

### **Theoretical estimate of the probability for macromolecule formation**

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**Abstract:** We estimate the polymerization probability of a macromolecule, where the macromolecule is made of distinct monomers; and there are different values of the fugacity for the addition of the monomers in the chain to form an infinitely long linear macromolecule of distinct monomers. A lattice model of the random walk is used to mimic the conformations of an ideal chain in two and three dimensions, and this ideal chain is made of macromolecules of distinct monomers. It has been shown through analytical estimates that the stiff macromolecule of distinct monomers may be easily formed than the flexible macromolecules for both two and three dimensional cases.

**Key words:** Macromolecule, Theoretical estimate, Polymerisation, Gaussian chain, Analytical method

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## 1. Introduction

There are four major types of the Biological macromolecules which are known to form various living organisms. These macromolecules are *Lipids*, *Carbohydrates*, *Nucleic Acids* and the *Proteins* [1]. The Lipids are non polymeric macromolecules. These Biological macromolecules are the backbone of the living creatures and the structures of these macromolecules are formed by distinct monomers and therefore understanding the possibility of polymerization of such macromolecules may be useful. There are artificial macromolecules which are known to be useful for various applications [2-3]. The macromolecules are formed by the process of dehydration; and the solute molecules which are in the solutions and these solutes act as the monomers and these monomers may combine to form long macromolecules and but the Biomolecules are evolved in the complex manner[1-4].

We consider structure of a macromolecule in the form of random polymer chain which is organized in the two and three dimensions. The structure of the macromolecule has been realized using a square lattice and a cubic lattice to study polymerization of such structure of an infinitely long linear macromolecule in two and three dimensions, respectively to mimic the formation of an infinitely long linear macromolecule made of four different repeat units or the monomers. The distinctions have been incorporated in the model of the macromolecule in such a manner that one monomer may connect to another type of monomer with a given Boltzmann weight, while addition of other type of the monomers with third type of the monomers have different Boltzmann weight. Such means has been used to mimic conformations of a macromolecule which is made of different types of the monomers so that we have some theoretical estimates about the structural aspects of the complex macromolecules through over simplified current mathematical model.

The manuscript is organized in the following manner; in the section two we define the random walk lattice model and we describe methods for calculating the partition function of an infinitely

long chain where the polymer chain is made of different type of the monomers. We analyze results obtained through simplified artificial model of the linear chain to mimic conformations of the chain and also to calculate the probability of the formation of an infinitely long linear macromolecule in the section three. We summarize our findings and conclude the discussion in the section four.

## 2. Model and Method

We consider a linear ideal polymer chain to mimic the conformations of a macromolecule in two and three dimensions. The conformations of an ideal polymer chain were enumerated using under lying lattices, i. e. a square and a cubic lattice for two and three dimensions, respectively. The lattice models were widely used to study the thermo-dynamical behaviour of the linear polymer molecules [5-13] in the thermodynamic limit; and we have also relied to lattice model of an ideal polymer chain to analyze the possibility of the macromolecule formation. The generating function technique is used to enumerate the conformations of the polymer chain [5, 8-11]; and all possible directions *i. e.*  $\pm x$  and  $\pm y$  directions on the square lattice were accessible to the walker for enumerating the chain conformations, but in the cubic lattice  $\pm z$  directions were also permitted to the walker in addition to  $\pm x$  and  $\pm y$  directions while enumerating the conformations of the polymer chain in three dimensions.

