

ENAS 606 : Polymer Physics

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Non-Ideal Chains: Size, Statistics, Free-Energy

1 Interactions Between Monomers

Just as the ideal gas equation of state $PV = nRT$ assumes no interactions between the constituent atoms or molecules of a gas, so to have we assumed no energetic interactions between the monomers of our polymer. The Van der Waals equation of state results from correction terms to the ideal gas EOS based on physical excluded volume and energetic interactions which decrease (or increase) the pressure of the gas relative to the ideal state. Here, we will treat real polymer chains via consideration of excluded volume, derived by comparison with the non-interacting or ideal case. The Mayer f-function $f(r)$ describes the probability of locating a monomer at r , relative to the non interacting system where $U(r) = 0$:

$$f(r) = \exp(-U(r)/kT) - 1 \quad (1)$$

The excluded volume, v , is defined as

$$v = - \int 4\pi r^2 f(r) dr \quad (2)$$

The excluded volume v is negative for systems with net attractive interactions, and positive for those with net repulsive interactions.

1.1 Excluded Volume and Solvency

Excluded volume scales as $v \approx b^2d$ where b is the Kuhn monomer size (length) and d is the diameter (Kuhn segments are rod-like).

- **Athermal Solvents** Here, v is independent of temperature. The system only features hard core repulsion and $v \approx b^2d$. Monomer-monomer contact is energetically indistinguishable from monomer-solvent contact, for example.
- **Good solvents** Excluded volume is reduced due to monomer-monomer attraction. The effect of this attraction is greater at lower temperatures, causing a reduction in the excluded volume. $0 < v < b^2d$
- **Theta solvent** The (positive) contribution to excluded volume from hard core repulsion is exactly balanced by that (negative) due to attractions and so $v = 0$. The chains thus have nearly ideal conformations. This occurs at a temperature called the theta temperature, Θ , which is analogous to the Boyle temperature in thermodynamics.

- **Poor solvents** Excluded volume is negative due to large attractive interactions between the monomers, which prefer monomer-monomer contact strongly over monomer-solvent contact. Chain dimensions are reduced relative to ideal. $-b^2d < v < 0$.
- **Non-solvents** Here, $v \approx -b^2d$ and the polymer collapses into a very compact structure that excludes all solvent.

2 Flory Theory

Flory treated the question of equilibrium conformation of real chains using a mean field approach. The equilibrium size is set by a balance between excluded volume which tends to expand the chain size, and a restoring force due to loss of conformational entropy due to swelling. The energetic contribution due to excluded volume is given by the number of *excluded volume interactions* within a coil and the cost of each exclusion, kT . The number of excluded volume interactions is just the probability of finding a monomer within the excluded volume of another. If we assume a mean density of monomers in the coil, N/R^3 , then the number of excluded volume interactions per monomer is vN/R^3 and for N monomers in the coil, the energetic contribution is

$$F_{excl} \approx kTv \frac{N^2}{R^3} \quad (3)$$

The entropic energy due to expansion of the coil is given as

$$F_{entropic} \approx kT \frac{R^2}{Nb^2}$$

The equilibrium coil size is determined as the minimum in the total energy function $F_T(R) = F_{excl}(R) + F_{entropic}(R)$. For positive v we have

$$\begin{aligned} F_T &\approx kT \left(v \frac{N^2}{R^3} + \frac{R^2}{Nb^2} \right) \\ \partial F / \partial R &= 0 \\ R_F &\approx v^{1/5} b^{2/5} N^{3/5} \end{aligned} \quad (4)$$

Comparison of R_F with $N^{1/2}b$ provides a quantity known as the chain interaction parameter, z where

$$\frac{R_F}{bN^{1/2}} \approx \left(\frac{v}{b^3} N^{1/2} \right)^{1/5} \approx z^{1/5} \quad (5)$$

2.1 Problems with Flory Theory

The simple approach taken by Flory provides surprisingly good results - more modern theories/calculations provide $R \sim N^{0.588}$. However, the success of the Flory theory is due to a cancelation of errors. The excluded volume contributions are overestimated as correlations between monomers (which decrease the probability of overlap) are not considered. At the same time, the entropic restoring force is also overestimated. Nevertheless, such approaches based on a mean field approximation of density combined with ideal chain conformation-derived entropy can provide quite useful results, for example in the case of an adsorbed chain.

