THE STATISTICS OF POLYMER CHAINS IN RANDOM MEDIA AND THEIR ADSORPTION ON A RANDOM SURFACE

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CERTIFICATE

This is to certify that the thesis bound herewith is an authentic record of research work carried out by the author under my supervision, in partial fulfillment of the requirements for the degree of Doctor of Philosophy of Cochin University of Science and Technology, and further that no part thereof has been presented before for any other degree.

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PREFACE

The work presented in this thesis was carried out at the Department of Applied Chemistry, Cochin University of Science and Technology, Cochin, Kerala. It is a theoretical investigation of polymer chains in quenched random media and their adsorption on chemically random surfaces.

Statistics of polymer chains in random media has been a subject of great theoretical interest because of their importance in a wide variety of phenomena such as exclusion chromatography, diffusion in porous media, transport across membranes, viscoelasticity of polymer solutions etc. The statistical behaviour of polymer chains in random media and their adsorption on random surfaces has been investigated both experimentally and theoretically [1,2].

The evaluation of statistical mechanical quantities for polymer molecule in solution or in melt is a tough many-body problem. Due to the free rotation about the single bonds in a single polymer chain, usually they have a large number of available conformations. Therefore a complete description of the conformational statistics of a polymer chain is becomes extremely difficult. There are powerful mathematical techniques, such as the 'path integral techniques' [3] by which such many body problems could be handled. Functional integrals and the techniques of many body theory were first applied to polymers in the pioneering work of S.F. Edwards [4]. Using the path integral approach, it is possible to estimate the probability of finding a particular chain conformation and hence the thermodynamic properties of the polymer chain. The relation between the path integral formulation for the distribution functions of polymer chains and the general concepts of the theories of Brownian motion and the random walks are also very interesting. This problem is interesting because of its analogy to the binding of an electron to a potential well.

There have been many theoretical attempts to find the average end-to-end vector distribution (the size) of a Guassian chain trapped in a random medium using the variational approach for estimating path integrals [3]. Related, interesting problem is the adsorption of polymers on random surfaces. The basic criterion of adsorption of polymer chains is the competition between the gain in potential energy obtained by the monomers by binding to the attractive surface and the loss in chain entropy associated with the reduction in the number of possible chain conformations of the adsorbed chains when compared to the free chains. Most theoretical attempts on adsorption of polymers have focused on the adsorption on a planar, uniform surface [5]. There have been investigations on both physically and chemically random surfaces [6]. Chemical and physical roughness are expected to show distinctive effects on adsorbed polymers.

The work embodied in this thesis is an investigation of the statistics of polymer chains in random media and their adsorption on a planar, but chemically random surface, and is based on the variational path integral approach [3] and the replica formalism [7].

Chapter I gives an overview of the study of polymers in disordered media. This chapter summarizes various theoretical treatments such as scaling theories, renormalization group techniques, numerical simulations etc. that have been carried out in the past to investigate the size of polymer chains in a random medium. Behaviour of polymer chains in both quenched and annealed random media are also discussed.

A review of adsorption of polymers on various types of surfaces (both regular and random) is presented in Chapter II. Results of the theoretical investigations, done in the past regarding the problem of adsorption of polymer chains on a planar and uniform, planar but chemically random, spherical, cylindrical and physically random surfaces, with differing extents of roughness, are discussed with special reference to the various theoretical investigations into adsorption on random surfaces. This chapter also outline results of numerical simulations on the adsorption on a corrugated surface.

In Chapter III the theoretical investigation that has been carried out on the statistics of polymer chains in random media is discussed. The Chapter gives an outline of the replica theory, used in the calculation, which was originally developed by Edwards [7] to study the amorphous materials and the variational formulation of the problem. A simple model of a flexible polymer chain in quenched random media, where the obstacles to polymer chain are kept fixed is considered. The difficulty that one encounters while treating the quenched randomness around the polymer chain is the averaging of the logarithm of the partition function over the disorder. The replica method employed in this investigation enables one to perform this averaging. The investigation which include the study of behaviour of polymer chain with randomness and the determination of the size of the polymer chain are discussed in detail in this chapter.

In Chapter IV the adsorption of polymer chains on a planar random surface is discussed with special emphasis on the de Gennes'approach for the study of adsorption on planar surfaces. It uses the variational path integral approach, to study the problem. It discuss in detail the behaviour of the adsorbed polymer in terms of the thickness of the adsorbed polymer on the random surface and the size of the polymer chain in the directions parallel to the surface.

Finally in Chapter V of the thesis, we give a brief summary of the results of our investigations.

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CHAPTER - I

POLYMER MOLECULES IN DISORDERED MEDIA

I.1. PATH INTEGRAL APPROACH TO POLYMER PROBLEMS

It is well known [1-3] that due to free rotation about the single bonds in a polymer chain, it can have an infinite number of conformations. In order to calculate the thermodynamic properties of the chain molecules, it becomes essential to calculate the probability distribution for the end-to-end vector for the chain. This can be evaluated exactly only for a few idealized models. Thus one encounters difficulty in completely describing the conformational statistics of the polymer chain, which is essentially a many body problem. The path integral approach is an elegant way of attacking such problems.

A polymer chain is composed of monomers joined together by single bonds. But if one makes use of the limit in which the polymer chain becomes a continuous one, one can make use of the mathematical analogies between polymers and other many body problems in chemical physics. For example, one can think of the polymer chain as being analogous to the path followed by a Brownian particle. This leads to the introduction of functional or path integral techniques [4,5] for the study of statistical mechanics of polymeric systems.

The path integral techniques were first applied to the polymer problems by Edwards [6], who studied the conformational probabilities of polymer chains in thermodynamic equilibrium. One of the first problems to be treated by these methods was the excluded volume problem [6,7], which arises from the fact that two different constituent atoms of a polymer chain cannot occupy the same region of space (See Yamakawa [8] for a review of theoretical approaches to the excluded volume problem). It has also been applied to polymer chains in random media [9], stiff chains [10] etc.

The basic idea of the path integral approach is the following. If we consider a particle executing Brownian motion, the path that it follows is analogous to the conformations of a polymer chain. One imagines a Brownian particle, starting at the origin at the time $\vec{0}$ and tries to calculate the probability density of finding the particle at a position $\vec{R}$ at time T_f. This probability or propagator is usually denoted as $P(\vec{R},T_f|\vec{0},0)$. The Brownian particle is free to move along any continuous path which satisfy the conditions $\vec{r}(0)=\vec{0}$ and $\vec{r}(T_f)=\vec{R}$. The particle can take an infinite number of paths, analogous to the the polymer chain which can have an infinite number of conformations. Of these paths some will be more probable than all the others and the probability density $P(\vec{R},T_f|\vec{0},0)$, has contribution from all paths.

In the path integral representation $P(\vec{R},T_f|\vec{0},0)$ is given by

$$P(\vec{R},T_f|0,0) = \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(t_f)=\vec{R}} D\vec{r}(t)\ e^{-S[\vec{r}(t)]} \tag{1}$$

where $S[\vec{r}(t)]$ is referred to as 'Action' or 'Hamiltonian'. $\int Dr(t)$ stands for summing over the infinite number of paths. For a free chain, the action is given by

$$S[r(t)] = \frac{3}{2l} \int_0^N ds \left[\frac{d\vec{r}(s)}{ds}\right]^2 \tag{2}$$

where N is the contour length of the polymer chain and l is the effective bond length between monomers in the chain. It is often referred to as the Kuhn effective step length.

One can do a path integral formulation of the polymer conformations by heuristically introducing the concepts of the Brownian motion. For that first of all, one has to consider a continuous chain representation for the polymer chain in which the rigid bonds are replaced by fuzzy effective bonds. The end to end vector distribution in such a case will be Gaussian. If we consider a polymer chain with one end at the origin and the other at $\vec{R}$, then the end-vector distribution is given by the path integral,

$$P(\vec{R},N;\vec{0},0) = \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{R}} D\vec{r}(s)\exp\{-[S[\vec{r}(s)]]\}. \tag{3}$$

I.2. POLYMERS IN DISORDERED MEDIA - AN INTRODUCTION

The study of polymer chains in random media has practical applications in important fields like transport across membranes, gel permeation chromatography, diffusion in porous media, viscoelasticity of polymer solutions, oil recovery etc. A large number of experiments have been performed in this field [11-27]. Moreover, the statistical properties of a polymer chain surrounded by a random medium is potentially relevant in the study of adsorption of polymers on random surfaces, in chromatography and also in the growth of an interface.

The randomness can be either quenched or annealed. In the case of quenched randomness, the obstacles to the polymer chain are fixed at their locations so that they are immobile whereas in the annealed case, they are mobile. Trapped polymer chains in a random medium is relevant to a large variety of technologies [17-25]. Most of the experiments have concentrated on the transport of polymers through porous media.

The experiments are of fundamental interest for testing the scaling arguments developed for polymer solutions [28]. There have been a large number of experiments performed for measuring the diffusion constants of flexible polymers in porous materials [18,24,25]. One of the goals of these experiments is to relate the measurements to the size characteristics of the polymer as well as to the parameters of the porous material such as porosity and permeability [12,13].

Many theoretical and experimental studies have indicated that the transport of macromolecules in solution in a porous medium is less efficient than the unrestricted transport in an unbound solution (i. e., in the absence of porous structure). This reduced efficiency is referred to as hindered or restricted transport [20] and was first pointed out by Renkin [29]. Bohrer *et al.* [20] have studied the hindered diffusion of dextran and ficoll in microporous membranes.

Theories based on scaling concepts and continuum hydrodynamics have been useful [28,30-36], for some of these experiments, such as transport of polymers through membranes where pore sizes are well characterized. However, for porous media whose microscopic characterization is difficult, it is more difficult to obtain simple theories that can be used to study the properties of polymers trapped in such media.

The characterization of pore structures by experimental techniques is extremely difficult. This makes the analysis of the data and the use of theory to interpret them, complicated. Experimental studies using scanning electron microscopy on a variety of sandstones have suggested that pore structures are fractals [37] having dimensions ranging from 2.57-2.87.

Thus the experimental situations described above regarding the polymer chain in a random medium are extremely complex and mean field theories [23,28,29,38] have been proposed and a few computer simulations [39-43] has been performed to mimic the experimental situation using well characterized models. The statistical properties of polymer chains in quenched random media have recently attracted renewed interest [9,39-64] due to their importance in science and technology.

I.3. SELF AVOIDING WALKS ON A RANDOMLY QUENCHED LATTICE

The statistical mechanics of macromolecules has benefited much from their analogy with the problem of a random walker [28,65]. The statistics of linear polymer chains in random media has been studied with great interest, employing a model having self avoiding walks (SAW) on randomly bond dilute (quenched) lattices [50-64,66-68], leading to conflicting conclusions. SAW are very good models for polymer chains [28,65]. Such a walk consists of N+1 monomers, connected by N bonds of equal length l. The monomers are not allowed to intersect. The major quantities of interest in such a problem are the mean square radius $\langle \vec{R}^2 \rangle$ and the radius of gyration $\langle \vec{R}_{gyr}^{\,2} \rangle$ of the polymer chain. For very long chains ($N \to \infty$), it is well known that,

$$\langle \vec{R}^{\,2} \rangle \propto N^{2\nu} \text{ and } \langle \vec{R}_{gyr}^{\,2} \rangle \propto N^{2\nu},$$

where ν is a universal exponent.

A very good estimate for ν is given by Flory's mean field formula [28], which gives $\nu=3/(2+d)$, where d is the dimensionality of the system. if d = 3, the above predicts a value of 0.60, while new calculations based on scaling and renormalization concepts give a slightly lower value : $\nu \approx 0.59$ [59,60]. Kremer [53] has performed a Monte Carlo study of SAW on randomly diluted lattice and found that the exponent ν does not change by dilution and $\nu=0.59$ as in the undiluted case, in contrast to the original conclusion of Chakrabarti and Kertesz [51]. Based on renormalization group ideas, they [51] proposed that $\nu=1/2$ for SAW on dilute lattices and that the dilutions are meaningful only up to the percolation threshold [69]. However it was pointed out that their [51] original treatment is inconclusive.

Kremer's result [53] was not in agreement with the Harris criterion [70] (This suggest that the critical behaviour of random magnetic systems depend upon the specific heat exponent α of the pure system. If α is positive, then the phenomenon exhibited by the random system differs from those of the pure system ; otherwise the randomness is irrelevant. Harris criterion could be applied heuristically to the problem of polymer in quenched random media. Thus one expects that ν for a self avoiding polymer in a quenched random medium should be different from that for a polymer in a regular medium). Kremer [53] found a higher exponent at the percolation threshold of the lattice, $\nu=2/3$.

A scaling form of the crossover between these exponents near the percolation threshold is also proposed and is found to be consistent with the Monte Carlo results. There have been other investigations [56] which is based on computer simulations to study the statistics of the SAW. It was found that [56] the critical behaviour remained unchanged below a certain dilution and a cross over to a higher order critical behaviour occurs beyond that point.

A rigorous analysis of the problem was made by Harris [52] who studied it directly and also by the use of replica formalism [71-73]. He showed that dilution does not affect the exponents and a careful use of Harris criterion [70] also leads to the same conclusion. The statistics of the SAW in the presence of dilution is found to be the same as that in the undiluted case and therefore it is found that no modification is needed even for concentrations near the percolation threshold.

This result [52] has been supported partially by the field theoretical renormalization group study of SAW on a random lattice carried out by Kim [54]. Using the replica trick, he [54] noted that there is some sort of instability of the system as randomness grows beyond a certain limit. This has also been proved by other investigations [50,58]. Rammal *et al.* [56] gave arguments for a change of the exponent ν at the percolation threshold.

Derrida [58] had argued that a change in all the statistics of the SAW should occur for any amount of disorder. Nadal and Vannimenus [57] considered a directed SAW on a dilute lattice, using various approaches. They found that for any amount of disorder, the mean value for the number of directed SAW is different from its most probable value. There have been a few recent investigations on SAW [66-68] on random lattices. The results of Lee and Nakanishi [66] suggests that the exponent ν

will remain unchanged even at the percolation threshold. But Monte Carlo calculations by Grassberger [68] found that $\langle \vec{R}^2 \rangle$ scale with a new, larger exponent.

