

Notes for Learning Polymer Physics

Yi-Fang, Tsai

December, 2021

Abstract

This is the notes for learning polymer physics from the book "*Scaling Concepts in Polymer Physics*" published in 1979, written by the 1991 Nobel Prize Winner Pierre-Gilles de Gennes. The main content in the notes is from Chapter I and Chapter X, which talk about the properties of ideal chain and its relationship with critical phenomena, respectively.

1 Ideal Chain

One of the simplest idealization of a flexible polymer chain consists in replacing it by a random walk on a periodic lattice. The walk is a succession of N steps, starting from one end (α) and reaching an arbitrary end point (ω). At each step the next jump may proceed toward any of the nearest-neighbor sites, and the statistical weight for all these possibilities is the same. The length of one step will be called a . **Notice that in high T , we enumerate the domains of Ising model to calculate its partition function.**

1.1 Define the number $R(r)$

From a pedagogical (could be too naive, though) point of view, all chain properties are easy to visualize. For instance, the entropy $S(r)$ associated with all chain conformations starting from an origin ($r=0$) and ending at a lattice point r , is simply related to the number of distinct walks $R_n(r)$ going from (0) to (r) in N steps

$$S(r) = \ln[\mathcal{R}_n(r)]$$

And if each lattice site has z neighbors, the number of distinct possibilities at each step is z , and the total number is

$$\sum_{(r)} \mathcal{R}_N(r) = z^N$$

where each of the a terms is a vector of length a with z possible orientations. Different a vectors have completely *independent* orientations (**obviously, it is not realistic**).

1.2 Some Important Equations from Numerical Data on Self-Avoiding Walks

It seems that the direct data are not quite conclusive¹, so we turn to numerical calculations on *self-avoiding walk* (SAW). The mathematical properties of simple random walks are , but somehow the mathematical properties of SAWs are complex.

There are two numerical methods used to study the SAWs:(1) exact counting of walks for finite N plus extrapolation methods to extend the results to $N \rightarrow \infty$. (2) Monte Carlo methods. All different dimensionalities are computed. The results of numerical studies on SAWs are usefully summarized in a review by McKenzie².

1. The total number of SAWs of N steps has the asymptotic form(at large N)

$$\mathcal{R}_N(tot) = constant \tilde{z}^N N^{\gamma-1} \quad (1)$$

The first factor \tilde{z} is very similar to the z^N which we had for ideal chains, but \tilde{z} is somewhat smaller than z . For the 3-dimensional simple cubic lattice, $z = 6$ and $\tilde{z} = 4.68$. The second factor is called the enhancement factor. The exponent γ depends only on the dimensionality, d , e.g., for all 3-dim lattice $\gamma \cong 7/6$, and for all 2-dim ones $\gamma \cong 4/3$.

We can say that γ is a universal exponent in contrast to \tilde{z} , but \tilde{z} depends on the dimensionality d and also the particular lattice chosen (e.g. face-centered cubic/simple cubic)³.

2. The end-to-end distance r of a polymer has a mean square average R_F^2 and which scales as

$$R_F \cong aN^\nu \quad (2)$$

And the distribution law for r depends on r only through the ratio r/R_F

$$p_N(r) = \frac{1}{R_F^d} f_p\left(\frac{r}{R_F}\right) \quad (a \ll r \ll Na) \quad (3)$$

and the prefactor $\frac{r}{R_F}$ is a normalization factor, R_F is the root mean square value defined by random walks. So the most important part in this equation is the $f_p(x)$ part.

¹Page. 38, the main experiments on real chains in a dilute solutions.

²C. Domb, *Adv. Chem. Phys.* 15,229(1969). D.S. McKenzie, *Phys. Rept.* 27C(2)(1976)

³I'm not quite sure what's going on here...

