Effect of confinement on coil-globule transition

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Abstract

The equilibrium thermodynamic properties of a linear polymer chain confined to a space between two impenetrable walls (lines) at a distance $D$ under various solvent conditions have been studied using series analysis and exact enumeration technique. We have calculated the end to end distance of polymer chain, which shows a non-monotonic behaviour with inter wall separation $D$. The density distribution profile shows a maxima at a particular value of $(D =) D^*$. Around this $D^*$, our results show that the collapse transition occurs at higher temperature as compared to its bulk value of $2d$ and $3d$. The variation of $\theta$– temperature with $D$ shows a re-entrance behaviour. We also calculate the force of compression exerted by the walls (lines) on the polymer.

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I. INTRODUCTION

In last few years\textsuperscript{1–6} much attention has been paid on the subject of confinement of polymer and its scaling relations. This is due to the fact that a polymer chain in restricted geometries exhibits specific and interesting properties which find application in steric stabilization of colloidal dispersions, thin films, adsorption behaviour of gels, surface coatings, membrane in nano pores etc\textsuperscript{6,7}. Several theoretical and numerical attempts has been made to understand these properties\textsuperscript{1,6,10} A polymer chain is said to be confined when the spacing $D$ between the parallel walls (lines in 2$d$) is less than the average end to end distance $< R_E >$ of the chain. The parallel ($< R_{E||} >$) and perpendicular component ($< R_{E\perp} >$) of $< R_E >$ is expected to behave as\textsuperscript{2,3,4} in 3$d$,

\begin{equation}
< R_{E||} > \sim aN^4 \left( \frac{D}{a} \right)^{1 - \frac{4}{\nu}}
\end{equation}

and

\begin{equation}
< R_{E\perp} > \sim D.
\end{equation}

Where $N$ is the total number of monomers in the chain, $a$ is the lattice parameter and $\nu$ is the end to end distance exponent respectively. When $D$ is greater than $< R_E >$, the effect of confinement on its conformational properties vanishes i.e.

\begin{equation}
< R_{E||} >=< R_{E\perp} > \sim aN^\nu
\end{equation}

The monomer density ($\rho(z)$) profile near the wall is expected to behave as

\begin{equation}
\rho(z) \sim z^{\frac{1}{\nu}}
\end{equation}

here $z$ is the perpendicular distance from the surface. It is assumed that the force exerted by the polymer on the wall is proportional to the monomer density near the wall. It has been shown that\textsuperscript{9}

\begin{equation}
\lim_{z \to 0} k \frac{\rho(z)}{z^{\frac{1}{\nu}}} \sim B \frac{f}{k_BT}
\end{equation}

where $k$ is the non-universal amplitude which relates the end to end distance $< R_E >$ of a polymer to the chain length $N$, $B$ is the universal amplitude ratio, $f$ is the force exerted on the wall due to confinement of the chain and $T$ is the temperature of the system respectively.
Considerable efforts have been made\textsuperscript{1−10} to verify the scaling relations and determine the value of $B$ in two and three dimensions. In a recent simulation by Hsu and Grassberger\textsuperscript{1} much better value of $B(=2.04 \pm 0.04 \text{ (in } 2d) \text{ and } 2.13 \pm 0.11 \text{ (in } 3d))$ has been obtained as compared to the previous Monte Carlo estimates\textsuperscript{2,10}.

The complete phase diagram of surface interacting polymer chain in poor solvent condition has been studied recently\textsuperscript{11,12}. Our aim in this paper is to analyze the effect of geometrical confinement such as the one given by a slit(or strip) on coil-globule transition under good and poor solvent conditions. In any Monte Carlo simulation, and particularly in the study of polymeric system, improper sampling of hyper-space under finite number of steps being considered which some time overlook some of the interesting features of these systems\textsuperscript{11,13}. Keeping this in mind, we have analyzed the partition function through series analysis and exact enumeration technique. We prefer this technique because in this case the complete partition function can be analyzed exactly and the scaling corrections are correctly taken into account by a suitable extrapolation scheme\textsuperscript{13,14}. For the sake of simplicity and comparison with the previous results the walls here have been considered as neutral.

The work is organized as follows; In Section 2, we briefly describe the model and the method. Section 3 deals with the monomer density profile in two and three dimensions where we compare our results with the known results. In Section 4 we study the effect of confinement on the coil-globule transition and establish the phase diagram which shows the reentrance behaviour in three dimensions. The paper ends with the discussion in Section 5.