Baumgärtner and Chakrabarti [74] recently investigated the problem of polymer chains in annealed random media using Monte Carlo methods. Their observations strongly lead to the conclusion that any amount of unconstrained annealed impurities do not affect the critical behaviour of strict self avoiding polymer chains, as observed originally by Harris [52], due to the cancellation of the disorder effects on the average polymer size. They also found that the treatment made earlier [52] have been wrongly applied to the quenched disorder case. With weaker self-avoidance they found an influence of annealed impurities on the configurational properties of the polymer chain. Their observations are in disagreement with the theoretical investigations, which indicated a tricritical theta point and collapse behaviour [75] for polymer chains in a random medium with annealed impurities, whereas it is in agreement with the early conjecture [70].

There have been several theoretical investigations on the problem of a polymer chain in random media [23,28-64,76-90]. Most of them have concentrated on the study of diffusion and transport of a polymer chain in porous media [23,44,48,86,90].

I.4. POLYMER CHAIN IN POROUS MEDIA

Diffusion of polymers through porous media controls a wide variety of experiments such as gel permeation chromatography, membrane separations etc. Experiments have been carried out on the transport of polymers into pieces of porous glass [15-17]. Porous media have in general very complicated, random interconnected pore structures [12,37,94]. In fact the experimental situations involving such media are extremely complex.

Porous media are the best realizations of quenched random media. The diffusion of a single structureless particle in such media has been extensively studied using the `ant in the labyrinth' model [69,91-93]. It has been suggested that the pore structures in a wide variety of porous media are fractals [94]. It is possible to deduce the structure of the porous media by experimentally [95] monitoring the diffusional behaviour of a particle present in the material.

The model problem of an isolated, flexible macromolecule in a quenched random environment has been suggested as a caricature for experimental situations like polymer molecule trapped in porous media. There have been several theoretical investigations focusing on the static and dynamic properties of polymer molecules in random porous media [9,44,86,87,96,97]. For a review on polymer molecules in disordered porous solids see Ref [45]. From the theoretical point of view, Casassa [23,27] was the first to calculate the partition coefficient (i.e., the ratio of the solute concentration inside the pore to the solute concentration outside) for both flexible chains and rigid rods, from a statistical analysis of the chain conformations. For an ideal polymer chain trapped in a pore, the entropy and all related thermodynamic properties have also been discussed.

Taking advantage of the scaling approach for polymer solutions [28], Daoud and de Gennes [48] have investigated the conformations of large flexible polymer chains in good solvent trapped in to small cylindrical pores as a function of polymer concentration. They have taken into account the repulsive interactions between the monomers (i.e., excluded volume interactions), by a scaling approach which goes beyond the usual Flory-Huggins approach [28]. But their [48] results were found to be weak, because of the lack of precise numerical coefficients.

Daoudi and Brochard [33] have later evaluated the partition coefficient both in the dilute regime and in the high concentration regime where the chains become highly entangled inside the pore. Also, de Gennes and Brochard [30,32] have calculated the diffusion coefficient of isolated chains inside a cylindrical pore and Daoudi and Brochard [33] have studied the transport under low concentration. Both approaches, static and dynamic, predicted that large flexible polymer chains penetrate small pores much more easily when the concentration is increased. Available experimental data [16] were in good qualitative agreement with this prediction, but quantitative comparisons were difficult to make because of the difficulties with the experiments such as polydispersity of the experimental sample.

There has been a scaling approach based on Flory-Huggins theory carried out by Daoud *et al.* [90]. But several experimental systems showed deviations from this theory. For a single ideal chain trapped in a pore, the theory due to Casassa [23], explains the behaviour very well. It was Daoud and de Gennes [48] who did [90] the rigorous calculation of the same, including the repulsive excluded volume interactions between the monomers, which are very important in practice. They have considered both dilute solutions, where different chains do not overlap, and semi-dilute solutions where there is a significant overlap.

In their calculations, they [48] have considered, the close relation that exists between polymer statistics and magnetic phase transitions [98]. In fact there exist an abundant theoretical literature on magnetic transitions in systems of restricted dimensionality [99]. However, it is found that only a small fraction of this work can be transposed immediately to the polymer problem [48].

Baumgärtner and Muthukumar (BM) [44] have performed a Monte Carlo simulation to study the behaviour of polymer chains in porous media. They [44] have introduced a very simple, but well defined model for a system of polymer in quenched random media. The model describes the polymer as consisting of a Gaussian chain in a medium where a large number of obstacles are frozen at random locations. de Gennes [28,100] has used exactly the same model [100] for proposing the reptation dynamics, for describing the diffusional behaviour of polymer chains in polymer melts. These authors [44] have also attempted to study the predictions of the reptation model and of the experimental results.

Dynamic and static properties of such a polymer chain without excluded volume, which performs Brownian motion between randomly distributed impenetrable fixed obstacles have been simulated and the results [44] were analyzed using scaling arguments [28].

BM [44] modeled the solid phase of the porous medium by the site percolation algorithm [69]. In their simulation a given volume was divided into a large number of equivolume cells. A known fraction of these cells were randomly occupied by the obstacles using this algorithm. The obstacles are frozen in their positions. Taking the cells unoccupied by the obstacles to constitute a continuum, a Gaussian chain was introduced. New chain conformations were created using the kink-jump technique, subject to the constraint that the chain segments can not occupy the cells of the obstacles. Both the equilibrium and dynamic properties of the chain were followed by averaging over the chain conformations and the conformations of the random medium for different chain lengths and densities of the obstacles.

BM [44] found that the equilibrium size of the chain is smaller than that in the absence of the obstacles and that the radius of gyration of the chain shrinks to a size independent of the chain length. They found a crossover from random coil to "collapsed" chain configurations as the impurity concentration is increased. This phenomenon was attributed to the effects of both, the lack of self-excluded volume and the presence of an effective self attractive potential arising from random repulsion between the polymer and the solid particles of the medium. For the idealized random walk model that they considered, the limiting collapsed chain dimensions are found to be independent of the chain length and dependent in a universal way on the impurity concentration. They have also analyzed the molecular weight dependence of various quantities such as diffusion coefficient, relaxation time, and radius of gyration etc. using scaling arguments.

It is well known that the chain dynamics can be adequately described by the Rouse Model [101] when the medium contains only one chain free from any solid particles. For this model, the diffusion coefficient of the center of mass of the chain D and the chain relaxation time τ depend on the chain length N according to $D \sim N^{-1}$ and $\tau \sim N^{2}$. The mean square displacement of a single monomer $r^{2}(t)$, relative to the position of the center of mass of the chain depends on time t (for times smaller than the configurational relaxation time τ) scales as $r^{2}(t) \sim t^{1/2}$. Recently there has been an experimental check [102] on the reptation arguments, by following polymer diffusion over small distances, using Neutron reflectometry and nuclear reaction analysis. The results were in excellent agreement with the reptation model.

For the entangled polymer chains it is found that [38,40] $D \sim N^{-2}$, $\tau \sim N^{3}$ and $r^{2}(t) \sim t^{1/4}$ (for $t < \tau$). If a polymer chain is confined inside a tube or slit-like pores

[30,34], eg. in nuclepore filters [30,34] and entanglements with different chains are negligible, then the chain dynamics is again altered.

In this problem BM [44] have found very strong dependence of D on N. They found that D $\sim$ $N^{-2.9\pm0.3}$ and $\tau \sim N^{4\pm0.4}$. Furthermore the mean square displacement of a single bead does not scale as $t^{1/4}$. Therefore it is clear that reptation is absent in this problem, where the solid particles are randomly distributed. This observed absence of the reptation dynamics has to be contrasted with the case where the particles are arranged in a regular array. In the case where the obstacles arranged in a regular fashion reptation dynamics has been observed.

Therefore, their investigations clearly indicate that the regular and random medium attribute different dynamical features to the chain. It is interesting to note that even the equilibrium properties of the chain are different in regular and random media. The chain shows shrinkage in random media. The diffusion in a random porous medium is slower due to the presence of randomly distributed bottlenecks [44]. The polymer chain is forced to squeeze through narrow channels to occupy positions which are entropically favourable. The entropic barrier arising from such bottlenecks slows down the dynamics significantly. Therefore, the N dependence of D is much stronger in the random medium than in the case of a regular one.

Dynamic properties of a self avoiding chain which performs Brownian motion between randomly distributed impenetrable fixed obstacles were also investigated by Monte Carlo simulations [46] by BM. The chain dynamics was found to be slower than even the reptation dynamics analogous to the case of a random walk.

They have also performed a Monte Carlo simulation on the dynamics of polymer chains in random media [47]. The investigations revealed three distinct regimes for the time evolution of the mean square displacement of the center of mass of the chains. Classical diffusion occurred in the early and late time regimes. The duration of the intermediate crossover regime was longer as the chain length increased and the statistical porosity of the lattice decreased. In this case also the data did not support the reptation theory.

There has been a theoretical investigation of the role of quenched random impurities in the statistical behaviour of polymer chains by Douglas [83] whose results were in excellent agreement with the simulations of BM [44]. He performed a simple dimensional analysis to discuss the relevance of impurity interactions on the molecular dimensions of flexible polymers in the limit of high and low impurity densities. Scaling arguments proposed by him [83] account for the universal behaviour of static properties observed (for eg. the collapse transition) by BM [44] in their Monte Carlo simulations. He introduced an approximate model of the random impurity interaction by considering the random impurities as being analogous to an "effective surface" with which the polymer interacts.

A close quantum mechanical analog of this problem is the scattering of an electron in an array of randomly distributed impurity centers. This has been studied extensively for the last thirty five years and can be translated with little variation to the polymer problem [103]. The polymer collapse transition due to impurities in a quantum mechanical context corresponds to a change from a free electron state to a localized state with increasing impurity concentration. It was de Gennes [104] who first noted the connection between the electron localization and the localization of a network chain in rubber. He also proposed the "tube model" for such localized chains.

Calculations by Edwards [7] indicate that such a transition occurs because, the randomly distributed impurities generate a net attraction, resulting in the localization of the polymer chain. BM [44] give the same interpretation to the polymer collapse. Edwards [7] and Touless[105] also noted the close analogy between electron localization and polymer collapse due to binary self-attractive excluded volume interactions.

These studies, which deal with effective interactions generated by the random density fluctuations in the medium surrounding the polymer provides a new perspective for understanding some of the most basic polymer solution properties. It was experimentally noted by Chu *et al.* [106] that many polymers exhibited two critical solution temperatures, upper and lower, above and below which the chain undergoes gradual contraction. It is difficult to understand on the basis of the usual two parameter model of excluded volume [8], why polymers frequently exhibit an upper critical solution temperature above which the molecular dimensions of the chain begins to contract.

Douglas [83] has considered the density fluctuations of the solvent as being impurities whose density grows with temperature (i.e., as critical point of the pure solvent is reached), and assumed the polymer collapse with increasing temperature as a kind of localization transition due to random impurities. But such a situation will correspond to collapse in an annealed random medium.

A two dimensional analog of the model put forward by BM [44], has been recently simulated by Chandler *et al.* [43]. They performed a Monte Carlo simulation for two dimensional freely jointed polymers, without excluded volume interaction, in equilibrium with a quenched random lattice of obstacles. The equivalent problem of random walks in a field of random traps has been extensively studied for the model on a lattice [107].

Their calculation [43] exploits an equivalence between the quenched and annealed averages valid when the polymer may equilibrate to the quenched material (i.e., a polymer is free to wander in an infinite volume). In addition to the obstacle density there are two additional parameters in the problem ; the obstacle side length 'a' and the polymer step length 'l'. Their calculations begin to exhibit standard Flory-Lifshitz scaling [87] only at extremely large values of monomer polymer units, N. For some choices of the parameters, a non-universal, inverted behaviour is found. This behaviour includes a nonmonotonic mean-square end-to-end length $\vec{R}^2$ as a function of N.

There are many theoretical and experimental investigations on the transport of polymer through small pores. Useful static and hydrodynamic theories of macromolecular transport in small pores have been developed by several authors [30,31] and scaling concepts have been used to study the same [23,28].

Transport of macromolecules in porous media has been recently investigated by Sahimi [85]. He has developed three models for flow and diffusion of macromolecules in a porous medium. The first model is fully deterministic and is exact for a given pore space and molecular configurations. The second model is stochastic in which the macromolecule execute a random walk in the pore space. The third model is based on an effective medium approximation. The porous medium is represented by a two or three dimensional network of interconnected cylindrical pores and the macromolecules are represented by hard spheres of a given hydrodynamic radius.There has been a recent investigation on the diffusion of polymer chains in disordered media performed by the renormalization group (RG) techniques [108]. Below the critical dimension of disorder, anomalous diffusion occurred and the polymer chain followed the diffusion of a Brownian particle. The results of the RG study of the anomalous diffusion below the critical dimension were used to compute the renormalization diffusion constant above the critical dimension.

A theory of the dynamics of a semi rigid polymer molecule in a porous medium has been recently formulated [109] on the basis of reptation theory. More recently Panyukov [110] has derived a theory for localized states of polymer chains.

I.5. VARIATIONAL REPLICA THEORY CALCULATIONS

The analytical treatment of the effect of quenched impurities on chain statistics is a difficult problem due to the necessity of averaging the logarithm of the partition function of the system over the disorder. This has been performed recently by Edwards and Muthukumar (EM) [9] using the replica formalism [71-73] and by the variational formulation of path integration [4,5]. This formalism has been extensively used in the study of amorphous materials. For example, it is used in the calculation of the order parameter for spin glasses [111] (Spin glasses are dilute magnetic alloys). The mean field theory for spin glasses has been obtained in the framework of replica approach [112]. These studies revealed that replica theory could be used effectively whenever there is problem of averaging over quenched disorder. One can find reviews on disordered systems in Ref. [113] where this formalism has been used extensively.

EM have [9] investigated the equilibrium behaviour of a Gaussian chain trapped inside a quenched random medium. They have given an analytical derivation of the size of the polymer chain. It has been suggested [9] that the effect of localization of a polymer (in a region where the attractive potential between the monomers is strongest) can be mimicked by using a harmonic potential. With this in mind, a variational estimate of the free energy for this problem was made by them. The variational method introduced by Edwards for handling the complex problem of the interacting replica theory is quite powerful. They have made use of the same to compute the size, $\langle \vec{R}^2 \rangle$, for the polymer in a quenched random medium.