The chain is made of four type of the monomers *i. e.* the monomers are *a*, *b*, *c* and *d*; where the bonding in between *a* & *b* monomers leads the release of an extra energy which is equal to  $2*E_s$  and similarly bonding in between the *c* and *d* monomers leads a release of an extra energy  $3*E_s$ . The first monomer of the chain is grafted at a point O; as it is shown in the figure no. 1, and a walk of five monomers is shown in the Figure no. 1 (i); and the Boltzmann weight of this walk is  $g^5k^4$ ; and the Boltzmann weight of the walk shown in the Figure no. 1 (ii) is  $g^9k^7\omega^4$ . The semi-flexible behaviour is incorporated in the polymer model by adding the stiffness weight in the conformations of the chain [5-11].

$$\begin{aligned} < N_u > \\ = & \frac{e^{2E_s}(-2 - 3e^{E_b} + e^{E_b+3E_s})^2}{(-1 + e^{E_s})(8 + 24e^{E_b} + 18e^{2E_b} + 8e^{E_s} + 4e^{2E_s} + 24e^{E_b+E_s} + 3e^{2(E_b+E_s)} + 18e^{2E_b+2E_s} + 8e^{E_b+2E_s} - 8e^{E_b+3E_s} - 12e^{2E_b+3E_s} - 7e^{E_b+4E_s} - 10e^{2E_b+4E_s} - e^{E_b+5E_s} + 2e^{2E_b+6E_s} + e^{2E_b+7E_s})} \dots (6) \end{aligned}$$

And average number of c-d monomers pairs is written as,

$$\begin{aligned} < N_v > \\ = & \frac{e^{3E_s}(-2 - 3e^{E_b} + e^{E_b+2E_s})^2}{(-1 + e^{E_s})(8 + 24e^{E_b} + 18e^{2E_b} + 8e^{E_s} + 4e^{2E_s} + 24e^{E_b+E_s} + 3e^{2(E_b+E_s)} + 18e^{2E_b+2E_s} + 8e^{E_b+2E_s} - 8e^{E_b+3E_s} - 12e^{2E_b+3E_s} - 7e^{E_b+4E_s} - 10e^{2E_b+4E_s} - e^{E_b+5E_s} + 2e^{2E_b+6E_s} + e^{2E_b+7E_s})} \dots (7) \end{aligned}$$

While, the average length of the polymer chain may be written using following equation

$$\begin{aligned} < N_g > \\ = & \frac{e^{-E_b}(1 + e^{E_b})^2(8 + 24e^{E_b} + 18e^{2E_b} - 6e^{2(E_b+E_s)} - 4e^{E_b+2E_s} - 4e^{E_b+3E_s} - 6e^{2E_b+3E_s} + e^{2E_b+4E_s} + e^{2E_b+6E_s})}{(-1 + e^{E_s})(8 + 24e^{E_b} + 18e^{2E_b} + 8e^{E_s} + 4e^{2E_s} + 24e^{E_b+E_s} + 3e^{2(E_b+E_s)} + 18e^{2E_b+2E_s} + 8e^{E_b+2E_s} - 8e^{E_b+3E_s} - 12e^{2E_b+3E_s} - 7e^{E_b+4E_s} - 10e^{2E_b+4E_s} - e^{E_b+5E_s} + 2e^{2E_b+6E_s} + e^{2E_b+7E_s})} \dots (8) \end{aligned}$$

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The number fractions for a-b monomers pairs and also the c-d monomers pairs are written as,

$$< N_a > = \frac{e^{E_b+2E_s}(-2 - 3e^{E_b} + 4e^{E_b+3E_s})^2}{(-1 + e^{E_b})^2(8 + 24e^{E_b} + 18e^{2E_b} - 6e^{2(E_b+E_s)} - 4e^{E_b+2E_s} - 4e^{E_b+3E_s} - 6e^{2E_b+3E_s} + e^{2E_b+4E_s} + e^{2E_b+6E_s})} \dots (9)$$

$$< N_b > = \frac{e^{E_b+3E_s}(-2 - 3e^{E_b} + e^{E_b+2E_s})^2}{(-1 + e^{E_b})^2(8 + 24e^{E_b} + 18e^{2E_b} - 6e^{2(E_b+E_s)} - 4e^{E_b+2E_s} - 4e^{E_b+3E_s} - 6e^{2E_b+3E_s} + e^{2E_b+4E_s} + e^{2E_b+6E_s})} \dots (10)$$