II. MODEL AND METHOD

We represent a polymer chain by self-avoiding walks (SAWs) on a square ($2d$) and cubic ($3d$) lattices. The polymer chain is confined in between strip of two impenetrable surface of height $D = 0, 1, 2..16$ in case of square lattice and $D = 0, 1, 2..8$ for cubic lattice, respectively. The walk originates from the middle of the surface (kept fixed) and spreads along all possible directions. This ensures that the chain is not affected by the presence of the upper surface for large values of $D$ and one recovers the usual statistics of SAWs. The thermodynamic properties associated with the confined polymer may be obtained from the partition function
which can be written as a sum over all possible configurations confined in distance $D$ i.e.

$$Z_N(D) = \sum_{C_N} C_N(D) x^N$$

(6)

here $x$ is the fugacity associated with each step of the walk and $C_N(D)$ is the number distinct SAWs of $N$ steps confined in width $D$. We have obtained $C_N(D)$ up to $N \leq 28$ in two dimensions (for $D \leq 16$) and $N \leq 19$ (for $D \leq 8$) in three dimensions. In general, it is appropriate to assume that for large $N$,

$$C_N(D) \sim N^{\gamma - 1} \mu(D)^N$$

(7)

here $\mu(D)$ is the connectivity constant of the lattice and $\gamma$ is the associated critical exponent. The value of $\mu(D)$ can be estimated using the ratio method\textsuperscript{13–14} with an associated Neville table. These values are found to be in good agreement with the result obtained by the exact transfer matrix calculation\textsuperscript{15}. The end to end distance exponent $\nu$ may be found using the relation

$$\nu = \frac{\log(<R_N>/<R_{N-2}>)}{\log(N/N - 2)}$$

(8)

where $<R_N>$ is the end to end distance exponent of $N$ steps walk. The values of $\nu = 0.748 \pm 0.002(2d)$ and $0.58 \pm 0.01(3d)$ are in good agreement with the known results in the limit $D \to \infty$. For finite value of $D$, we restore the scaling proposed by Milchev and Binder\textsuperscript{2}. The slopes found for $2d$ and $3d$ for parallel and perpendicular component of end to end distance are in good agreement with Eqs. (1–2) as shown in Figs. (1–2). However,
the variation \(< R_E >\) is non-monotonic with \(D\) as shown in Fig. 3. We find that \(< R_E >\) first decreases with decreasing \(D\) before it starts to rise. This behaviour was ascribed earlier to a lateral squeezing of chains with increasing \(D\), followed by an elongation in the direction parallel to the walls\(^{16-17}\).

FIG. 3: The variation of end to end distance (\(< R_E >\)) of polymer chain for various length with inter wall separation \(D\) for 3d and 2d.

III. MONOMER DENSITY DISTRIBUTIONS

In the present model, one end of the chain is anchored at the middle of one of the walls. Consequently, it introduces asymmetry in the distribution of monomer density in the direction perpendicular to the plane of wall. In earlier simulations\(^1\), the walker has
been allowed to start from any of the planes in between the walls, therefore, the monomer distribution in such case is found to be symmetric. The density distribution of polymer attached to the surface has been shown in Fig. 4 for $2d$ and $3d$. From these figures it is obvious that when the thickness of the strip decreases, the monomer density near the wall increases. In Fig. 5, we show the monomer density for fixed $D$ which increases with $N$, and therefore, is not a finite size effect. In fact the peak shifts away from surface, at which polymer is grafted, as $N$ increases.

The force exerted on the wall is proportional to the monomer density on the surface and may be expressed in terms of the work done by moving one of the surfaces

$$f = - \frac{\partial G}{\partial D} = \frac{k_B T}{\mu} \frac{\partial \mu}{\partial D}.$$  \hspace{1cm} (9)

Using the simple scaling ansatz

$$\rho(z) = \frac{1}{D+1} f_\rho(\xi) = \frac{1}{D+1} A \xi (1 - \xi)^{1/\nu_d}$$  \hspace{1cm} (10)

where $\xi = y/D + 1$ and $\nu_d$ is the end to end distance exponent of $d$ dimension, with $A = 10.38(2d)$ and $18.74(3d)$, as proposed by Hsu and Grassberger\(^1\) we find the value of the
universal amplitude ratio B to be equal to 2.01(2d) and 2.1(3d), respectively. These values are in good agreement with the exact result\textsuperscript{9} and simulations\textsuperscript{1}.