It is found that, for long Gaussian chain in three dimensions, the mean square end-to-end vector is proportional to $(u\rho_o)^{-2}$, where $u\rho_o$ is the scattering power of the medium ; ρ_o is the number of density scatterers and u is the strength of the pseudopotential between the chain segments. They [9] showed that a long chain gets localized for sufficiently high impurity density ν and that the radius of gyration of the chain in the localized state is proportional to $\nu^{-1/4-d}$ in space dimensions d=2 and d=3. They have been able to show that in the asymptotic regime of long chain lengths and high density of obstacles the chain assumes, in three dimensions an average radius which is inversely proportional to the obstacle density and is independent of its length.

A simple extrapolation formula was found for the size at intermediate values of $(u\rho_o)^2$. It is found that

$$\langle \vec{R}^2 \rangle = (Nl/z)\,[1-\exp(-z)], \qquad (4)$$

where N is the chain length, l is the Kuhn step length, and $z = \varepsilon u^2 \rho_o^2 N l^5$ with ε being a numerical coefficient. When the obstacle density is sufficiently high to allow the empty space to be below its percolation threshold [69], they found that the chain will get trapped in one of the "islands" of empty space and the chain size is then determined by the size of the island [9].

These results of replica calculation were in excellent agreement with the simulation results of BM [44]. They found that this problem differs from the Anderson problem of a random walker in random potentials [69,91,114]. In the Anderson problem it is well known that the mean square displacement of the particle is proportional to the time for asymptotically long times if ρ is above the percolation threshold. Since the trajectory of a random walker is the same as the Gaussian chain in the absence of impurities, one expects this equivalence to be valid even in the presence of impurities. Thus one expects $\langle\vec{R}^{\,2}\rangle$ to be proportional to the chain length, $\langle\vec{R}^{\,2}\rangle \sim N$, for asymptotically long chains. But their [9] results were quite different.

They have also elucidated the difference between the quenched and annealed situations. The problem of polymer in an annealed state where the obstacles are mobile, is easier and is well understood [74,75,115-118].

There have been some analytical investigations on the problem of a polymer in a quenched random medium with excluded volume effects [88], using the replica formalism [71-73] and Feynman's variational procedure for calculating the free energy of the chain [4,5]. Muthukumar [88] has calculated the size of such a chain with excluded volume interactions. He [88] has encountered the general phenomenon of shrinkage of the size of the polymer chain as the density of the impurities is increased.

He has also studied the consequences of the two-body and three-body interactions, long-range interactions, and the dimensionalities of both the object and the embedding space on the collapse of the object. He has demonstrated that the collapse of a polymeric system in a quenched random medium is a general phenomenon due to the screening of the potential interactions between monomers by the impurities. When the impurity density is increased, the polymer chain is found to attain a theta state with Gaussian statistics and then the excluded volume effects were found to be screened.

The static properties of a polymer molecule in a porous medium has been recently investigated by Honeycut and Thirumalai [86], who simulated the problem using a site percolation model [69] in which various sites are occupied randomly. Using a combination of scaling concepts, generalized Flory arguments, computer simulations, and an approximate variational theory based on replica formalism [9], they have investigated a number of interesting static properties of polymers in random media. Effects of excluded volume interactions have also been studied.

For the polymer chain in random media they have argued that the density fluctuations leading to spatial inhomogeneity are responsible for the localization of the polymer in obstacle free regions. They have shown that the variational replica theory developed by EM [9] gives reasonable qualitative predictions of a number of properties of Gaussian chains in random media, but breaks down in the details of its predictions.

Using a generalized Flory theory, they have been able to predict the scaling of $\langle \vec{R}^{\,2} \rangle$ with N, when the effective attractive interaction induced by the random medium is strong enough. It is shown that when the strength of the disorder is large enough, the mean square end-to-end vector scales as $N^{2\nu}$, where N is the number of links in the chain and $\nu = 1/(d+2)$ a value different from that for a free chain. Under these conditions the polymer was found to assume a compact, globule like conformation, due to shrinkage compared to the obstacle free case for which $\nu = 1/2$.

This prediction is in contradiction with the variational replica theory. For the polymer with excluded volume interactions, they found that when the disorder is strong enough to cause substantial shrinkage of the polymer, then $\nu = 1/d$. The chain with excluded volume interactions is shrunk in the random media where as it is found to be slightly stretched in the regular media. But for sufficiently weak interactions, they confirmed using simulations that ν is unaffected by the presence of the disorder and retains the value of $\nu = 3/(d+2)$ within the accuracy of the Flory theory.

They have also studied excluded volume effects and the shape fluctuations that the polymer molecule undergoes in a random environment and have argued that the shape fluctuations are relevant to the transport mechanism of polymers in random media. This argument have been established in a study of velocity fluctuations in dilute polymer flow [119].

Various shape parameters that they had calculated from simulations indicate that polymers in porous media are considerably more spherical (less anisoptropic) than random coils. They have suggested that the diffusion of a polymer in a random medium occurs once the chain acquires the optimal shape. The results that they obtained were is different from that of a polymer chain in regular medium. The limitations and the general validity of the replica variational theory has also been assessed by an application to the directed polymer in a quenched random environment. This has already been established by Kardar [120] who applied the technique to the exactly solvable problem of a directed polymer in a quenched random environment in 1+1 dimensions, using the Bethe ansatz technique [121].

Honeycut and Thirumalai [86] found that the variational technique gives a correct estimation of the bound to the free energy of the quenched random system, but the prediction of the exponent ν, which describes the scaling of mean square distance with length is incorrect.

Honeycut and Thirumalai have continued their investigations [87], on the effect of random environment on the shape of polymer molecules. The effect of nonspherical cavities which arise as a result of density fluctuations in the environment, in determining the size of the polymer in random media is studied with Monte Carlo simulations. This theory predicts that when one end is anchored, $\nu=2/3$ which suggests a certain similarity between this problem and that of the directed random walk in a random environment [77].

Using replica formalism [71-73], there have been theoretical studies on directed polymers in random systems [122]. Parisi [122] has applied the replica approach to study directed polymers in two dimensional random medium with short range noise. He has been able to show the predictions of the replica symmetry theory and has compared it with the exact results. In the one dimensional case, it is found that the replica symmetry is nearly broken. This result is in perfect agreement to the one found for the directed polymer with some minor differences. The possibility of spontaneous symmetry breaking is also addressed in this paper. In the two-dimensional model that he has considered, it is found that replica symmetry is weakly broken. There has been other investigations dealing with the effect of randomness on directed polymers [77,78].

The replica calculation on quenched disorder has been examined recently by Cates and Ball [49] using scaling arguments and the essential results of EM [9] were recovered. They examined the statistics of a Gaussian polymer chain in a quenched random potential, by mapping the problem into a nonlinear evolution equation for a growing interface in the presence of a time-independent random flux. Additional logarithmic corrections depending on the size of the system have also been proposed by them. They [49] have also analyzed the case where one end of the polymer chain is fixed. According to their calculations the mean end to end vector scale as

$$R \sim \nu^{(1/d-4)} [\ln V]^{(1/d-4)} \qquad (5)$$

where V is the volume of the system containing the polymer chain.

Natterman and Renz [82] have mapped this problem of polymer in random media onto the localization of a quantum particle in a random potential [123] and their results were in good agreement with that of EM [9].

I.6. POLYMER MOLECULES IN RANDOM CONSTRAINT ENVIRONMENTS

There have been many investigations on the problem of a macromolecule in topologically constraint environments. For example, a computer simulation of the dynamics of a polymer chain in the random constraint cage have been performed by Geurts and Wiegel [42]. They have considered a model in which the cage represents the average topological constraints on the motion of a particular polymer, imposed by the other polymers in the system. Such a model of a random chain in a constraint cage has been used frequently to model the complex equilibrium dynamics of highly entangled polymer chains [40]. They have used an algorithm described by Evans and Edwards [40] and Needs and Edwards [124].

Edwards and Evans [40] were able to determine the center of mass diffusion constant D and the chain relaxation time τ of the macromolecule moving through the regular constraint cage. It was found that $D \propto N^{-2}$ and $\tau \propto N^{3}$ when the lattice constant of the cage c is sufficiently small (c=2) where N is the total number of results obtained by Wiegel and Geurts could not derive much of physical interpretation of the problem of a polymer chain in random medium.

One of the recent investigations on the study of polymer chains in random media is that of Gersappe and de la Cruz [125]. They have analyzed the effect of disorder on the statistics of a ring macromolecule by computer simulation. They found that when the size of the ring or the disorder concentration is increased, the ring macromolecule will start obeying the 'lattice animal' or highly branched polymer statistics. This result is in contrast to that of the linear macromolecules, where a disordered medium does not induce a change in the chain statistics, as long as the impurity concentration is below the percolation threshold [122]. They also showed that this problem maps onto a related study on two dimensional vesicles with a pressure difference.

There has been several investigations on the study of a flexible polymer chain in a dynamically disordered medium [126]. The problem is analogous to a random walk problem in which a single random walker moves on a lattice of finite extent with dynamical bond disorder. Random walks on infinite lattices with dynamical disorder have been the subject of several recent investigations [127].

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CHAPTER - II

THE ADSORPTION OF POLYMERS ON SURFACES

II.1. INTRODUCTION

Adsorption of polymers on surfaces play a part in a wide variety of natural, inorganic, biological and technological processes and is also of major theoretical interest. The physics of polymer adsorption has attracted much interest in the past 25 years due to its practical application to processes like colloidal particle stabilization [1,2,12,13], polymer coatings [1], adhesion, chromatography etc.

In many cases of practical interest, the polymer is in solution and there is a surface with a lot of structure of its own, for eg., the surface can be a cell membrane. In these cases, attractive forces exist which favour the adsorption of polymer on the surface (polymer can be attracted by a solid surface for eg., polystyrene on metallic chromium or by a limiting surface of the solution). A general discussion of adsorption can be found in the monograph of de Gennes [8]. Rubin has given rigorous solutions to certain lattice problems related to the adsorption of a polymer to a plane, line and a point [14]. Conformational states of macromolecules adsorbed at solid-liquid interfaces has been studied by Eirich [15]. Adsorption isotherms and adsorbate layer thicknesses of about 20 different dilute, polymeric systems were determined. Most of them were found to form monolayers on surfaces where as a few remained as individual macromolecules.

The basic physical origin of the criterion of adsorption of polymer chains on a surface is the competition between two conflicting effects viz., the gain in potential energy obtained by the monomers by adsorbing to the attractive surface and the loss in chain entropy associated with the reduction in the number of possible chain conformations of the adsorbed chains, when compared with that of free chains.

When a surface is physically rough, it may be thought of as consisting of "hills" and "valleys" made of protrusions of spheres and cylinders. In such cases three major effects are to be taken into account. (i) Entropy consideration alone will lead to the preferential adsorption at the hills rather than at the valleys, because the chain can assume a larger number of conformations at the top of the hill than at the bottom of a valley. (ii) The consideration of energy alone will lead to preferential adsorption in the valleys, where a larger number of contacts with the surface are possible. (iii) The potential energy of interaction between the monomers and the surface is a function of the local curvatures, which will modify the boundary conditions used in determining the characteristics of adsorption [60]. The effective result is that depending upon the local curvatures and the nature of the surface potential, adsorption will take place either on the valleys or at the hills.

The chemical randomness may be caused by impurities on the surface or because the adsorption is on the surface of an alloy, which has a random distribution of its components on the surface. Among the many mathematical formulations of adsorption of polymer chains to a surface, the simplest is the *propagator method* introduced by Edwards and later reviewed by de Gennes [4] and Weigel [9].

II.2. RANDOM WALK MODEL FOR ADSORPTION

Most of the early investigations on the problem of polymer adsorption on surfaces make use of the analogy between random walk paths and polymer conformations. The most important problem in the statistical mechanical theories of polymer chain adsorption at a surface is to enumerate the infinite number of conformations of the polymer chain and to keep track on the number of monomer units in each chain conformation.

Rubin [14] has done rigorous calculations for the problem based on a lattice model in which there is one to one correspondence between the random walk paths on the lattice and the polymer chain conformations. These treatments have been later reviewed by Barber and Ninham [16].

Silberberg [17] has given an approximate treatment for a variety of lattice models. He noted that if self excluded volume interactions of the polymer chain is neglected and if all surface sites are equivalent, then the problem of determining the dimensions of the chain molecules in the direction normal to the adsorbing surface is essentially a one dimensional problem. Polymer chains of sufficiently large size are found to be adsorbed in a surface phase whose composition and structure are essentially independent of molecular weight and of the concentration of the macromolecule in the equilibrium bulk phase.

It was also found that the concentration of polymer segments in the surface is high and the layer of polymer segments held to the surface in loops is compact, even in cases where the interaction energy between the adsorbate and the adsorbent is low.

DiMarzio and McCrackin [18], using a combinational theorem and Monte Carlo calculations, have carried out a comprehensive investigation of the distribution of polymer chain units by considering a one dimensional polymer molecule. The end-to-end length and the distribution of segments with respect to the distance z from the surface were computed as functions of the chain length N of the polymer and the attractive energy of the surface. They have shown that many of the results that they obtained for the one dimensional case could be applied to real systems.

Rubin [14] obtained an analytical solution to the problem of determining the average number of polymer chain units in the surface layer as well as the mean dimensions of the chain in the direction normal to the surface for a class of lattice models introduced by Silberberg [17]. Rubin has also performed calculations taking into account the excluded volume interactions [14] in the polymer chain.

A statistical mechanical treatment of a polymer chain adsorbed on a surface when the surface coverage is very low has been considered by Hoeve *et al.* [19]. Hoeve [20] and his co workers [19] have also noted the similarities between the problems of adsorption and the DNA denaturation. Their results were in contradiction with that of Silberberg [17]. Their theory predicts large loops and few units adsorbed for small adsorption free energies and small loops and more units adsorbed at large adsorption free energies. But Silberberg predicted small loops for all values of the adsorption free energy.