While, the number ratio of a-b monomers pairs to that of c-d monomers pairs is written as,

$$< N_c > = \frac{e^{-E_s}(-2 - 3e^{E_b} + e^{E_b+3E_s})^2}{(-2 - 3e^{E_b} + e^{E_b+2E_s})^2} \dots (11)$$

Since, it is assumed that there are four different kinds of the monomers present in the solution, and these monomers are assumed to form the macromolecule by the process like dehydration [1-4]. Any of these four types of the monomers may form bond to remaining three types of the monomers and the Boltzmann weight corresponding to the bonding of the monomer is at least  $g$  (where  $g$  is the step fugacity). While,  $a$  type monomers can connect to  $b$  type monomer with the Boltzmann weight  $g\omega^2$  [where  $\omega = \text{Exp}(\beta E_s)$ ]; and similarly  $g\omega^3$  is the Boltzmann weight corresponding to bonding of the  $c$  type monomers to the  $d$  type monomers in the polymer chain. The Boltzmann weight  $k[\text{Exp}(-\beta E_b)]$  corresponds to bending energy 90 degree, but 180 degree bending energy corresponds to the stiffness weight  $k^2$  [12-13].

The grand canonical partition function ( $F$ ) of the polymer chain, in general may be written as ( $2 \leq n$ ):

$$F(g, \omega, k) = \sum_{N=1}^{\infty} \sum_{n=0}^{\infty} \sum_{N_B=0}^{N-1} g^N \omega^n k^{N_B} \dots (1)$$

### 1. The Calculations and the Results

We use the generating function technique [5-14] to obtain the partition function of the polymer chain in the thermodynamic limit, and the singularity of the partition function of the chain is used to find the conditions required for the polymerization of an infinitely long chain. The admissible values of  $\omega_c$ ,  $u_c$  &  $v_c$  are shown in the table no. 1; and the nature of the corresponding phase diagram is shown in the figure no. 1. It is to be noted here that  $\omega_c$  (i. e.  $u_c$  &  $v_c$ ) is the minimum Boltzmann weight, which is required for the polymerization of an infinitely long chain of different monomers; while the  $g_c$  is the weight for the formation of an infinitely long chain of identical monomers.

We obtained the values of the relevant parameters of the semi-flexible polymer chain of distinct monomers, i. e. the average number of  $a$ - $b$  monomers pairs and also the number of  $c$ - $d$  monomers pairs using following equations:

$$\langle N_u \rangle = \frac{\partial \text{Log}(F)}{\partial \text{Log}(u)} \dots (2)$$

$$\langle N_v \rangle = \frac{\partial \text{Log}(F)}{\partial \text{Log}(v)} \dots (3)$$

Where  $u = g\omega^2$  and  $v = g\omega^3$ , and  $N_u$  is the number of  $a$ - $b$  monomers pairs, while  $N_v$  shows number of the  $c$ - $d$  monomers pairs; and the average length of the chain is obtained using the following well known equation,

$$\langle N_g \rangle = \frac{\partial \text{Log}(F)}{\partial \text{Log}(g)} \dots (4)$$

The fraction of  $a$ - $b$  and  $c$ - $d$  monomers pairs may be obtained using following relations,

$$n_a = \frac{\langle N_u \rangle}{\langle N_g \rangle}, \quad n_b = \frac{\langle N_v \rangle}{\langle N_g \rangle} \quad \& \quad n_c = \frac{n_a}{n_b} \dots (5)$$

Where,  $n_a, n_b$  is the average number of  $a$ - $b$ ,  $c$ - $d$  monomers pairs and  $n_c$  is the ratio of  $a$ - $b$  to  $c$ - $d$  monomers pairs number.

