Interpenetration of two chains different in sizes: Some Exact Results

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Abstract

A model of two interacting polymer chains has been proposed to study the effect of penetration of one chain in to the other. We show that small chain penetrates more in comparison to the long chain. We also find a condition in which both chains cannot grow on their own (or polymerize) but can grow (polymerize) in zipped form.

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In recent papers [1-3] it has been shown that the lattice model of self-attracting-self-avoiding walks (SASAWs) [4-5] may be used to study the critical behavior of two chemically different interacting polymer chains in a solution which may be of different types (good or poor) for different chain. We reported transition from zipped state to segregated state by varying the solvent quality, the temperature and the interaction between monomers of inter-chain and intra chain. The model proposed by us takes into account of the physical condition that the interaction between monomers is repulsive at short distance and attractive at large distance. The non crossing constraint represents the repulsion, and the attraction between monomers occupying the neighboring lattice site is due to the attractive part of the interaction. This model is termed as two-interacting walks (TIWs) and is solved exactly for truncated n-simplex lattice (n=4,5 and 6) using real space renormalization group calculation. The mean number of monomers $M$ of one chain in contact with the other chain at the vicinity of transition point is expected to behave as [2].

$$M \sim N^y$$  \hspace{1cm} (1)

Where $N$ is the total number of monomers in one chain and $y$ is the contact exponent.

The aim of this letter is to study the influence of chain length distribution. This problem has got considerable attention in past years from experimental and theoretical point of view. Experiments have been done with mixture of polystyrene [10-11] and poly-$\alpha$-methylstyrene [12] and the results were interpreted by various two parameter perturbation theories assuming that polymer coil behaves like the hard sphere. Recent theoretical studies have been devoted to this problem [13-15] and renormalization group analysis showed that chains small in sizes penetrate more compared to the long chain. Deviation to the hard sphere model has already been seen by the experimentalists [10-12] and their argument also lead to the conclusion that the polymers of lower molecular weights penetrate more [10-11]. In another experiment [16] several mixtures of same chemical species with very different sizes, confirms the prediction.

To study the interpenetration of small chains, we consider a grand canonical ensemble of
polymers. By grand canonical we mean, of course, not the number of chains are fluctuating but the number of monomers in the chain are fluctuating i.e. the chain length is fluctuating. The generating function of our interest is

\[
\Omega(x_1, x_2, x_3, u_1, u_2, u_3) = \sum_{\text{all walks}} (x_1^{N_1} u_1^{R_1})(x_2^{N_2} u_2^{R_2})(x_3^{N_3} u_3^{R_3})
\]

(2)

where \(N_1(N_2)\) is the number of steps (monomers) in the polymer \(P_1(P_2)\) and \(x_1(x_2)\) denotes the fugacity weight attached to each step of polymer \(P_1(P_2)\) respectively. Here \(u_1(u_2)\) represents the Boltzmann factor associated with the attractive interaction between monomers of polymer \(P_1(P_2)\). \(x_3\) and \(u_3\) denote, respectively, the fugacity weight attached with zipped walks and the Boltzmann factor associated with the attractive interaction between monomers of \(P_1\) and \(P_2\). \(N_3\) is the total number of zipped steps. \(R_1(R_2)\) is the number of monomers of \(P_1(P_2)\) occupying the nearest neighboring sites of the lattice and \(R_3\) is the number of monomers of different chains occupying the nearest neighbor lattice points. The complete phase diagram with these fugacities is given in [2].

For present study we consider situations in which \(x_1(x_2) < x_1^c(x_2^c)\) and or \(u_1(u_2) < u_1^c(u_2^c)\) such that long chains are exponentially suppressed and the ensemble is dominated by the short chains. We shall use this condition in our further study. The generating function expressed in terms of Eq.(2) for 4-Simplex lattice[1-5] can be represented in terms of restricted partition functions shown in Fig. 1 and their corresponding recursion relations are given below

\[
A_{r+1} = A^2 + 2A^3 + 2A^4 + 4A^3B + 6A^2B^2
\]

(3)

\[
B_{r+1} = A^4 + 4A^3B + 22B^4
\]

(4)

\[
C_{r+1} = C^2 + 2C^3 + 2C^4 + 4C^3D + 6C^2D^2
\]

(5)

\[
D_{r+1} = C^4 + 4C^3D + 22D^4
\]

(6)
\[ E_{r+1} = (AC)^2 + 2ACE(A + C) + 2E^4 + 6E^2(B^2 + D^2) + 4E^3(B + D) \] (7)