Silberberg has also done [21] a generalized (approximate) statistical mechanical treatment of adsorption of an isolated macromolecule, taking into account the self exclusion effects. Monte Carlo simulations of the same have also been performed [22,23]. The statistical mechanical problem of adsorption from solution has also been discussed, taking into account the critical importance of solvent-polymer and solvent-surface interactions [24].

Another investigation which could properly account the conformations of a polymer chain near the surface was that of DiMarzio [25]. He found that the characteristic dimensions of a polymer chain near the surface is larger than the polymer away from the surface. His method was that of a random walk with a reflecting boundary. Exclusion effects have also been taken into account in a general equation.

II.3. ADSORPTION - SCALING APPROACH

Scaling analysis has provided many useful theoretical results for the adsorption of polymer chains at interfaces. In flexible polymer solutions, the perturbation of the polymer conformations due to the presence of a surface extends to a large distance, the effect of which is solely due to the large size of polymer chains. A diffuse polymer layer is then formed and this is in close relationship with the existence of scaling laws for these systems.

Such diffuse layers have been studied in the past [19]. Scaling laws were introduced for the study of polymer adsorption on surfaces by de Gennes [26] and Alexander [27]. Scaling laws have been discussed in detail in Ref [4] and the application of the scaling theories to adsorption has been reviewed by Bouchaud *et al.* [28].

de Gennes [26] had investigated the equilibrium properties of flexible polymer chains adsorbed on a flat surface using scaling theory arguments. He assumed very long polymer chains whose adsorption on the surface is weak, resulting in a large thickness 'D' for the adsorption layer and a good solvent, so that the excluded volume effects become important.

The repulsion between the monomers were incorporated through a scaling theory, which goes beyond the usual mean field approximations. The central assumption in this investigation was that the polymer concentrations in the first and in the next layers scale in the same way (although they do differ by a constant factor). He was able to find out three regimes of adsorption.

i. In the dilute limit (separate chains) D is independent of the polymerization index N, and varies with the strength of the effective monomer surface attraction (measured by a small parameter δ) according to $D \sim \delta^{-3/2}$ instead of $D \sim \delta^{-1}$ in mean field.

ii. There is a semi dilute regime, where the coils begin to overlap, but where D remains essentially the same.

iii. The most important case corresponds to the plateau in the adsorption isotherm ; he showed that the correlations inside the layer are similar to those in a three dimensional system. Then $D \sim N \delta (\ln c_B)^{-1}$ where c_B is bulk concentration. The dependence on N is stronger than in mean field $D \sim N^{1/2}$ but compatible with the existent data.

de Gennes [29] had constructed the equilibrium concentration profiles for a polymer solution near a solid wall including all scaling exponents. He considered both the adsorption and depletion layers (layer formed when the polymer chains are repelled by the wall). Here he restricted the investigation to weak coupling i.e. the situations where the sites are not saturated with polymer.

In a later work [30] he has made use of the same scaling arguments to analyze the concentration profiles and interaction energy of flexible polymer chains and a solvent inside a narrow gap between two weakly adsorbing plates. He concluded that two flat plates carrying irreversibly adsorbed polymer chains in good solvents, repel each other. But in cases where the chains can exchange reversibly with the bulk solution, the interaction is always found to be attractive (this holds in good/bad solvents).

The influence of a hard wall on the conformations of long polymer chain with one end fixed near the wall which exerts short range attractive forces on each monomer has been investigated by Eisenriegler *et al.* [31]. They have investigated the problem with special emphasis upon the region around the adsorption temperature T_a , below which the polymer becomes adsorbed to the wall. They considered both ideal non-interacting chains and chains with excluded volume effects. The dimensions of the polymer parallel and perpendicular to the wall and their probability distribution were also calculated.

The predictions of the scaling theory were well confirmed by Monte Carlo studies of self-avoiding walks on the tetrahedral lattice with a free surface and estimates for the exponents were presented. A new sampling technique in favor of adsorbed polymer was also developed by them. This discussion of a single polymer chain has been extended by Eisenriegler [32] who generalized the above to dilute (weak interaction between the chains) and semi dilute (strong overlap between polymer chains) solutions of polymer chains.

Universal amplitude ratios for the surface tension of polymer solutions [33] were also calculated. This has later been modified by evaluating universal amplitudes for a single chain, fixed with one end at the surface (such a chain is referred to as a surface chain) at the critical point of adsorption [34]. He has calculated the ratios for mean square end-to-end distances of surface and bulk chains as well as short distance amplitudes for the end-to-end distance distributions of a surface chain.

Using scaling theory arguments Johner *et al.* [44] have carried out a mean field calculation for the conformation of a polymer chain with one end fixed at a distance z from the adsorbing surface. For the single ideal chain adsorption, it was previously noted that in addition to the thickness of the polymer chain D, there exists a characteristic length Z_o, corresponding to the capture distance by the attractive surface of a chain with an end fixed. A polymer at a distance larger than Z_o does not feel the attraction by the surface. A chain at distance equal to or smaller than this distance adopts a stretched configuration and it is found that an external force has to be applied in order to keep the fixed end at a given distance.

Using scaling theory arguments they [44] have generalized these to the case of a good solvent, when the excluded volume interactions are important. It is found that $D \sim \delta^{-1}$ where δ is the energy for a monomer on the surface and $Z_o \sim N\delta^{-2/3}$. They have also studied the relaxation of the polymer chain when the fixed end is released. It is found to be strongly attracted by the surface and it adopts a stretched conformation.

Johner and Joanny [45] have investigated polymer adsorption in a poor solvent. The most important result that they have obtained is that the adsorption of a polymer chain can be viewed as a wetting problem i.e., in the same way as wetting by liquid drops.

The adsorbed chains are found to form a two dimensional dilute polymer solution which is either in a poor solvent or in a good solvent at very low bulk concentrations. At a higher bulk concentration the surface layer becomes continuous, its thickness grows and diverges when the concentration is made even higher. Their results could be applied to diblock co polymer adsorption in a selective solvent.

Scaling predicts a great variety of structures, all characterized by a concentration profile. The most spectacular predictions concern the variation of this structure with the adsorption energy near the surface. Most of the experiments on polymer adsorption have been carried in situations of strong adsorption or depletion [13]. In these situations, scaling laws has been tested, and the results were found to be in excellent agreement with the predictions.

II.4. SELF AVOIDING WALKS INTERACTING WITH A LATTICE

Most of the early theoretical investigations [14,17] of polymer adsorption modeled the polymer molecule as a random walk. One of the principal predictions of this model is that if the polymer chain interacts with the interface via. a short range attractive potential, there is a critical value of the temperature below which the polymer is adsorbed and above which it is desorbed.

Whenever the repulsive forces between the monomer units in a polymer chain are taken into account, the calculation of the number of conformations becomes much more difficult. The problem then consists of calculating the number of self avoiding walks on a lattice.

Theoretical attempts to include the excluded volume effects by considering a self avoiding walk (SAW) on a lattice, interacting with a lattice plane which represents an interface has also been studied [21-23,35-40]. There has been exact enumeration studies [35-38] (on short walks) to find the effect of excluded volume constraints exactly on the conformational properties of polymer molecules adsorbed on a planar surface which used extrapolation techniques to obtain information on longer walks.

It has been found [37] that the excluded volume effects have a marked effect on the conformational properties of the adsorbed polymer molecule. Wittington [38] gave results on the existence of some limits and bounds on the partition functions of infinitely long walks using rigorous calculations. Most of these studies of excluded volume effects were consistent with the existence of a critical temperature analogous to that of a random walk model.

Most of these treatments have been directed towards a SAW terminally attached to an interface i.e., with the first vertex of the walk in the interfacial plane [35,36]. Torrie *et al.* [41] have considered SAW which are attached, but not terminally attached, to the interface. They have presented exact enumeration data on the numbers of walks with various numbers of vertices in the interfacial plane for three different lattices and also rigorous results on the form of the partition function.

II.5. ADSORPTION ON COLLOIDAL PARTICLES

It is well known that adsorption of polymers can take place on the surfaces of colloidal particles [13]. Colloidal particles in non polar solvents are often maintained dispersed by means of adsorbed polymers [13]. Polymeric steric stabilization against aggregation of colloidal particles requires [13,30] that (1) the solid particle provides an adsorbing substrate for the polymer. (2) the polymer is irreversibly adsorbed and (3) the solvent is good for the polymer i.e., the solvent mediated polymer segment-segment interactions are strongly repulsive.

When two colloidal particles approach, the reduction in the number of available conformations of the polymer chains give rise to an entropic repulsive force, stabilizing them. Some interesting theories of stabilization of colloids by adsorbed polymers with and without excluded volume interactions have been proposed by Dolan and Edwards [42] and by Pincus *et al.* [43].

Dolan and Edwards [42] have modeled the polymer stabilized colloidal particles by planar surfaces on to which the polymer chains are adsorbed by one end only. Interactions between segments of the polymer were treated as excluded volume effect. It is found that a positive value of excluded volume greatly increases the repulsive free energy compared with that for chains with zero excluded volume, particularly at large separation distances of the surfaces. It is therefore concluded that excluded volume effects play an important part in the stabilization of colloids by adsorbed polymer.

Pincus *et al.* [43] considered the adsorption of polymers on colloidal particles, both spherical and cylindrical particles, whose dimensions are comparable to the solution polymer radii of gyration. They found that adsorption occurs if the sticking energy per monomer exceeds a certain threshold and that for a colloidal particle this threshold increases by an amount inversely proportional to its radius. It is found that, the repulsive interactions between the monomers limit the number which may be attached to a given particle. There have been scaling laws proposed [27] to describe the adsorption of polymers onto micelles.

II.6. ADSORPTION ON PLANAR, UNIFORM SURFACES

There have been studies on the ideal situation of polymer adsorption i.e., adsorption on a planar, uniform surfaces. The most interesting of these investigations is that of de Gennes [8]. He considered the problem of a long chain weakly adsorbed to a planar surface, a problem closely related to the ground state of microscopic particles. The problem has been solved by de Gennes by employing a Schrödinger-like equation and the eigen values (bound state) and the eigen functions were found [8]. (See chapter IV for details of the de Gennes approach).

The conformational properties of a polymer chain interacting with a surface were studied by Stratouras and Kosmas [77]. New features for the cases of a chain free to move in the whole space and for a localized chain fixed with one of its ends at a point were also illustrated. The macroscopic behaviour of these localized and non localized chains were studied as a function of the molecular weight of the chain, the chain-surface interaction parameter and the distance of localization z_o for the localized or a perpendicular bound L of the volume for the non localized chains, respectively.

The effect of adsorbed homopolymer on the elastic moduli of impenetrable surfactant bilayers, considering adsorption on both sides of the bilayer has been recently studied theoretically by Brooks *et al.* [46]. They formulated the energy of adsorption for both spherical and cylindrical surfaces. In the limit of weak adsorption, analytic expressions for the polymeric contribution to the mean and Gaussian elastic moduli of the bilayer were derived, using both mean-field and scaling functional approach. For stronger adsorption, numerical calculations has been made, and in the limit of very strong adsorption, asymptotic functional forms for the elastic moduli were found. They have arrived at the conclusion that the presence of adsorbed polymer can greatly influence the elasticity of surfactant bilayers.

There have been a few recent studies on the adsorption of star polymers at planar interfaces. Adsorption of star like micelles has also been studied [47]. Recently Halperin and Joanny [48] analyzed the adsorption of a star polymer on a flat surface using scaling arguments. Equilibrium properties of linear polymer chains grafted at one end to a repulsive cylindrical surface were also studied using molecular dynamic simulation [49]. Adsorption of branched polymers at surfaces have also been carried out and exact results for the three dimensional case have been given by Jansses and Lyssy [50].

Dill *et al.* [51] has reviewed the adsorption of macromolecules at high densities at interfaces recently. The general principles of interfacial constraints on highly concentrated polymers are well described. The chain in such cases has two different types of constraints. They are constrained from penetrating to the surface. They are also constrained due to the interaction between different chains, which is prominent when they are at high concentration.

The formation of large loops in adsorbed polymer layers when the concentration of the bulk, C is large has been discussed by Daoud and Jannik [52]. They have introduced a new characteristic length Λ corresponding to the extension of the loops in the bulk. They found that $\Lambda \sim N\ C^{3/4}$.

Shull [53] have used a detailed self-consistent field theory to calculate the properties of end-adsorbed polymer chains, and polymer "brushes" in equilibrium with a blend of adsorbing B polymer and non adsorbing A polymer. There have been studies on the adsorption of grafted polymer layers (polymeric brushes) on a planar surface [54].

There have been a recent study on the conformations of chain molecules at an impenetrable surface [55]. They have explored how the conformations depend on the distance of the center of mass of the chain from the surface, by exhaustive enumeration of short chains on three dimensional simple cubic lattices. They found that the conformational ensemble becomes restricted as the chain approaches the surface ; hence there is an entropic repulsion and the conformations become distorted as they flatten to the surface. They observed that as the chain approaches the surface, there is an enrichment of certain conformations namely helices, turns parallel and anti parallel sheets. They confirmed the well known results that the open chains (chains with no intra chain attraction) undergo an adsorption transition onto the surface.

des Cloizeaux [56] have considered polymer adsorption near the attractive surface of a polymer solution in a good solvent. He found that concentration profile is given by a universal law. Stratouras *et al.* [57] have investigated the average conformational properties of a free polymer chain interacting with a surface and free to move in a space perpendicular to the surface.

Cattarinussi and Jug [58] have carried out detailed investigations of a geometrical model of collapse and adsorption of a polymer chain near an attractive surface. They have estimated the size exponents by means of cell renormalization methods in d=2 and d=3 dimensions which provided some evidences for the surface induced enhancement of the collapse transition temperature.

Recently, Adriani and Chakraborty [59] have investigated the effect of chain architectures on the relaxation of a polymer chain that is chemisorbed on a surface, using molecular dynamic simulations. They found that strong and specific interaction of the chemisorptive functional groups give rise to energy hyper surfaces with deep energy minima separated by high transition barriers between states.

They have examined two different polymer chain architectures consisting of one and two chemisorbing functional groups respectively. In both architectures, the adsorbed chains were found to get trapped in local energy minima and there were slow transitions between conformational states of the adsorbed chain. The relaxation to equilibrium was found to be slow and conformation of the trapped chains are found to relax with highly cooperative dynamics. The two architectures were found to show distinctive effects on adsorption.