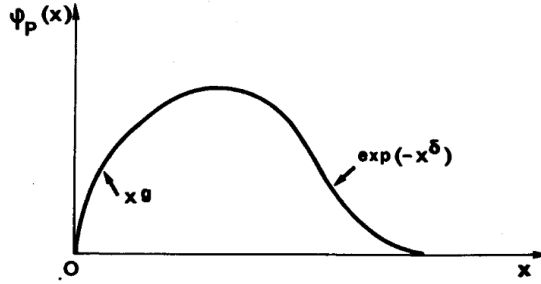


Figure 1: Distribution of end-to-end distance r in a SAW of N steps. x is r/R_F , and you can see the exponential decrease at large x .

2 Derive Some Useful Properties from Ising Model

In this section we'll going to derive(or mention) some properties that we can make a comparison with that of polymer physics.

2.1 The n Vector Model

There are two assumptions on this model:

1. We assume that the magnetic atoms are located on a periodic lattice. Each magnetic atom(i) carries a spin S_i ; thi is a vector, with n components $S_{i1}, S_{i2}, \dots S_{in}$. In our considerations we ignore all quantum effects.
2. The total length S of each spin is fixed, so we choose the following normalization:

$$S^2 \equiv \sum_{\alpha=1}^n S_{i\alpha}^2 = n \quad (4)$$

If neighboring spins are coupled, and their energy is minimized when they are parallel. This leads to a quantity similar to Hamiltonian we define it as \mathcal{H} :

$$\mathcal{H} = - \sum_{i>j} K_{ij} S_i \cdot S_j - \sum_i H \cdot S_i \quad (5)$$

K is constant and positive, and K_{ij} is K for nearest neighbor pairs (ij) and vanishes for all other choices. And H is the incorporated term describing the external field H . Remember that

The partition function of the spin system is

$$Z = \prod_i \int d\Omega_i \exp(-H/\tau) \quad (6)$$

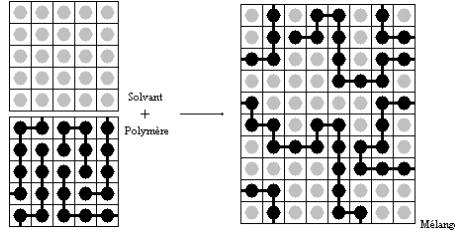


Figure 2: from Wikipedia:Flory-Huggins solution theory

where $\int d\Omega_i$ represents an integration over allowed orientations of spin S_i . For example, if we choose n to be 3, then the integration is like to integrate over the solid angle of a 2 dimensional sphere. It has been a traditional temptation to expand the partition function in power of the coupling energy K_{ij} for each pair:

$$\exp(-K_{ij}(S_i \cdot S_j))/\tau = 1 - \frac{K_{ij}}{\tau}(S_i \cdot S_j) + \frac{1}{2}\left(\frac{K_{ij}}{\tau}\right)^2(S_i \cdot S_j)^2 + \dots \quad (7)$$

Usually when such expansions are inserted into the above equation for Z , they result in a complicated structure. **If we go to the limit $n = 0$, however, they become simple.** This is a very formal step since our definition of n implied that it was a positive integer. However, this step can be performed and is useful. We shall see that when $n = 0$ the expansion leads to a problem of **self-avoiding chains on a Flory-Huggins lattice**, which is a famous theory discussing the thermodynamic properties of polymer solution.

3 Single-Chain Problem

3.1 Average over Orientations and Moment Theorem

Let us first define an average over all orientations of each spin. It is different from a thermal average, so its not weighted by the Boltzmann factor. The relation between an **average over all orientations** and **thermal average** for any function $G(S_1, S_2, \dots)$ is

$$\langle G \rangle = \frac{\langle \exp(-\mathcal{H}/\tau) G \rangle_0}{\langle \exp(-\mathcal{H}/\tau) \rangle_0} \quad (8)$$