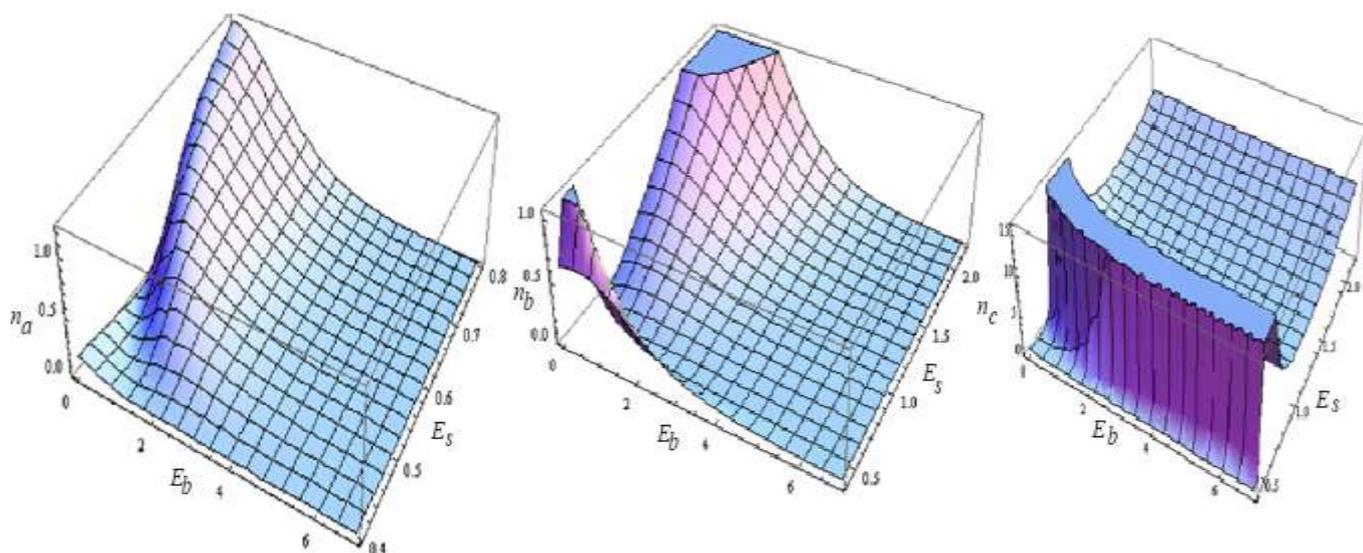
#### (a) Macromolecule in two dimensions

A macromolecule of distinct monomers is assumed to polymerize in the two dimensions; and there are four types of the monomers which forms an infinitely long semi-flexible polymer chain. The grand canonical partition function ( $F$ ) and the average number of  $a$ - $b$  and  $c$ - $d$  monomers pairs were calculated for two dimensional case in the following manner (here  $g_c = \frac{1}{(1+k)^2}$ , i. e.  $1/4$  for  $k=1$ ; [5-6]),

We have shown the variations of the parameters  $n_a, n_b$  and  $n_c$  in the figure no. (3) for the two dimensional ideal polymer model of distinct monomers for the chosen values of the bonding energy of the monomers pairing and the bending energy of the polymer chain. It is shown that the variation of  $n_b$  is complex and involved.



<b>Table No. 1: We have shown the critical values of the pairing fugacity for the monomers of the chain to form an infinitely long macromolecule; the molecule is made of four different types of the monomers for two dimensional, and the macromolecule is made of six monomers in three dimensional model</b>						
$k$	$\omega_c(2d)$	$u_c(2d)$	$v_c(2d)$	$\omega_c(3d)$	$u_c(3d)$	$v_c(3d)$
0.001	1.58394	2.50888	3.97392	1.75709	3.08736	5.42478
.1	1.62722	2.64785	4.30864	1.78409	3.18297	5.67872
.2	1.669451	2.78707	4.65287	1.81083	3.27912	5.9379
.3	1.71033	2.92521	5.00307	1.83708	3.37485	6.19989
.4	1.74996	3.06238	5.35905	1.86285	3.4702	6.46448
.5	1.78847	3.19862	5.72063	1.88816	3.56517	6.73157
.6	1.82593	3.33401	6.08767	1.91305	3.65978	7.00130
.7	1.862421	3.46861	6.46002	1.93754	3.75404	7.27364
.8	1.898016	3.60247	6.83754	1.96163	3.84798	7.54833
.9	1.932776	3.73562	7.22013	1.98535	3.9416	7.82548
.999	1.966418	3.8668	7.60375	2.00848	4.03398	8.10219