II.7. ADSORPTION ON ROUGH SURFACES

In almost all practical problems of polymer adsorption, surfaces are neither homogeneous in composition nor smooth. Although the heterogeneity (chemical or physical) may strongly influence the adsorption of polymer chains, these non-ideal situations have received relatively little theoretical attention [60-66]. Experimental study is often very difficult due to the difficulty in carrying out controlled adsorption studies on rough surfaces. There has been some theoretical studies focusing on the adsorption of polymers on rough surfaces [10,64-66] of which one study deals with the adsorption on a fractal surface [64].

If we consider a rough surface with a root mean square amplitude variation of order z_o and characteristic horizontal length λ for surface fluctuation, and if both of them are larger in comparison with the size of the polymer chain, then the polymer chain near the surface can be mapped into the problem of a chain in two dimensional random media as discussed by several authors [66-72].

This situation is similar to the case of chemically rough surface where the impurities are non adsorbing. In such a case, the locations corresponding to the chemical impurities or the steep hills introduce an effective attraction between monomers by essentially denying the monomers to occupy the locations. This can lead to the shrinkage of the polymer chains. Moreover one expects the adsorption to be stronger due to the presence of the impurities with the consequent suppression of the critical adsorption temperature.

If the randomness on a surface is not so strong, one can study about the influences of surface roughness on the adsorption behaviour by considering periodic fluctuations of the rough surface from a flat plane as

$$z = z_o \cos(2\pi x/\lambda) \cos(2\pi y/\lambda) \qquad (1)$$

where z is the local height of the surface with respect to the reference plane and x and y are the coordinate axes in the plane perpendicular to z. Such an attempt was first made by Hone *et al.* [73] who modeled the rough surface as a sinusoidal grating geometry, $z = z_o \cos(2\pi y/\lambda)$, and performed detailed calculations for the adsorption of an infinitely long, ideal Gaussian chain. They have employed the ground state dominance approximation, assuming that the periodically varying rough surface is transparent allowing the chain to adsorb on both sides of the interface. The effect of excluded volume between chain segments on these results were studied by Ji and Hone [74]. They have formulated a mean field theoretical approach to study the effect of surface curvature on polymer by considering the adsorption of a polymer on the interior and on the exterior surface of a sphere in a good solvent. Both perturbation expansion and the numerical simulation shows that surface tension and monomer density tend to be lowered when the surface is curved towards the polymer solution. But when the surface is curved away from the solution, it increases.

For the polymer solution confined to the interior of a sphere, it is found that there exists a critical radius, at which the surface tension is minimized. A study of the surface excess per unit area showed that it slowly decreases with surface roughness. It remains to be seen how much of these predictions get modified by the curvature dependence of the realistic potentials from the surface.

Stimulated by the work of BM [75] and that of EM [66] on the statistics of polymer chains in three dimensional random media, Edwards and Chen [10] have studied a polymer chain adsorbed on a rough surface. They have included the excluded volume effects and suggested a model of how the statistics of a polymer chain lying on a surface is affected by the roughness on the surface.

It is shown that an appropriate equation for the mean size of the polymer is derived from an entropy,

$$R^2/N + N/R^2 + w\,(N/R)^2 - \nu N \ln R, \qquad (2)$$

where w is the excluded volume interaction and ν is a measure of the concentration of the disorder and N is the length of the polymer. It is found that for small w, the polymer localizes, but for sufficiently large enough N, the excluded volume is dominant, however small w is.

A recent theoretical study which deals with the adsorption of polymers on a rough surface is that of Ball *et al.* [76] who found that under certain circumstances, a surface which is curved, or corrugated, or rough, will adsorb polymer/trap electrons when its flat equivalent does not. Qualitatively, when the magnitude of the curvature exceeds that of the bare de Gennes boundary parameter c_o, then the former will control the adsorption.

They [76] found that the entropy/kinetic energy effects alone favour adsorption at the protuberances of the surface, but they have to compete against the attractive potential. For a range of pair wise additive power law interactions they found that the effect of potential dominates, but in the limit of a surface of much higher dielectric constant than the solution, the entropy effects win.

They have compared their results on the binding at spheres, cylinders and flat surfaces with the earlier investigations [73] and found that there is no quantitative agreement with them for the curved cases.

A theoretical investigation on the disorder induced adsorption of polymers has been carried by Baumgärtner and Renz [72]. They have studied the competition between adsorption and entropic repulsion of a single self avoiding polymer trapped in quenched random media consisting of parallel, adsorbed rods, distributed at random and in the perpendicular plane, by simulations and by analytical arguments.

The chain undergoes an adsorption transition at finite temperature which is not observed in a regular medium. Below and above the transition temperature, the chain is found to be stretched parallel to the rods and shrunk in lateral directions. These phenomena are based on two different mechanisms, localization by adsorption at low temperature and localization by entropic repulsion at high temperatures.

An interesting theoretical investigation was recently carried out by BM [65], who studied the influence of both physical and chemical roughnesses on the adsorption characteristics of polymer chains using scaling arguments and by Monte Carlo simulations. They investigated the problem using Edwards Hamiltonian, representing the polymer chain as a random walk statistics without any monomer-monomer excluded volume interactions.

For the chemically rough surface they found that the surface adsorption temperature is depressed by an amount proportional to the concentration of the impurities. This result was found to be supported by a Flory type argument and by Monte Carlo simulations.

For the physically rough surface, the adsorbed state of the polymer was found to be different and more complex as compared to that in the case of a flat homogeneous surface. They have modeled rough surfaces by checker board corrugations. The adsorbed state of the polymer exhibited three different regimes. At low temperatures the chain is localized in one of the wells.

At higher temperatures they found a diffusive regime, where the chain units are diffusing and this regime was found to be equivalent to the conduction band of the polymer analog model of a one-dimensional electron in a periodic potential. These conclusions were supported by the Monte Carlo estimates of various quantities i.e., adsorption energy, specific heat, density profile, parallel component of the radius of gyration and diffusion coefficient. Bouchaud and Vannimenus [78] have investigated the polymer adsorption on an impenetrable attractive surface. They have considered a few models in which the polymer resides on a fractal surface. In one of these models, they find a multicrititcal point where a bulk collapse transition and a surface adsorption transition coexist. They have also carried out a simple real space renormalization scheme for the square lattice. Recently much of the attention has been focused on the adsorption of directed polymers on surfaces [79,80].

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CHAPTER - III

THE SIZE OF A FLEXIBLE POLYMER CHAIN IN RANDOM MEDIA

III.1. INTRODUCTION

There has been a lot of investigations on the problem of polymer chains in random media [1-5]. The behaviour of polymer chains in an annealed random medium, where the obstacles to the polymer chains are mobile, is fairly well understood [6-8]. We consider a quenched random medium, where the relaxation time of the medium is much larger than the thermal relaxation time of the polymer chain. The simplest system one can think of in such a case, is a Gaussian chain in a medium, where a large number of obstacles to the polymer chain are kept fixed at random locations.

Such a system has been simulated by Baumgärtner and Muthukumar (BM) [1] who found that the size of the chain is decreased as one increases the randomness, finally resulting in a limiting, collapsed configuration for the polymer chain. The analytical treatment of the same model has been done by Edwards and Muthukumar (EM) [2] whose results were in agreement with the simulation results [1] of BM.

In this chapter, our investigation on the effect of quenched randomness on the flexible polymer chain is discussed. We study a generalization of the problem posed by EM [2] - we consider the randomness of the medium to be correlated on a length scale R_o. We follow EM [2] and make use of the replica trick and variational technique to estimate the size of the polymer. Our study goes beyond that of EM in that we make use of a non-local trial action to describe the polymer chain, which has the property of being translationally invariant, unlike the local harmonic oscillator action used by them. We also comment on the use of the local harmonic oscillator for this problem.

III.2. THE MODEL

The polymer chain is modeled by Edwards Hamiltonian [9,10], which has been extensively used in the theoretical investigations of polymer problems. One can derive the thermodynamic properties from the partition function of the polymer chain and can also relate the dimensions of the chain with one of the most important quantities of experimental interest, the molecular weight. For a flexible polymer chain, the probability distribution $P(\vec{R})$ describing the end-to-end vector $\vec{R}$ of the chain will be Gaussian. For detailed description of configurational statistics of flexible (with and without excluded volume) and stiff polymer chains see in the monograph by Freed [11]).

We consider such a Gaussian chain in a quenched system of obstacles where the obstacles to the polymer are held fixed at random locations. The problem addressed here is quite different from the Anderson problem of a random walker in random potentials [12-14].

The probability density functional for a polymer chain $\vec{r}(t)$, $0\leq t\leq N$ interacting with n random obstacles, located at $\vec{R}_\alpha$, $\alpha=1,2,\ldots$ n is determined by the the action [2]

$$S_{ran} = \frac{3}{2l}\int_0^N ds \left[\frac{d\vec{r}(s)}{ds}\right]^2 + \sum_{\alpha=1}^{n}\int_0^N W(\vec{r}(s)-\vec{R}_\alpha)ds, \tag{1}$$

where W is the potential describing the interaction between the obstacles and the polymer. Introducing the density of obstacles as,

$$\rho(\vec{r}) = \sum_{\alpha=1}^{n}\delta(\vec{r}-\vec{R}_\alpha) , \tag{2}$$

we can write

$$\sum_{\alpha=1}^{n}\int_0^N W(\vec{r}(s)-(\vec{R}_\alpha))ds = \int d\vec{r}\int_0^N W(\vec{r}(s)-\vec{r})\rho(\vec{r})ds . \tag{3}$$

The density of obstacles $\rho(\vec{r})$ is a random function of the position $\vec{r}$. We can write,

$$\rho(\vec{r}) = \rho_o + \delta\rho(\vec{r}), \tag{4}$$

where ρ_o is the average density of obstacles and $\delta\rho$ is the fluctuation. Introducing Eq. (4) into (3), we get,

$$\sum_{\alpha=1}^{n}\int_0^N W(\vec{r}(s)-(\vec{R}_\alpha))ds = \int_0^N ds\int d\vec{r}\; W(\vec{r}(s)-\vec{r})\rho_o + \int_0^N ds\int d\vec{r}\; W(\vec{r}(s)-\vec{r}_1)\delta\rho(\vec{r}_1). \tag{5}$$

The first term on the RHS of Eq. (5) is just a constant term and does not make any contribution to the probability functionals that we shall be calculating. Therefore we shall omit this term from now on. Defining,

$$\nu(\vec{r}) = \int d\vec{r}_1 W(\vec{r}-\vec{r}_1)\delta\rho(\vec{r}_1), \tag{6}$$

we can write Eq.(1) as,

$$S_{ran}[\vec{r}(s)] = S_o[\vec{r}(s)] + \int_0^N \nu(\vec{r}(s))ds. \tag{7}$$

It is clear that $\langle\nu(\vec{r})\rangle = 0$. We shall, further take $\nu(\vec{r})$ to be correlated on a length scale R_o and to be Gaussian, i.e., we take,

$$\langle\nu(\vec{r})\nu(\vec{r}')\rangle = B(\vec{r}-\vec{r}'). \tag{8}$$

Usually, the potential W is a short range repulsion and hence, if one takes

$$W(\vec{r}) = W_o\delta(\vec{r}). \tag{9}$$

Then

$$\nu(\vec{r}) = W_o\delta\rho(\vec{r}) , \tag{10}$$

and the assumption in Eq. (8) means

$$W_o^2\langle\delta\rho(\vec{r})\delta\rho(\vec{r}')\rangle = B(\vec{r}-\vec{r}'). \tag{11}$$

If one lets,

$$B(\vec{r}-\vec{r}') = u\ell^4\,\delta(\vec{r}-\vec{r}'), \tag{12}$$

with u being dimensionless, we get the special case considered by EM [2] (See Eq. 2.19). We consider a slightly more general case, where we take,

$$B(\vec{r}-\vec{r}') = V^2\, e^{-(\vec{r}-\vec{r}')^2/R_o^2} . \tag{13}$$

Clearly, if we let $V^2 = (\pi R_o^2)^{-3/2}\, u\ell^4$ and let $R_o \to 0$, then one gets the limit considered by EM [2]. From the above analysis the distribution function $\mathcal{G}(\vec{R},N;\vec{0},0)$ for the end-to-end vector $\vec{R}$, in the presence of randomness $\nu(\vec{r})$ is given by,

$$\mathcal{G}(\vec{R},N;\vec{0},0) = \int_{\vec{r}(0)=\vec{0}} D\vec{r}(s)\exp\{-S_{ran}[\vec{r}(s)]\}\,\delta(\vec{r}(N)-\vec{R})/\mathcal{N}_{ran} . \tag{14}$$

Here $\mathcal{N}_{ran}$ is the normalization factor ensuring that,

$$\int \mathcal{G}(\vec{R},N;\vec{0},0)d\vec{R} = 1 . \tag{15}$$

Therefore,

$$\mathcal{N}_{ran} = \int d\vec{R} \int_{\vec{r}(0)=\vec{0}} D\vec{r}(s)\exp\{-S_{ran}[\vec{r}(s)]\}\,\delta(\vec{r}(N)-\vec{R}) . \tag{16}$$

Our interest is in the calculation of the quenched average $G(\vec{R},N;\vec{0},0)$, defined by

$$G(\vec{R},N;\vec{0},0) = \langle\mathcal{G}(\vec{R},N;\vec{0},0)\rangle_{\upsilon} , \tag{17}$$

where $\langle \quad \rangle_{\upsilon}$ indicates the averaging over all random functions $\nu(\vec{r})$. As is clear from the Eq. (17), $G(\vec{R},N;\vec{0},0)$ is the ratio of two random quantities and hence calculating the average is difficult, and one has to adopt the replica trick [15-17].

A modification of the work done by EM has been done by Muthukumar [3] who incorporated the repulsive excluded volume interactions between the monomers into calculation. He found that collapse of the polymer chain is a universal phenomenon exhibited by polymer chains in quenched random media and that the excluded volume interactions were screened out. We do not, however, investigate the effect of the excluded volume interactions in this thesis.