We call it the **rule of average**. And the partition function becomes

$$Z = \Omega \langle \exp(-\mathcal{H}/\tau) \rangle_0$$

where $\Omega = \prod_i \int d\Omega_i$ is the total volume of the phase space for the spins. After we expand the partition function, we are going to deal with terms like:

$$\langle S_\alpha \rangle_0$$

$$\langle S_\alpha S_\beta \rangle_0$$

$$\langle S_\alpha S_\beta S_\gamma \rangle_0$$

where α, β , etc are component subscripts. when we formally set $n = 0$, only the quadratic term is non-vanishing

$$\langle S_\alpha S_\beta \rangle_0 = \delta_{\alpha\beta}$$

and the higher moments all equal to zero! e.g.

$$\langle S_\alpha^4 \rangle_0 = 0$$

We'll skip the proof⁴.

3.2 The Magnetic Partition Function Expanded in Self-Avoiding Loops

Because of moment theorem, we can rewrite partition function as

$$\begin{aligned} Z/\Omega &= \langle \prod_{i>j} \exp(\frac{K_{ij}}{\tau} \sum_{\alpha} S_{i\alpha} S_{j\alpha}) \rangle_0 \\ &= \langle \prod_{i>j} [1 + \frac{K_{ij}}{\tau} \sum_{\alpha} S_{i\alpha} S_{j\alpha} + \frac{1}{2} (\frac{K_{ij}}{\tau})^2 \sum_{\alpha\beta} S_{i\alpha} S_{j\alpha} S_{i\beta} S_{j\beta}] \rangle_0 \end{aligned} \quad (9)$$

You can see that all higher terms in the expansion of exponential vanish, the highest term in the expansion is to the power of two. And **just as the high temperature expansion we see in Ising model**, to each site i must be associated two spin components $S_{i\alpha}, S_{i\alpha}$ to obtain a nonzero average. These rule means that **the only allowed graph are closed loops**(Figure. 3). And the loop **cannot intersect itself** otherwise it contributes an average $\langle S_i^4 \rangle$ which vanishes by moment theorem.

Note that each loop has a single value of component index α occurring at all its sites. It means that the two factors S_i at one point involve the same component. When sum over the component index α for one loop, we get

$$(K/\tau)^N n \quad (10)$$

Where N is the number of bonds in the loop, and n is the component index. When n approaches zero, we get a trivial result

$$\frac{Z}{\Omega} \equiv 1 \quad (11)$$

so far that's what we get.

⁴If you're interested, check page 273-275.

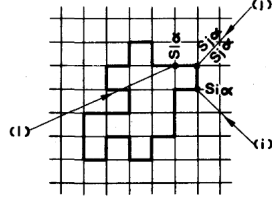


Figure 3: a close loop without intersecting itself



Figure 4: a minimal loop

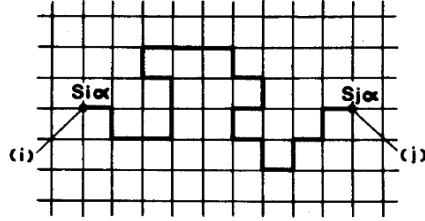


Figure 5: a self-avoiding walk linking site i and j

3.3 Spin Correlations and the One-Chain Problem

We have a spin spin correlation function as below:

$$\langle S_{il} S_{jl} \rangle$$

Here we choose one component(l) to compute. Apart from normalization condition, it is identical to the magnetization correlation function. Apply the **rule of average** in eq. (8), we get

$$\langle S_{il} S_{jl} \rangle = \frac{\langle \exp(-H/\tau) S_{il} S_{jl} \rangle_0}{\langle \exp(-H/\tau) \rangle_0} \quad (12)$$

And the denominator is equal to 1.

Since **the index is (i) and (j)**, and the only loop which contributes are self-avoiding loops, so what we have is a sum over **all self-avoiding walks sites i and j**.