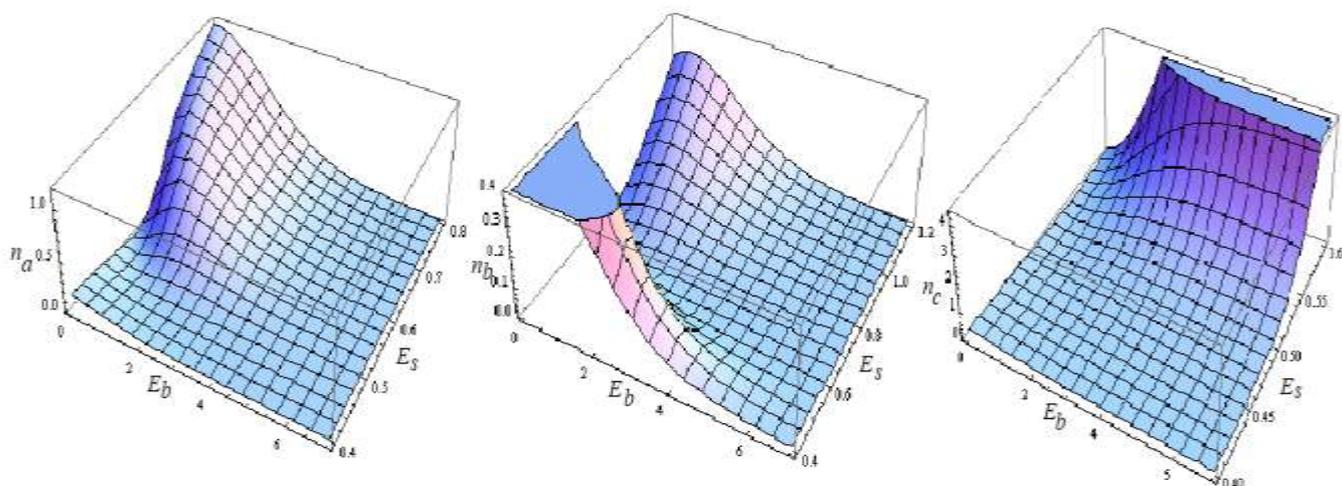


**Figure No. 3:** We have variation of the fractions  $n_a$ ,  $n_b$ , and  $n_c$  for two dimensional case is shown for the value of monomer-monomer pairing energy ( $E_s$ ) and the bending energy ( $E_b$ ) of the polymer chain. The energy values  $E_s$  &  $E_b$  are shown in the units of the inverse thermal energy ( $\beta$ ), and for the sake of mathematical simplicity we have taken the value of  $\beta=1$ .

### Macromolecule in three dimensions

We followed the methods that had been described in the above section 3 (a) regarding calculations of the relevant parameters of our interest for the two dimensional ideal chain to calculate relevant parameters of the chain for the case of three dimensional ideal polymer chain of distinct

monomers; and plotted the variation of the parameters  $n_a$ ,  $n_b$  and  $n_c$  in the figure no. (4) for an ideal chain in the three dimensional semi-flexible polymer model. We have also shown the possible critical values of the monomer-monomer pairing energy for different stiffness weights of the chain in two and three dimensions in the table no. 1 for the sake comparison and the completeness.



**Figure No. 4:** We have shown the variation of the relevant parameter  $n_a$ ,  $n_b$  and  $n_c$  for the possible values of the monomer-monomer pairing energy ( $E_s$ ) and the bending energy ( $E_b$ ). These energy values were reported in the unit of  $\beta$  and the  $\beta=1$  for the sake of mathematical simplicity in the proposed model. This figure corresponds to the case of an infinitely long chain which is made of four type of the monomers  $a$ ,  $b$ ,  $c$  and  $d$  and the chain is polymerised the three dimensions.