III.3. THE REPLICA FORMALISM

In presence of quenched randomness $\nu(\vec{r})$, one can calculate the free energy of the system as

$$\beta F = - \ln Z, \tag{18}$$

where Z is the partition function and is a functional $\nu(\vec{r})$. Now the average value of the free energy is

$$\beta\langle F\rangle = - \langle \ln Z\rangle. \tag{19}$$

Calculating the average of lnZ is difficult. Therefore, Edwards introduced the replica trick, which makes use of the fact that,

$$\ln Z = \left[\frac{\partial Z^n}{\partial n} \right]_{n\to 0} . \tag{20}$$

Eq. (18) becomes

$$-\beta\langle F\rangle = = \left[\frac{\partial \langle Z^n\rangle}{\partial n} \right]_{n\to 0} . \tag{21}$$

Even now, one has the difficult job of calculating $\langle Z^n\rangle$ for $n\to 0$. However, calculating $\langle Z^n\rangle$ is easy, if n is an integer. Therefore, one does the calculation, thinking of n as an integer and then one analytically continues the result to n = 0! We now adopt the same kind of approach to calculate $\mathcal{G}(\vec{R},N;\vec{0},0)$.

The distribution function in Eq. (14) could be written as,

$$\mathcal{G}(\vec{R},N;\vec{0},0) = \lim_{n\to 0} \int_{\vec{r}(0)=\vec{0}} D\vec{r}_1(s)\exp\left[-S_{ran}[\vec{r}_1(s)]\right] \delta[\vec{r}_1(N)-\vec{R}]$$

$$\left[\int_{\vec{r}(0)=\vec{0}} D\vec{r}_1(s)\exp\left[-S_{ran}[\vec{r}_1(s)]\right]\right]^{n-1} . \tag{22}$$

Imagining n to be an integer, we have,

$$\mathcal{G}(\vec{R},N;\vec{0},0) = \lim_{n\to 0}\left[\prod_{\alpha=1}^{n}\int_{\vec{r}_\alpha(0)=\vec{0}} D\vec{r}_\alpha(s_\alpha)\exp\left[-\sum_{\alpha=1}^{n}\int_0^N S_{ran}[r_\alpha(s_\alpha)ds_\alpha\right]\right.$$
$$\left.\delta[\vec{r}_1(N)-\vec{R}]\right] . \tag{23}$$

Now the quenched average is,

$$G(\vec{R},N;\vec{0},0) = \langle\mathcal{G}(\vec{R},N;\vec{0},0)\rangle_\nu . \tag{24}$$

On performing the average, we get,

$$\mathcal{G}(\vec{R},N;\vec{0},0) = \lim_{n\to 0}\left[\prod_{\alpha=1}^{n}\int_{\vec{r}_\alpha(0)=\vec{0}} D\vec{r}_\alpha(s_\alpha)\exp\,[-S)]\right]\delta[\vec{r}_1(N)-\vec{R}], \tag{25}$$

where

$$S = \sum_\alpha S_o[\vec{r}_\alpha(s_\alpha)] - S_1, \tag{26}$$

with

$$S_o[\vec{r}(s)] = \frac{3}{2l}\int_0^N ds\left[\frac{d\vec{r}(s)}{ds}\right]^2 \tag{27}$$

and

$$S_1 = \frac{1}{2}\sum_{\alpha,\beta=1}^{n}\int_0^N ds\int_0^N dt\; B(\vec{r}_\alpha(s)-\vec{r}_\beta(t)) . \tag{28}$$

If there are now n polymer chains, they all will start at the origin = $\vec{0}$. The first polymer will have its end at $\vec{R}$ while there is no restriction on the remaining chains. As the path integrals in Eq. (25) cannot still be performed, we adopt the variational approach (see ref. (18 & 19)).

III.4. THE FREE ENERGY

Our approach to the calculation of the free energy of the chain is the following. We consider F(n), the free energy of the n replicas of the polymer chain defined by,

$$e^{-F(n)\beta} = \left[\prod_{\alpha=1}^{n} \int_{\vec{r}(0)=\vec{0}} D\vec{r}_\alpha(s_\alpha)\right] \exp(-S) \tag{29}$$

and estimate F(n) using the variational method, using a trial action. As we are interested in the n → 0 limit, we can think of expanding F(n) as a series in n. In the n → 0 limit, only the term linear in n is important and so we consider

$$\beta F_1 = \lim_{n\to 0} \left\{\frac{\partial F(n)}{\partial n}\right\}, \tag{30}$$

where F_1 is the free energy of a single polymer chain.

We now proceed to calculate F(n) and choose our trial action in such a fashion as to get the minimum value for F_1. The trial action that we use is,

$$S_T = \sum_{\alpha=1}^{n} S_t[\vec{r}_\alpha(s_\alpha)]. \tag{31}$$

S_t is defined by,

$$S_t[\vec{r}(s)] = \frac{3}{2\ell}\int_0^N ds \left[\frac{d\vec{r}(s)}{ds}\right]^2 + (q^2/12\ell N)\int_0^N ds \int_0^N dt\, [\vec{r}(s)-\vec{r}(t)]^2, \tag{32}$$

where q is a trial parameter that has to be variationally determined. The choice of the above trial action is motivated by the expectation that the chain might be bound inside some of the potential wells created by the randomness and also in view of analytical solvability of the problem. The action in Eq. (32) has a harmonic oscillator like non-local part. In comparison, the trial action that has been used by EM is

$$S\,[\vec{r}(s)] = \frac{3}{2l}\int_0^N ds\left[\frac{d\vec{r}(s)}{ds}\right]^2 + (q^2/6l)\int_0^N ds\;\vec{r}(s)^2, \tag{33}$$

which is a local harmonic action. We prefer to use the non-local action rather than the local one as the non-local one is translationally invariant, while the local one is not. Note also that this harmonic oscillator like trial action gives a special status to the origin i.e., one end point of the polymer and there is no physical justification for doing this. Our trial action also has the advantage that, all path integrals that are needed for our purpose can be analytically evaluated. To see how this may be done consider the integral,

$$I(\vec{R},N;\vec{0},0) = \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{R}} D\vec{r}(s)\exp\{-[S_t[\vec{r}(s)]]\}. \tag{34}$$

$S_t[\vec{r}(s)]$ involves the non-local, quadratic term. Analytical evaluation of path integrals involving such a general non-local quadratic action is possible [20,21]. This particular action is quite easy to handle, as one has the identity,

$$\exp(-S_t) = q^3(N/6\pi l)^{3/2}\int_{-\infty}^{\infty} d\vec{y}\,\exp-\left[\frac{3}{2l}\int_0^N ds\left(\frac{d\vec{r}(s)}{ds}\right)^2 + (q^2/6l)\int_0^N (\vec{r}(t)-\vec{y})^2 dt\right]. \tag{35}$$

(See Appendix A1 for details of the derivation of Eq. (35)).

Therefore,

$$I(\vec{R},N;\vec{0},0) = q^3(N/6\pi\ell)^{3/2} \int d\vec{y} \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{R}} D\vec{r}(s) \exp\{-[S_{ho}^{\vec{y}}[\vec{r}(s)]\} ,\tag{36}$$

where

$$S_{ho}^{\vec{y}}[\vec{r}(s)] = \frac{3}{2\ell} \int_0^N ds \left[\frac{d\vec{r}(s)}{ds}\right]^2 + (q^2/6\ell) \int_0^N ds\ (\vec{r}(s)-\vec{y})^2 .\tag{37}$$

So we see that the path integral having the non-local quadratic action of Eq. (32) can be expressed in terms of path integral over a harmonic oscillator type action, with the origin of the harmonic oscillator being at $\vec{y}$ and subsequent integration over $\vec{y}$. The identity is quite easy to verify, for which one simply has to perform the Gaussian integral over $\vec{y}$. Now clearly,

$$\int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{R}} D\vec{r}(s) \exp\{-[S_t^{\vec{y}}[\vec{r}(s)]\} = G_{ho}^{\vec{y}}(\vec{R},N;\vec{0},0),\tag{38}$$

where $G_{ho}^{\vec{y}}(\vec{R},N;\vec{0},0)$ is the propagator corresponding to a harmonic oscillator action, with the minimum of the harmonic oscillator potential being at $\vec{y}$, instead of the origin. If $G_{ho}(\vec{r},N;\vec{r}',0)$ is the propagator corresponding to the usual harmonic oscillator (with minimum of the potential at the origin), obeying the Schrödinger- like equation of the form,

$$[\partial/\partial N - (\ell/6)\nabla_{\vec{r}}^2 - (q^2/6)\vec{r}^2]\ G_{ho}(\vec{r},N;\vec{r}',0) = \delta(N)\delta(\vec{r}-\vec{r}') ,\tag{39}$$

then

To determine the trial parameter q variationally, we write Eq.(29) as,

$$e^{-F(n)\beta} = \left[\prod_{\alpha=1}^{n} \int_{\vec{r}(0)=\vec{0}} D\vec{r}_\alpha(s_\alpha)\right] \exp(-S_T) \exp[-(S-S_T)]. \qquad (47)$$

Introducing the notation $\langle\mathcal{M}\rangle_T$ for the expectation value of any quantity $\mathcal{M}$ with respect to the trial action S_T, defined by

$$\langle\mathcal{M}\rangle_T = \frac{\left[\prod_{\alpha=1}^{n} \int_{\vec{r}(0)=\vec{0}} D\vec{r}_\alpha(s_\alpha)\right] \exp(-S_T)\ \mathcal{M}}{\left[\prod_{\alpha=1}^{n} \int_{\vec{r}(0)=\vec{0}} D\vec{r}_\alpha(s_\alpha)\right] \exp(-S_T)}. \qquad (48)$$

We can write Eq. (47) as,

$$e^{-F(n)\beta} = Z^n \langle\exp[-(S-S_T)]\rangle_T \qquad (49)$$

$$\geq Z^n \exp[-\langle S-S_T\rangle_T], \qquad (50)$$

where Z is defined as,

$$Z = \int_{\vec{r}_\alpha(0)=\vec{0}} D\vec{r}_\alpha(s_\alpha) \exp\{-S_t[\vec{r}_\alpha(s)\} . \qquad (51)$$

Using the definition given in Eq. (36) for $I(\vec{R},N;\vec{0},0)$, we find,

$$Z = \int d\vec{R}\ I(\vec{R},N;\vec{0},0). \qquad (52)$$

Using the identity of Eq. (37), we get

$$= [q^3(N/6\pi\ell)^{3/2}] \int_{-\infty}^{\infty} d\vec{y} \int_{\vec{r}(0)=\vec{0}} D\vec{r}(s) \exp\{-S_t^{\vec{y}}[\vec{r}(s)]\} \qquad (53)$$

$$= [q^3(N/6\pi\ell)^{3/2}] \int_{-\infty}^{\infty} d\vec{y} \int d\vec{R}\ G_{ho}(\vec{R}+\vec{y},N;\vec{y},0) \qquad (54)$$

$$= \left[\frac{qN/3}{\sinh\,(qN/3)}\right]^{3/2} . \tag{55}$$

(See Appendix A2 for details of the derivation Eq.(55)). In the ground state dominance approximation, i.e., when $(qN/3) \gg 1$ this reduces to

$$Z \approx [2qN/3]^{3/2} \exp\,(-qN/2). \tag{56}$$

The integrals that occur in $\langle S-S_T\rangle_T$ can be evaluated as follows. They are

$$\text{(i)} \qquad \sum_{\alpha,\beta=1}^{n} q^2/(12\ell N)\int_0^N ds\int_0^N dt\ \langle[\vec{r}_\alpha(s)-\vec{r}_\beta(t)]^2\rangle_t \tag{57}$$

$$= -(q/2)\,\frac{\partial}{\partial q}\left[\ \ln\left\{\left[\prod_{\alpha=1}^{n}\ \int_{\vec{r}(0)=\vec{0}} D\vec{r}_\alpha(s_\alpha)\right]\exp\,[-S_T]\right\}\right] \tag{58}$$

$$= -(3nq/4)\,\frac{\partial}{\partial q}\ \ln\left[\frac{qN/3}{\sinh\,(qN/3)}\right] \tag{59}$$

$$= -(3nq/4) + (nqN/4)\,\coth(qN/3) \tag{60}$$

$$\approx nqN/4, \text{ in the } (qN/3) \gg 1 \text{ limit.} \tag{61}$$

(ii) $I_{\alpha\beta}$

$$I_{\alpha\beta} = (1/2)\int_0^N ds\int_0^N dt\ \langle B(\vec{r}_\alpha(s)-\vec{r}_\beta(t))\rangle_T \tag{62}$$

Using Eq. (48) we find

$$= \frac{\frac{v^2}{2}\int_0^N ds \int_0^N dt \int d\vec{y}\int d\vec{R} \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{R}} D\vec{r}(t)e^{-S_t^{\vec{y}}} \exp\,[\,-[\vec{r}_\alpha(t)-\vec{r}_\beta(s)]^2/R_o^2]}{\int d\vec{R}\int d\vec{y} \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{R}} D\vec{r}(t)e^{-S_t^{\vec{y}}}} . \qquad (63)$$

(See Appendix A3 for details of the evaluation of $I_{\alpha\alpha}$) $I_{\alpha\alpha}$ (where $\alpha=\beta$) and $I_{\alpha\beta}$ can be calculated numerically. To attack the proble analytically, we can make use of the ground state dominance approximation to get the following: $I_{\alpha\alpha} \approx (NV)^2/\ 2\ [1+2\ell/(qR_o{}^2)]^{3/2}$ and $I_{\alpha\beta} \approx (NV)^2/\ 2\ [1+6\ell/(qR_o{}^2)]^{3/2}$. We combine the above results and introduce the dimensionless variables $\bar{N} = N/\ell$, $\bar{q} = q\ell$, $\bar{R}_o = R_o/\ell$ and $\bar{V} = V\ell$ to get the free energy,

$$\beta F_1(N) = \frac{(\bar{N}\ \bar{V})^2}{2}\ (\bar{q}\ \bar{R}_o{}^2)^{3/2} \left[\frac{1}{(6 + \bar{q}\ \bar{R}_o{}^2)^{3/2}} - \frac{1}{(2 + \bar{q}\ \bar{R}_o{}^2)^{3/2}} \right] + \bar{q}\ \bar{N}/4\ . \qquad (64)$$

Now we define $u = \bar{q}\ \bar{R}_o{}^2$ and Eq. (64) could be written as,

$$\beta F_1(\bar{N}) = \frac{(\bar{N}\ \bar{V})^2}{2}\ u^{3/2} \left[\frac{1}{(6 + u)^{3/2}} - \frac{1}{(2 + u)^{3/2}} \right] + \frac{u\bar{N}}{4\bar{R}_o{}^2}. \qquad (65)$$

Or

$$2\beta\bar{F}_1(N)/(\bar{N}\ \bar{V})^2 = f(u) + pu \qquad (66)$$

where $p = 1/(2\bar{N}\ \bar{V}^{\ 2}\ \bar{R}_o{}^2)$ and

$$f(u) = -[u/(2+u)]^{3/2} + [u/(6+u)]^{3/2}. \qquad (67)$$

We now define $\bar{F}_1(u) = 2\bar{F}_1(N)\beta/(\bar{N}\ \ \bar{V})^2$. In the above, pu represents the increase in free energy if one tried to localize the polymer chain to a size $\sim q^{-1/2}$, while $f(u)$ represents the increase due to effective attraction between different segments of the polymer, caused by the random potential. The size of the polymer chain can be estimated using the equation (44) for $G^t(\vec{R},N;\vec{0},0)$ to be,

$$\langle \vec{R}^2 \rangle = 6\ell^2 \bar{R}_o^{\,2} \tanh[u\bar{N}/(6\bar{R}_o^{\,2})]/u \ . \qquad (68)$$

(See Appendix A4 for the derivation of Eq. (68).)