If the walk involves N steps, the resulting contribution to eq.(10) is simply $(K/\tau)^N$. All along the walk the component index α must be equal to the chosen value, i.e. no summation to be carried on α . Finally, we are led to the fundamental theorem:

$$\langle S_{il}S_{jl} \rangle|_{n=0} = \sum_N R_N(ij) \left(\frac{K}{\tau}\right)^N \quad (13)$$

Where $\mathcal{R}_N(ij)$ is the number of self-avoiding walks of N steps linking points (i) and (j) on the lattice (we discussed \mathcal{R} in chapter I), This equation is the **basic link between chains and magnets**.

4 Self-Avoiding Walks(SAWs)

We now present some of its applications.

4.1 Total Number of Walks

The total number of SAWs of N steps, starting from point (i) is

$$R_{N(total)} = \sum_j R_N(ij) \quad (14)$$

$R_N \cong \bar{z}N^{\gamma-1}$ is the asymptotic form given in eq.(1). Susceptibility may be expressed by

$$\begin{aligned} \chi_M &= \frac{1}{\tau} \sum_j \langle S_{il}S_{jl} \rangle \text{ (def.)} \\ &= \frac{1}{\tau} \sum_N R_{N(total)} \left(\frac{K}{\tau}\right)^N \\ &\cong \frac{1}{\tau} \sum_N \left(\frac{K\bar{z}}{\tau}\right)^N N^{\gamma-1} \\ &= \left(\sum_j \text{ becomes } \sum_N \right) \end{aligned} \quad (15)$$

When τ reaches the critical value(\bar{z} is mentioned in section 1):

$$\tau_c = K\bar{z} \quad (16)$$

Consider $\tau = \tau_c(1 + \epsilon) \cong \tau_c \exp(\epsilon)$, then

$$\chi_M \cong \frac{1}{\tau_c} \sum_N \exp(-N\epsilon) N^{\gamma-1} \quad (17)$$

Replace the sum by an integral $\int_0^\infty dN$, we get

$$\chi_M \cong \frac{1}{\tau_c} \epsilon^{-\gamma} \quad (18)$$

It is in agreement with the singularity for the magnetic susceptibility of Ising model $\chi_M = \chi_0 |\epsilon|^{-\gamma}$.

4.2 N and ϵ are Conjugate Variables

Weve located the transition point⁵, we return to the general correlation $\langle S_i S_j \rangle$ and rewrite it for small ϵ in the form:

$$\langle S_{il} S_{jl} \rangle = \sum_N \exp(-N\epsilon) R_N(ij) \text{ for small } \epsilon \quad (19)$$

it is a Laplace transform since it involves the $\exp(-N\epsilon)$. So N and ϵ are conjugate variables. Small ϵ corresponds to a large N.

4.3 Scaling Law for Self-Avoiding Walks/ Asymptotic Form for Large r

All the properties for magnetic correlations now have their counterpart for self-avoiding walks. The first and most essential is the existence of a single correlation length. The analog of ξ is the range of the **self-avoiding walks** **Rf**. In the introduction of the main reference, Prof. de Gennes mentioned the difference between the **local and global properties of polymers**⁶. the eq.(0.1) in the introduction is of the form of Flory radius, or maybe the radius of gyration R_G . Both R_F and R_G shows the scaling law that is similar to ξ .

The spatial scaling law which corresponds to the existence of one single characteristic length is

$$\frac{R_N(ij)}{R_N(tot)} = p(r) = \frac{1}{R_F^d} \phi_\nu\left(\frac{r}{R_F}\right) \quad (20)$$

the definition of $p(r)$ is mentioned in section 1.2, as eq.(3).

The limiting behavior of the correlations at large distances is given by an Ornstein-Zernike form. Invert the Laplace transformation:

$$\phi_\nu \sim \exp - \left(\frac{r}{R_p}\right)^{1/(1-\nu)} \quad (21)$$

The justification of eq.(21) is in Chapter 1 of the main reference, using the simpler Pincus argument. It is not covered by this note⁷.