Here and below we adopt a notational simplification in which the index \( r \) is dropped from the right hand side of the recursion relations. It may be emphasized here that the recursion relations written above are exact for the model defined above. The recursion relations for \( A \) and \( B \) are independent of \( C, D \) and \( E \) (and \( C \) and \( D \) are independent of \( A, B \) and \( E \)) is the consequence of the definition of the model. This means that the model defined above take care of the criticality of one chain in dilute solution does not get affected in presence of other chain. However, The effect of a polymer chain on other has been taken through intercation mediated by configuration \( E \). Since the interaction between inter chain and or intra chain is restricted to bonds within a first order unit of the fractal lattice, \( u_1, u_2 \) and \( u_3 \) do not appear explicitly in the recursion relations. They appear only in the initial values [4-5] given below:

\[ A_1 = x_1^2 + 2x_1^3u_1 + 2x_1^4u_1^3 \] (8)

\[ B_1 = x_1^4u_1^4 \] (9)

\[ C_1 = x_2^2 + 2x_2^3u_2 + 2x_2^4u_2^3 \] (10)

\[ D_1 = x_2^4u_2^4 \] (11)

\[ E_1 = (x_3u_3)^4 \] (12)

Here index 1 and 2 on the right hand side of Eq.(8-11) correspond to chain \( P_1 \) and \( P_2 \) respectively and \( x_3 = (x_1x_2)^{1/2} \) is the fugacity of zipped walk. The fixed points corresponding to different configurations of polymers in the asymptotic limit are found by solving Eq.(3-4) for polymer chain \( P_1 \) and Eq.(5-6) for polymer chain \( P_2 \) respectively. A complete phase diagram of Eq.(3-4) or Eq.(5-6) is given in [4-5]. The state of polymer chain \( P_1(P_2) \) depends on the quality of the solvent and on the temperature and can therefore be any of three states.
Swollen, Compact globule and at $\Theta$ point described in the asymptotic limit by the fixed points $(A^*, B^*) = (0.4294, 0.0498), (0.0, 22^{-1/3})$ and $(1/3, 1/3)$ respectively. The fixed point corresponding to the swollen state is reached for all values of $u < u_c$ at $x = x_c(u)$. The end to end distance for a chain of $N_1$ monomers of $P_1$ in this state varies as $N_1^{\nu_1}$ with $\nu_1 = 0.6740$ [4-5] and connectivity constant $\mu = 1/x_c$ is found to be 1.5474. The fixed point corresponding to the compact globule state is reached for all values of $u > u_c$ at $x_1 = x_c(u)$. At $u_1 = 3.31607..$ and $x_c = 0.22913..$ the system is found to be at its tri-critical point or $\theta$-point.

We consider a situation in which either one or both chains have fugacity less than their critical value. This represents a state in which a long chain can not exist independently and system is dominated by small chains. It is indicated by $O$ state which corresponds to the fixed point $(A^*, B^*)$ and or $(C^* D^*) = (0.0, 0.0)$. The four independent combinations found in these cases are achieved by considering following conditions. $SO$ represents the situation in which one of the polymer chain is in the swollen state (indicated by $S$) with the condition $x_1 = x_1^c(u_1)$ with $u_1 < u_1^c$ while the other chain is in $O$ state with the condition $x_2 < x_2^c(u_2)$ with $u_2 < u_2^c$. $TO$ corresponds to the situation in which one of the chain is at $\theta$-point with the condition $x_1 = x_1^c(u_1)$ with $u_1 = u_1^c$ and second chain is in $O$ state $(x_2 < x_2^c(u_2)$ with $u_2 < u_2^c)$. $CO$ represents that one of the polymer chain is in collapsed state with the condition $(x_1 = x_1^c(u_1)$ with $u_1 > u_1^c$ while the second one is in $O$ state. $OO$ indicates the situation in which both the chains are at below of their criticality $(x_1 < x_1^c(u_1)$ with $u_1 < u_1^c$ and $x_2 < x_2^c(u_2)$ with $u_2 < u_2^c$).

The four non-trivial fixed points reached by Eq. (7) using Eqs(3-6) are given in table 1. These fixed points are reached by the system when $x_3$ and $u_3$ lie on the curve drawn in Fig. 2. We find that the value of $x_3$ as a function of $u_3$ depends on the states of individual chain. Linearization of Eq.(7) about these fixed points lead to the eigenvalue $\lambda_i > 1$ which gives contact exponent which we list in table 1 by the relation given below[1-3]

$$y = \ln(\lambda_i)/\ln(\lambda_b)$$
where $\lambda_b$ is the largest eigenvalue of the system. The curves between $u_3$ and $x_3$ are continuous without any multicritical point.