III.5. RESULTS

In the approximate case, we made a plot of $\bar{F}_1(u)$ as a function of u for different values of p (See Fig. III.1). For small chain lengths or weak randomness such that the value of p is greater than 0.1405, $F_1(u)$ has its minimum at $u=0$ and for this situation, Eq. (68) gives $\langle \vec{R}^2 \rangle = N\ell$, which is the value for a free polymer molecule. But as one decreases the value of p and when it becomes less than 0.1405, the function $\bar{F}_1(u)$ suddenly develops a new minimum at a non-zero value for u. This means that there is a discontinuous change over from the free polymer like behaviour ($\langle \vec{R}^2 \rangle \propto N$) to one that is not. In the limit where randomness or the length of the chain becomes very large, we have $p << 1$ and the first term on the right hand side of the equation (66) may be neglected so that $\bar{F}_1(u) = f(u)$. The best value of u is then given by

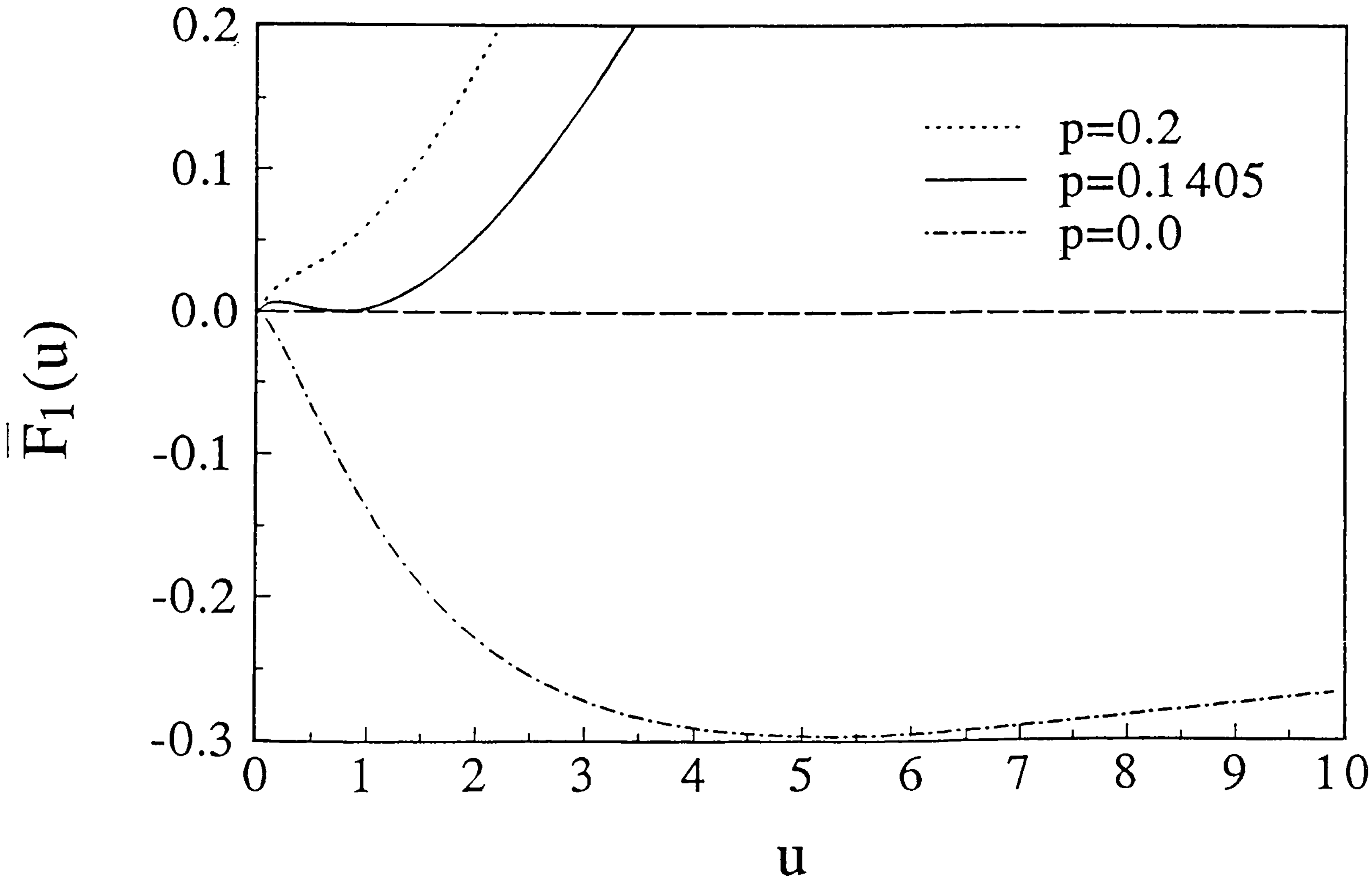

Fig. III.1. Plot of $F_1(u)$ against u for different values of p

$$\frac{3}{(6+u)^{5/2}} = \frac{1}{(2+u)^{5/2}} \,. \tag{69}$$

Eq.(69) can be solved to get $u = 5.248$. Therefore, the size of the polymer chain for $p \gg 1$ is given by, $\langle \vec{R}^2 \rangle = 6\bar{R}_o{}^2/5.248$,a constant, independent of the length of the polymer molecule.

It is interesting to compare the above predictions with what one would have obtained, if one used the trial action, given in Eq. (33), used by EM in their calculations. In this case, in the ground state dominance approximation, we find that $I_{\alpha\alpha} = I_{\alpha\beta}$, even if $\alpha \neq \beta$. Therefore, the free energy would not have any contribution from the interactions between the replicas and the only contribution is the first term, pu in the equation (66). So the minimum occurs always at $u = 0$ and thus the use of this local action does not predict the collapse of the polymer.

It is quite easy to generalize our results in one and two dimensions.

In one dimension we have,

$$2F_1/(\bar{N}\,\bar{V})^2 = -[u/(2+u)]^{1/2}+[u/(6+u)]^{1/2} + (u/6\bar{N}\,\bar{V}^2\,\bar{R}_o{}^2). \tag{70}$$

It is interesting to analyze Eq. (70) in the limit when $u \to 0$. In this case Eq. (70) will reduce to

$$2F_1/(\bar{N}\,\bar{V})^2 = u^{1/2}\left[\frac{1}{6^{1/2}} - \frac{1}{2^{1/2}}\right] + (u/6\bar{N}\,\bar{V}^2\,\bar{R}_o{}^2) \,. \tag{71}$$

The term in brakets in Eq. (71) is negative so that there is always a minimum at $u > 0$. As $\vec{V} \to \infty$, it is found that the polymer is collapsed to a chain size of $2\ell^2\bar{R}_o{}^2/1.7034$.

In two dimensions we have ,

$$2F_1/(\bar{N}\ \bar{V})^2 \ = \ -[u/(2+u)]+[u/(6+u)] + (u/3\bar{N}\ \bar{V}^2\ \bar{R}_o^{\ 2}). \qquad (72)$$

The first derivative F_1' is given by the expression

$$F_1' \ = (\bar{N}\ \bar{V})^2\ \{-[2/(2+u)^2]+[6/(6+u)^2]\} + \bar{N}/6\bar{R}_o^{\ 2}\ . \qquad (73)$$

In this case when the randomness is increased, we have minimum at $u = (12)^{1/2}$. The chain size then becomes $2\ell^2\bar{R}_o^{\ 2}/\sqrt{3}$.

We have also done the exact calculation of the free energy by evaluating the integrals $I_{\alpha\alpha}$ and $I_{\alpha\beta}$, defined by the Eq. (63) numerically (The derivations are given in the Appendix A3). $I_{\alpha\alpha}$ could be written as an integral,

$$I_{\alpha\alpha} = (\bar{V}^{\ 2}/2) \int_0^N t\ dt \left[\ 1+(4/\bar{q}\ \bar{R}_o^{\ 2}\ )\ \frac{\sinh(\bar{q}t/3)\ \sinh(\bar{q}(\bar{N}-t)/3)}{\sinh\ (\bar{q}\ \bar{N}/6)} \right]^{-3/2} \qquad (74)$$

and the expression for $I_{\alpha\beta}$ is given in Appendix A3.

We have made plots of the value of $\bar{q}$ that makes the free energy a minimum as a function of $\bar{V}$, for different values of the parameter $\bar{N}$ (See Fig. III.2). In the case of ground state dominance, $\bar{q} = 0$ remains the minimum for weak randomness but as one increases randomness, there is a discontinuous change over of the minimum to positive values of $\bar{q}$. In the exact calculations, we found that even for weak randomness, the minimum no longer remains at $\bar{q} = 0$, but at non zero values of $\bar{q}$.

As the value of $\bar{N}$ increases, it is clear from Fig. III.2 that the curves for the exact and approximate cases are almost identical for large values of $\bar{q}$, as expected. For large values of $\bar{q}$, the curves for the approximate and the exact cases are almost indistinguishable in the figure. But the two curves differ

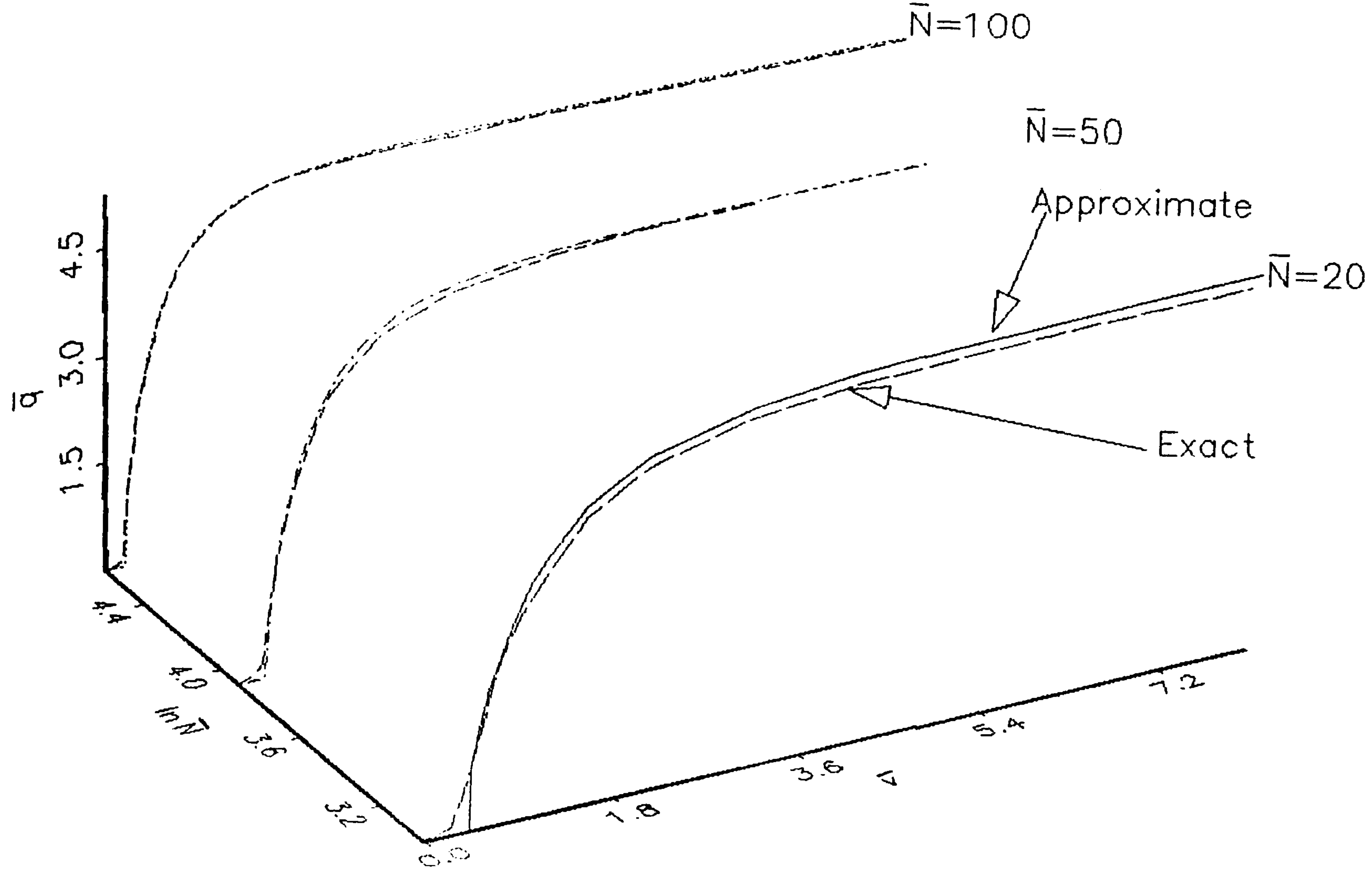

Fig. III.2. Plot of $\bar{q}$ as a function of $\bar{V}$ for different $\bar{N}$

considerably in the small $\overline{q}$ region as clear from Fig. III.3 which gives a plot of $\overline{q}$ as a function of $\overline{V}$ for $\overline{N} = 100$. The curve for the exact case show a smooth increase in $\overline{q}$ with randomness whereas that for the approximate calculations show that $\overline{q} = 0$ remains the minimum for small valus of randomness. For both cases, it is clear that the collapse transition occurs at a much lower magnitude of randomness $\overline{N}$ increases.