4.4 Self-Avoiding Walks Returning to the Origin

We announced that⁸

⁵I think the point is located by the numerical calculation we mentioned in section 1 since it mention the quantity \tilde{z} .

⁶Page. 28, if you're interested.

⁷This note only cover eq.(01) to eq.(24) of Chapter 1

⁸It's from eq.(I.28) of Chapter 1.

$$\mathcal{R}_N(a) \cong N^{-\nu d} = N^{-2+\alpha} \quad (22)$$

If we define the correlation function of magnetization $\langle M(0) \cdot M(r) \rangle$

$$\begin{aligned} \langle M(0) \cdot M(r) \rangle &= \text{correlation function} \\ &= \frac{1}{r^{d-2+\eta} f_M(\frac{r}{\xi})} \end{aligned} \quad (23)$$

f_M satisfies:

$$\begin{aligned} f(0) &= 1 \\ f(x) &\cong x^\eta \exp(-x) \quad (x \gg 1). \end{aligned}$$

and choose two neighboring points, i.e. $r = a$, $\langle M(0) \cdot M(r) \rangle$ becomes a measure of the coupling energy responsible for magnetic order ($\epsilon \equiv x \rightarrow 0$):

$$\begin{aligned} \langle M(0) \cdot M(a) \rangle_{\tau=\tau_{c-}} - \langle M(0) \cdot M(a) \rangle_{\tau=\tau_c} &= -C_v d\tau \\ &= -const \cdot \epsilon^{1-\alpha} \end{aligned} \quad (24)$$

What we mentioned above in eq.(23) and eq.(24) is derived with the concept of Ising model. The magnetic analog of $\mathcal{R}_N(a)$ is the correlation function in eq.(24). So by the Hamiltonian in eq.(5), we have

$$E = -\frac{1}{2} z K \langle S_i \cdot S_{jk} \rangle \quad (25)$$

i and j here is the nearest neighbors and the factor $1/2$ is to eliminate the over-counting. With eq.(22) and simple algebra, we have eq.(26) and eq.(27):

$$\begin{aligned} E &= -\frac{1}{2} z K \sum_N \exp(-N\epsilon) R_N a \\ &\cong -K \sum_N \exp(-N\epsilon) N^{-2+\alpha} \end{aligned} \quad (26)$$

Split into two parts and replacing the sum by an integral:

$$E(\epsilon) = E(0) + \int_0^{infy} dN (1 - \exp(-\epsilon N)) N^{-2+\alpha} \quad (27)$$

The integral has no singularities either for each extreme N . Set $\epsilon N = t$ and write

$$\int_0^{infy} dN N^{-2+\alpha} (1 - \exp(-\epsilon N)) = \epsilon^{1-\alpha} \int_0^{infy} dt t^{-2+\alpha} (1 - \exp(-t)) \cong \epsilon^{1-\alpha} \quad (28)$$

So we find the similarity with the previous equation (24)⁹.

$$E(\epsilon) = E(0) - const. \epsilon^{1-\alpha}$$

⁹Here's another comment that this derivation proves that "eq.(22) agrees with the scaling properties of the energy E ". This is one of the missing pieces. just a reminder for myself.

5 Summary

There are still lots of missing pieces I lost in the references, especially in the last section about SAWs. So I want to write down the key points mentioned by Professor de Gennes as a memo:

1. All properties of one self-avoiding walk on a lattice can be related to the spin correlation of a ferromagnet with an n -component magnetization when we formally set $n \rightarrow 0$.
2. a link between the exponents for self-avoiding walks and critical exponents. ($\nu = 1/2$, $\gamma = 1$)
3. phase transition like mean field behavior
4. The temperature T of the polymer system is not related to the temperature τ of the magnetic system, but $((\tau - \tau_c)/\tau_c = \epsilon$ is the conjugate variable of the degree of polymerization, N .)

I cannot totally understand these comments, but I hope that they can be the hints when someday I try to pick up the relevant knowledge in polymer physics.