## 2. Summary and the Conclusions

We model the Gaussian polymer chain on a square and a cubic lattice to enumerate the conformations of the polymer chain of distinct monomers, as the

chain is made of four different types of the monomers ( $a$ ,  $b$ ,  $c$  and  $d$ ) and therefore the bonding between different monomers has different fugacity. The Gaussian chain is shown schematically in the two and three dimensions using Figure no. (1). The Gaussian semi-flexible polymer chain is polymerized in the thermodynamic limit, provided  $g_c = \frac{1}{(1+k)^2}$  for the square lattice case, and  $g_c = \frac{1}{(1+4k+k^2)}$  for the cubic lattice case; thus it has value  $\frac{1}{4}$  and  $\frac{1}{6}$  respectively for flexible ideal chain for two and three dimensions [5-6].

There are two additional critical values of the fugacity of an infinitely long chain which corresponds to divergence of the number density fluctuations of the  $a$ - $b$  monomers pairs and also fluctuations in  $c$ - $d$  monomers pairs. In the proposed model system, it is assumed that there are two hydrogen bonds in between  $a$ - $b$  monomers pairs;

while there are three hydrogen bonds which are formed in between the  $c$ - $d$  monomers pairs.

Therefore, we have chosen  $u=\omega^2$  and  $v=\omega^3$ ; where  $u$  and  $v$  are the Boltzmann weights corresponding to the formations of the two and three hydrogen bonds in between  $a$ - $b$  and  $c$ - $d$  monomers pairs, respectively; and therefore, the powers on the Boltzmann weight  $\omega$  is nothing but the number of the hydrogen bonds in between these monomers i. e. ( $a$ ,  $b$ ) and ( $c$ ,  $d$ ) monomers pairs.

There are two values of  $\omega_c$  which corresponds to singularity of the partition function which is in addition to the critical value of the monomer fugacity for the formation of an infinitely long ideal chain of identical monomers, and it has been found that the value of  $\text{Log}[v_c]/\text{Log}[u_c]=1.5$  and it is due to fact that there are two or three hydrogen bonds were assumed in the proposed model. Therefore, we have shown  $\omega_{c1}$  &  $\omega_{c2}$  in the table no. 1 for different values of the stiffness weights for two and three dimensional models, for the sake of completion.

An infinitely long chain is polymerized in two and three dimensions where the chain is made of  $a$ - $b$  and  $c$ - $d$  monomers pairs, as shown in the figure no.

(2). The nature of variation of the relevant parameters *i. e.*  $n_a$ ,  $n_b$  and  $n_c$  for the possible values of the monomers pairing energy ( $E_s$ ) and the bending energy ( $E_b$ ) have been graphed in the figure no. (3) for the square lattice; and these parameters (*i. e.*  $n_a$ ,  $n_b$  and  $n_c$ ) are also shown in the figure no. (4) for the cubic lattice case, respectively.

There are reports on the single macromolecule formation and its thermodynamics [15-17], and we may infer little bit more useful information regarding macromolecule using an oversimplified such models for the polymer chain. Where the chain is seen as the Gaussian chain and the conformations of the chain were realized using the square and the cubic lattices; the stiffness weight is used to mimic the semi-flexible nature of the polymer chain. The distinction in between the monomers (*a*, *b*, *c* and *d*) was incorporated using different values for the fugacity of different type of the monomers addition in the polymer chain. It is shown in the figure no. (2) that the monomer-monomer pairing energy decreases with the bending energy of the chain, and *c-d* pair fraction and *a-b* pair fraction differ from each other and the ratio of *a-b* monomers pair to that of *c-d* monomer pairs are also the function energy  $E_s$  and the bending  $E_b$ . It is to be noted that above findings are function of ordering which is chosen in the four different types of the monomers. We have taken four types of the monomers in the cyclic manner such that it may follow a sequence A-T-C-G, which is shown in the figure no. 1.

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