For five simplex lattice the polymer chain [5] always remain in the swollen state for all values of intra-chain interaction and hence we have only two possible combinations of chains i.e. SO and OO. The results obtained by these combinations are given in table 2. However for 6-simplex lattice we do find the similar behavior as of 4-simplex lattice. The fixed points corresponding to SO, CO, TO and OO and corresponding contact exponents are given in table 3. The recursion relations and corresponding partition functions may be taken from[4-5] for 5 and 6-simplex lattices. It is interesting to compare our results with experimental observations. We find an unbinding transition from a configuration zipped states of the chain to a state where the chains are segregated. The unbinding transition point is a multicritical point. At this point the monomers of a chain in contact with the monomers of other chain scales with an exponent $y$ and is called the contact exponent.

The value of $y$ listed in table 1 for a single chain surrounded by small chains, exhibits an interesting behavior. As is evident from table 1, 2 and 3 that when one chain is in S-state and other is at O state the exponent $y$ is found to be greater than one. It may be noted here that O state corresponds to the situation in which long chain does not exist and system is dominated by small chain. It may be thought as instead of one chain combining all monomer dissolved in the solution, we may have several small chains. Therefore the monomers of swollen chain will be in contact with several monomers of the small chains, which make the exponent larger than one. This may not be the case when one of the chains is in compact globule or at tricritical state and the other at O state. Most of the monomers of the first chain are occupied by its own monomers and therefore making contact with other monomers of small chain less probable. Hence the contribution will come mostly from the surface of the collapsed polymer. Recent computer simulation with melt polymer have similar behavior where interpenetration is found to be the shape dependent[9]. However, when the polymer chain is at its tri-critical, we find that contact exponent is larger than the compact one. Because in this case, small chain can penetrate.
note that when two chains are in swollen state[1] the contact exponent was found to be 1 indicating that one monomer of a chain is in contact with a monomer of other chain and is in zipped state.

The other interesting feature which is obvious from table 1,2 and 3 is that in a solution in which none of the chain can polymerize on its own (i.e. the chains are individually are in O state but can polymerize in zipped form due to unlike monomer-monomer interaction. We note that this zipped state configuration of two chains in all cases is in compact phase as is evident from eigenvalue listed in table 1,2 and 3. Apart from this in all other cases when chains are in either T or C state, the value of y is found to be less than 1.

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TABLES

**TABLE I.** Fixed point of $E$ state, eigenvalues and contact exponent for 4-simplex lattice

| State of chain | $E_i^*$ | $\lambda_i$ | $\lambda_b$ | $y$   |
|----------------|--------|-------------|-------------|------|
| SO             | 0.7857 | 3.8617      | 2.7965      | 1.3138|
| CO             | 0.5036 | 2.8769      | 4.000       | 0.7622|
| TO             | 0.5231 | 2.9371      | 3.7037      | 0.8228|
| OO             | 0.7937 | 4.000       | —           | —    |

**TABLE II.** Fixed point of $E$ state, eigenvalues and contact exponent for 5-simplex lattice

| State of chain | $E_i^*$ | $\lambda_i$ | $\lambda_b$ | $y$   |
|----------------|--------|-------------|-------------|------|
| SO             | 0.4516 | 3.9809      | 3.1319      | 1.2101|
| OO             | 0.5694 | 4.6308      | —           | —    |

**TABLE III.** Fixed point of $G, H$ and $I_{[4-5]}$ states, eigenvalues and contact exponent for 6-simplex lattice

| State of chain | $G_i^*$ | $H_i^*$ | $I_i^*$ | $\lambda_i$ | $\lambda_b$ | $y$   |
|----------------|--------|--------|--------|-------------|-------------|------|
| SO             | 0.0    | 0.1039 | 0.1049 | 5.9929      | 3.4965      | 1.4304|
| TO             | 0.9628 | 0.0795 | 0.1048 | 5.3050      | 5.4492      | 0.9341|
| CO             | 0.0    | 0.0711 | 0.1050 | 5.057       | 6.00        | 0.9046|
| OO             | 0.0    | 0.1042 | 0.1042 | 6.0         | —           | —    |
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FIGURES

FIG. 1. diagrams representing the five restricted partition functions for two chains (indicated by black($P_1$) and white($P_2$) lines on 4-simplex lattice.

FIG. 2. critical fugacity $x_3$ for entanglement of two chains as a function of $u_3$ in a situation where one or both chains can not grow on their own. Results are shown here for CO and OO states of individual chains. Other configurations SO and TO have values in between these two curves. The letter O indicates a condition in which long chain can not grow and system is dominated by small chains.