FIG. 5: The density profile with $D$ for different chain length. These figures show that the peak height increases with $N$ but shifts out to larger $D$ as $N$ increases.

IV. EFFECT OF CONFINEMENT ON COIL-GLOBULE PHASE TRANSITION

As confinement affects the monomer density profile, one expects a significant change in the transition point if one varies the distance between the two walls. A square lattice with finite $D$ is essentially an one dimensional system and hence there is no phase transition as such. Keeping this in mind, we study such an effect, on a simple cubic lattice with variable wall thickness $D$. We consider self- attracting-self avoiding walks (SASAWs) and associate energy $-\epsilon_p$ for nearest neighbour monomers which are not chemically bonded. The partition function of the confined chain may be written as

$$Z_N(D,u) = \sum_{N_p} C_{N,N_p}(D)u^{N_p}$$

where $u$ is the Boltzmann weight defined as $u = e^{-\epsilon_p/\beta kT}$ and $N_p$ is the number of pairs of monomer of chain length $N$. $C_{N,N_p}(D)$ is the number of distinct configurations with $N_p$
number of nearest neighbour pairs confined between the walls at distance \( D \). The reduced free energy can be written as

\[
G(D, u) = \lim_{N \to \infty} \frac{1}{N} \log Z_N(D, u) = \log[\mu(D, u)].
\] (12)

To characterize conformational change in the system, we study specific heat defined as \( C_v = \partial^2 G / \partial \epsilon_p^2 \) as a function of temperature. The peak in the \( C_v - T \) diagram has been identified as a sudden change in conformation. Such changes in heat capacity in a narrow temperature range are due to large fluctuations in energy. Studying the distribution of end to end distance in this region we identify such transition as Coil - Globule transition. Of course, a sharp transition of a single chain occurs in the limit \( N \to \infty \) only, and hence the accuracy of the extrapolation in Eq. 12 is crucial. In the limit \( D \to \infty \), we find \( u_c = 1.93 \) and 1.76 for 2\( d \) and 3\( d \), respectively. These values are in good agreement with earlier results\(^{18-20}\). The variation of \( u_c \), with \( D \) has been shown in Fig. (6) which shows a re-entrance behaviour.
It can be seen from Fig. (6) that at a fixed value of monomer-monomer attraction with a change of inter wall separation $D$, a polymer which was initially in the coil phase goes into the globule phase. With further increase of $D$ the polymer again attains the coil phase.

V. CONCLUSIONS

In this paper, we have studied the effect of confinement on the equilibrium thermodynamic properties of a linear polymer chain in various solvent conditions. The scaling relations found by us for $< R_{||} >$ and $< R_{\perp} >$ are in agreement with earlier predictions. We show that due to the confinement, the end-to-end distance, $< R_{E\perp} >$ varies non-monotonically with inter-wall separation $D$. This is also reflected in variation of monomer density with maxima at particular $D^*$. In this region the number of non-bonded nearest neighbours increases due to confinement and hence there is a rise in the transition temperature (i.e. decrease in $u_c$) as shown in Fig. (6). The re-entrant behaviour can also be seen from Fig. (6). It has

![Graph 1](image1.png)

**FIG. 7:** The variation of force exerted by confining walls on per monomer of the polymer chain with $D$.

been observed that for a given value of monomer-monomer attraction a polymer which was initially in the coil phase goes into the globule phase due to the rise in nearest neighbour
pairs due to confinement at the particular $D^*$. With further increase or decrease of the wall’s separation $D$, the number of these pairs decreases and hence the polymer acquires the coil phase.

We also studied this effect on a square lattice with finite $D$. We do find a peak in the specific heat which signals that the system has a tendency to be in the ordered state, but this tendency will only turn into a phase transition when the slit width diverges i.e. $D > N^\nu$.

It is interesting to see the variation of force exerted by the confining wall with $D$ in Fig. (7). It is qualitatively similar to the one obtained in a simulation$^{10}$, in which the force has been applied by atomic force microscope tip on polymer chain attached to the surface. In such a case it has been found that polymer escapes from an approaching AFM tip (finite surface) by forming a stretched tether$^{10}$. Since in our work the surface has been considered as an infinite plane, ”escape transition” is not possible. However, the work with a finite surface of specific geometry is in progress.

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