as shown by Strobl on page 52. We define the number of persistence units in the chain as  $N$ , number of persistence units in a thermic blob as  $n_t$ , and the number of thermic blobs in the chain as  $N_t = N/n_t$ . The thermic blob size is given by,  $\xi_t = n_t^{1/2} l_p$ . The Flory radius for the chain is given by,

$$R_F = N_t^{3/5} \xi_t = (N/n_t)^{3/5} \xi_t = (N/(\xi_t/l_p)^2)^{3/5} \xi_t = N^{3/5} \xi_t^{-1/5} l_p^{6/5}$$

The expanded chain can also be described by the Flory-Krigbaum derivation in terms of the excluded volume,  $V = V_c (1-2\chi) = l_p^3 (1-2\chi)$ ,

$$R_F = N^{3/5} a_F = N^{3/5} l_p^{-3/5} V^{1/5}$$

where  $a_F = l_p^{2/3} V^{1/3}$  from our expression  $(R_F)^5 \text{ \AA} (V \tilde{N}/l_p^3) (l_p^5 N^{5/2}) = V l_p^2 N^{6/2}$ , or

$$R_F = V^{1/5} N^{3/5} l_p^{2/5}.$$

By setting the two expressions for  $R_F$  equal, an expression for  $\xi_t$  can be obtained,

$$V^{1/5} N^{3/5} l_p^{2/5} = N^{3/5} \xi_t^{-1/5} l_p^{6/5}$$

$$V^{1/5} l_p^{-4/5} = \xi_t^{-1/5}$$

$$\xi_t = l_p^4/(V) = l_p^4/(V_c (1-2\chi)) = l_p^4/(l_p^3 (1-2\chi)) = l_p/(1-2\chi) = l_p/(1-2z\Delta\epsilon/kT)$$

where the latter expression gives the temperature dependence of the thermic blob size.

### Why:

The last expression shows that the thermic blob decreases in size as the excluded volume increases. The function can be considered to enhance the persistence length,  $l_p$ , by the ratio of the hard-core volume to the enthalpic and hard core volume. We can look at certain conditions for this expression in terms of the interaction parameter  $\chi$ .

When  $\chi$  is 0,  $\xi_t = l_p$  and the solvent is a very good solvent. Since the thermal blob can grow no smaller than the persistence length this is the terminal value for all negative  $\chi$ 's.

When  $\chi$  is negative,  $\xi_t = l_p$  since the thermal blob can grow no smaller than the persistence length this is the terminal value for all negative  $\chi$ 's.

When  $\chi$  is positive but less than 0.5,  $\xi_t > l_p$  and the blob grows with temperature until the theta temperature is reached or until  $\xi_t = R_F$ . The equation above predicts that a thermal blob is only seen when enthalpic interactions oppose mixing of the polymer, i.e. positive  $\chi$ . ***The blob occurs to mitigate enthalpically driven demixing and entropically driven miscibility.*** Apparently the balance between these effects is size-scale dependent as discussed below.

When  $\chi$  is 1/2, the denominator goes to 0 and  $\xi_t$  goes to infinity or to  $R_F$  which is the largest possible size for a finite molecular weight. At this point the coil is Gaussian and the theta-state has been reached.

### **Size-scale dependence to the entropy/enthalpy balance for $0 < \chi < 0.5$ :**

The change in entropy on mixing per lattice site for a polymer coil of length,  $N$ , at a volume fraction  $\phi_p$  in a solvent ( $N_s = 1$ ) is given in the Gaussian, Flory lattice model as  $kT (1/N) \phi_p \ln \phi_p + (1-\phi_p) \ln(1-\phi_p)$ . The change in enthalpy on mixing per lattice site is  $kT \chi \phi_p(1-\phi_p)$ . In the context of renormalization using blobs it is clear that there is a size-scale dependence (through  $N$ ) to the free energy that has been ignored. That is, if we consider blobs of different size they must correspond to chains of different  $N$ . The source of this size scale dependence is the entropy of mixing term which is dependent on the size of the blob from the  $N$  term. ***That is, for chains of small blob size  $N$  is big,  $N = N_{\text{persistence}} l_p / \xi_t$ .*** Then, it is not surprising that miscibility differences at different length scales could drive the formation of a thermic blob when enthalpic conditions are poor for mixing, i.e. for a good solvent but not for a very good solvent. As the blob size becomes larger (i.e. when  $n_t$  becomes larger and  $N = N_{\text{persistence}}/n_t$  becomes effectively smaller) entropy drives good-solvent miscibility. As the blob becomes smaller (i.e. when  $n_t$  becomes smaller and  $N$  becomes larger) the miscibility limit (theta scaling), theta temperature, can be reached at a local level while maintaining miscibility (good solvent scaling) at large sizes. The chain has essentially phase separated at a local scale while maintaining miscibility at large scales. This discussion must remain of a qualitative nature since there is no expression for the free energy of a coil in either a very good solvent condition or a good solvent condition. That is, the use of the FH free energy expression is not appropriate where the chain scaling deviates from Brownian.