The treatment of the case for $v < 0$ in the preceding simple manner leads to an aphysical result for the coil size that minimizes the total free energy. Stabilizing terms need to be considered [2].

3 Thermal Blobs, The Thermic Length Scale

We can conceive of a blob that is associated with the balance between thermal energy and the energetic contribution due to excluded volume interactions. On length scales below ξ_T , the polymer is ideal whereas above ξ_T , excluded volume interactions dominate and the system executes a self-avoiding random walk.

The blob is ideal, so $\xi_T^2 \approx g_T b^2$. As above, using a mean field number density of monomers inside the blob, the excluded volume interaction energy is

$$kT v \frac{g_T^2}{\xi_T^2}$$

This energy is just balanced by the thermal energy, kT so that the thermal blob size is given by $\xi_T \approx b^4/v$ and the number of monomers in a blob as $g_T \approx b^6/v^2$. Comparison to Equation 5 shows that the number of monomers in the thermal blob is related to the chain interaction parameter by

$$g_T \approx N/z^2$$

If we now consider the conformation of the chain above the blob length scale, for excluded volume repulsion, the blobs follow a self-avoiding random walk, so

$$R \approx \xi_T (N/g_T)^\nu \approx b(v/b^3)^{2\nu-1} N^\nu$$

where $\nu \approx 3/5$ as provided by the Flory argument. For excluded volume attraction, the blobs condense onto themselves, and form a compact globule. The size of the globule is given assuming a fractal dimension of 3, that is

$$R \approx \xi_T (N/g_T)^{1/3}$$

4 Temperature Dependence of Coil Dimensions

The temperature dependence of coil dimensions is considered via the modification of the excluded volume provided via the Mayer f-function. The contributions from hard-sphere overlap and weak attraction are separated so that

$$\begin{aligned} f(r) &\cong -1; r < b \\ f(r) &\cong U(r)/kT; r > b \\ v &= 4\pi \int_0^b (1)r^2 dr + 4\pi/kT \int_b^\infty U(r)r^2 dr \\ v &\approx \left(1 - \frac{\Theta}{T}\right) b^3 \end{aligned} \tag{6}$$

where

$$\Theta \approx \frac{-1}{kb^3} \int_b^\infty U(r)r^2 dr$$

The theta temperature Θ is thus explicitly linked to the chain interaction parameter and the thermal blob size via

$$\begin{aligned} z &\approx \frac{T - \Theta}{T} N^{1/2} \\ g_T &\approx \left(\frac{T}{T - \Theta}\right)^2 \end{aligned} \tag{7}$$

5 Chain Statistics: End-End Distances

We can now return to the question of real chain statistics. Before, we derived the Gaussian distribution for ideal chains and used it to arrive at an expression for the free energy of an ideal polymer chain as a function of its end-end distance. Now, for real polymer chains, we have a free energy that is a function of the scaling exponent ν ($R \approx bN^\nu$) where

$$F(R) \approx kT \left(R / \langle R^2 \rangle^{1/2} \right)^\delta$$

with $\delta = 1/(1 - \nu)$.

The probability distribution function for end-end distances is given by the Boltzmann factor using the free energy $F(R)$

$$P(N, R) \sim \exp(-F(R)/kT)$$

This probability is further modified by the decreased likelihood of finding chain ends within a certain distance of each other that scales as R^g . If we define

$$x \equiv R / \langle R^2 \rangle^{1/2}$$

then

$$P(x) \cong 0.278x^{0.28} \exp(-1.206x^\delta) \quad (8)$$

For real chains, $\delta \cong 2.43$. The distribution of end-end distances is markedly lower at small distances than ideal chains.

References

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- [3] G. Strobl, *The Physics of Polymers: Concepts for Understanding Their Structures and Behavior*, Springer, 1997.
- [4] P. Flory, *Principles of Polymer Chemistry*, Cornell University Press, 1953.