

Thermal Blob: The Why and What of it.

What: (Following Strobl p. 52):

The thermic blob (thermal blob) is governed by the blob size ξ_t (or ξ_p) so it is desirable to obtain an expression for ξ_t in terms of known features of the system, the persistence length, l_p , the interaction parameter, χ , 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,

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

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 $(R_F)^5 = (V N/l_p^3) (l_p^5 N^{5/2}) = V l_p^2 N^{6/2}$, 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 ξ_t can be obtained,

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

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

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

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 χ .

When χ is 0, $n_t = l_p$ 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 χ 's.

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

When χ is positive but less than 0.5, $n_t > l_p$ and the blob grows with temperature until the theta temperature is reached or until $n_t = R_F$. The equation above predicts that a thermal blob is only seen when enthalpic interactions oppose mixing of the polymer, i.e. positive χ . ***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 χ is 1/2, the denominator goes to 0 and n_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 ϕ_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, $N = N_{persistence} l_p / r$*** 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 $N = N_{persistence} / n_t$ 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.