In the exact calculations, we found that the minimum of the free energy of the polymer chain always occur at a non zero value for $\overline{q}$, in contradiction with the prediction by the ground state dominance approximation. This is not surprising, as the ground state dominance approximation breaks down in the vicinity of $\overline{q} = 0$. In the approximate calculations, we have found that the transition to the collapsed state is sudden where as in the exact case, it is found to be smooth.

In order to confirm that the collapse transition is a discontinuous one in the approximate case, we have made plots of the free energy of the chain as a function of $\overline{q}$ in Fig. III.4. In the case shown in Fig. III.3, the collapse occurs for $\overline{V} = 0.1890$. So in Fig. III.4, we plot the free energy as a function of $\overline{q}$ for $\overline{V} = 0.1880$ and 0.1890. For $\overline{V} = 0.1880$, $\overline{q} = 0$ still corresponds to the lowest free energy, while for $\overline{V} = 0.1890$, one has a new minimum, at $\overline{q} = 0.7690$. So as $\overline{V}$ is increased from 0.1880 to 0.1890, the best value of $\overline{q}$ jumps from 0 to 0.7690, showing that the collapse of the polymer occurs suddenly. We have made a similar plot for the exact case in Fig. III.5, and found that the change of $\overline{q}$ with $\overline{V}$ is smooth, eventhough it is very rapid near $\overline{V} =$

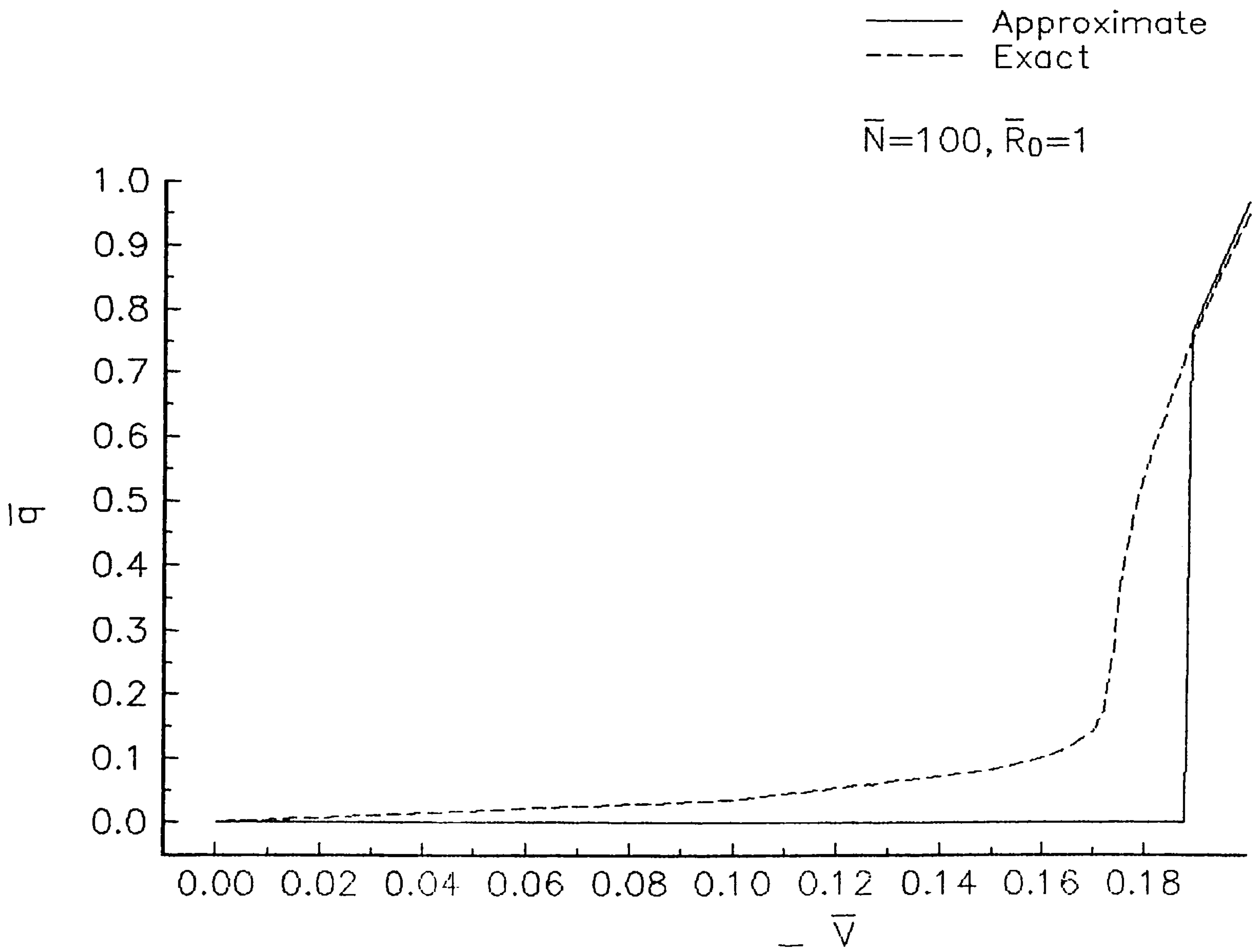

Fig. III.3. Plot of $\bar{q}$ as a function of $\bar{V}$

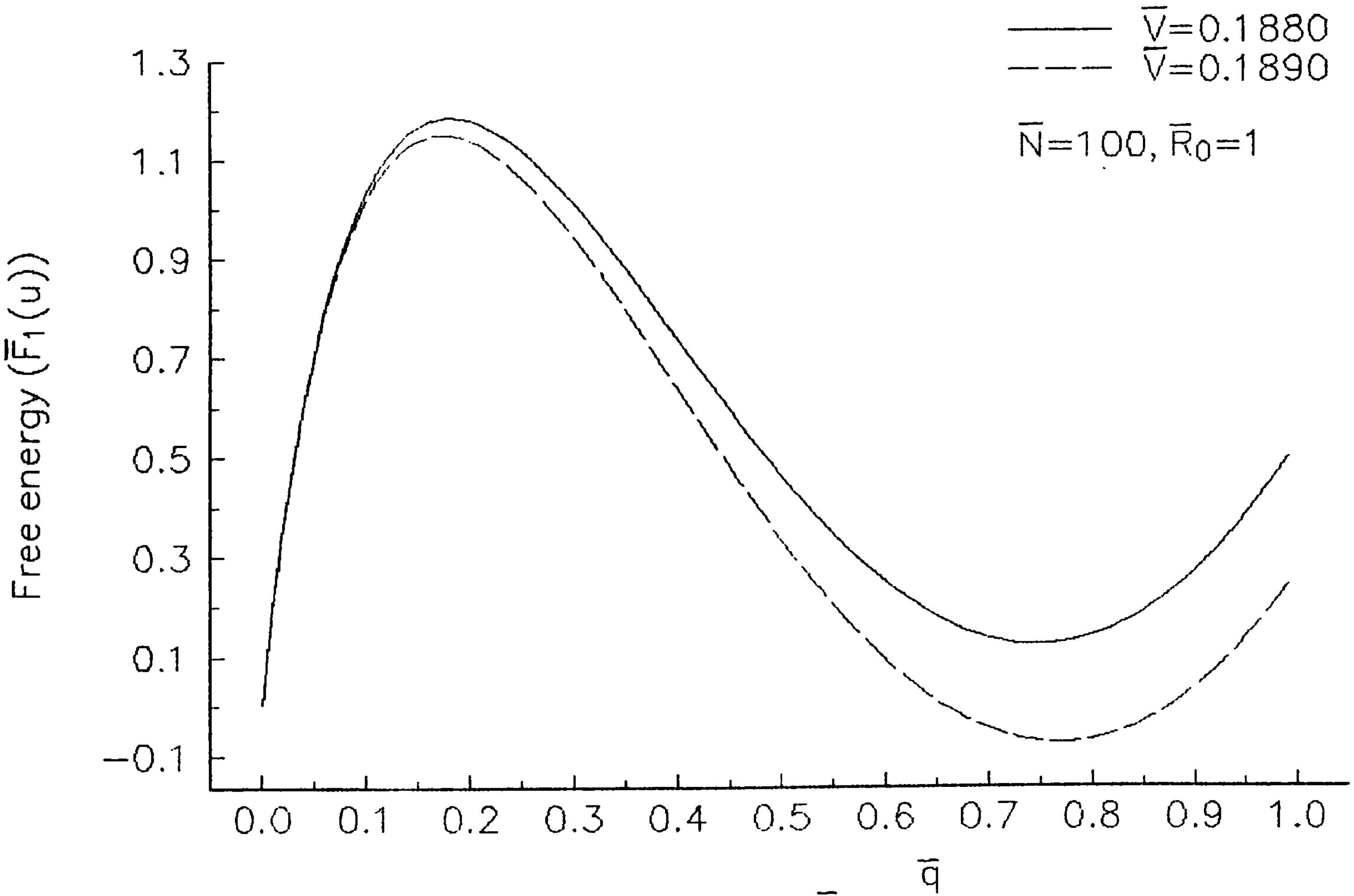

Fig. III.4. Plot of free energy vs $\bar{q}$

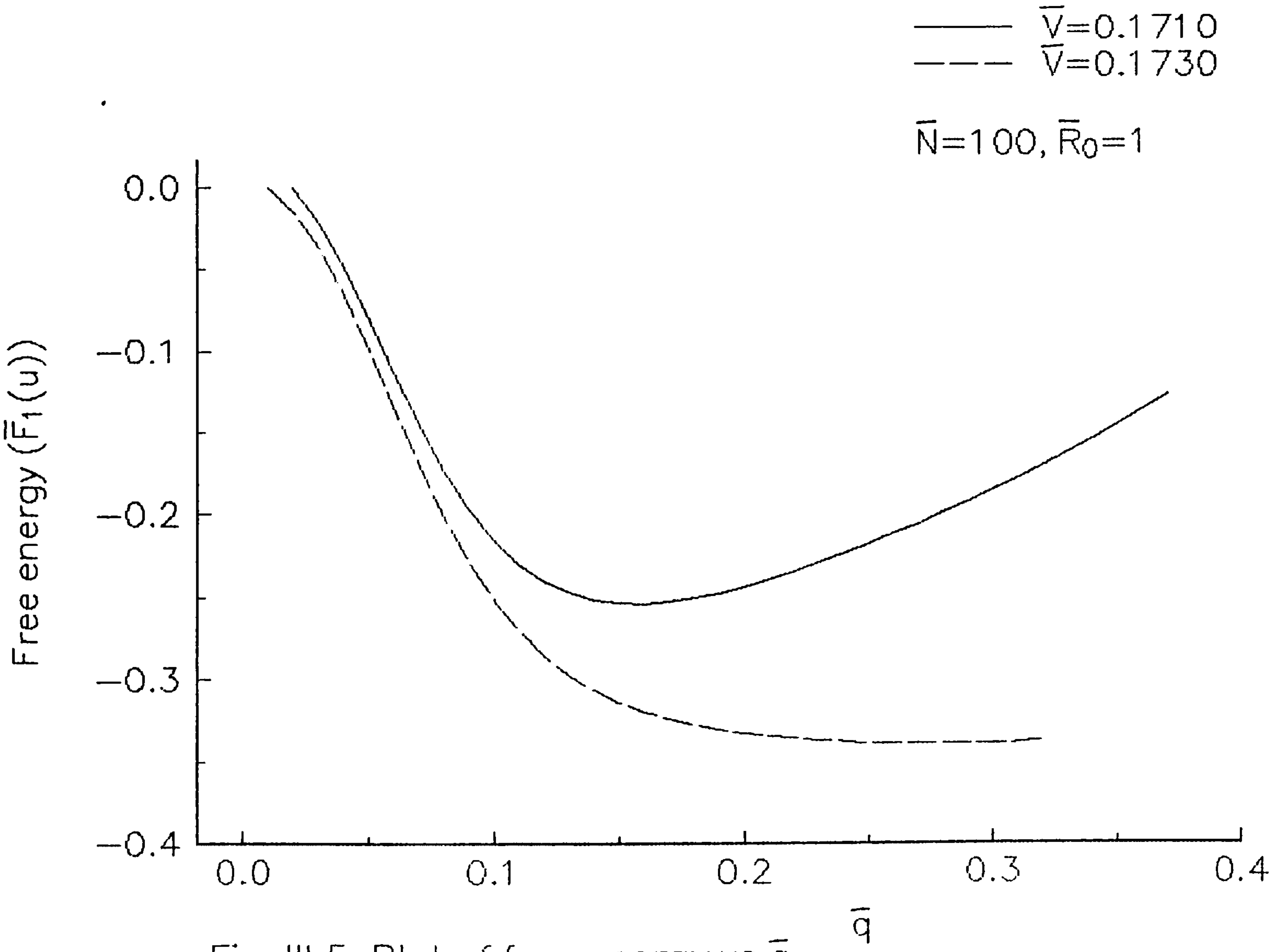

Fig. III.5. Plot of free energy vs $\bar{q}$

0.1710.

We have made plots of the size $[\langle \vec{R}^2 \rangle]^{1/2}$ as a function of randomness $\bar{V}$ in Fig. III.6. In the approximate case, the polymer chain does not show a reduction in the size with randomness until it reaches a certain limit, and a sudden reduction in the size as randomness goes beyond this limit. Therefore, the approximate calculations predict that the chain behaves like a free polymer initially followed by a sudden decrease in size to the collapsed state.

However in the exact calculations, we found that as randomness increases initially, there is a continuous reduction in the size of the polymer chain which implies that the polymer chain is no longer a free one. This has been made clear in Fig. III.6. Here we found that as randomness increases, the size of the polymer chain shows a smooth reduction, approaching a limiting N independent value.

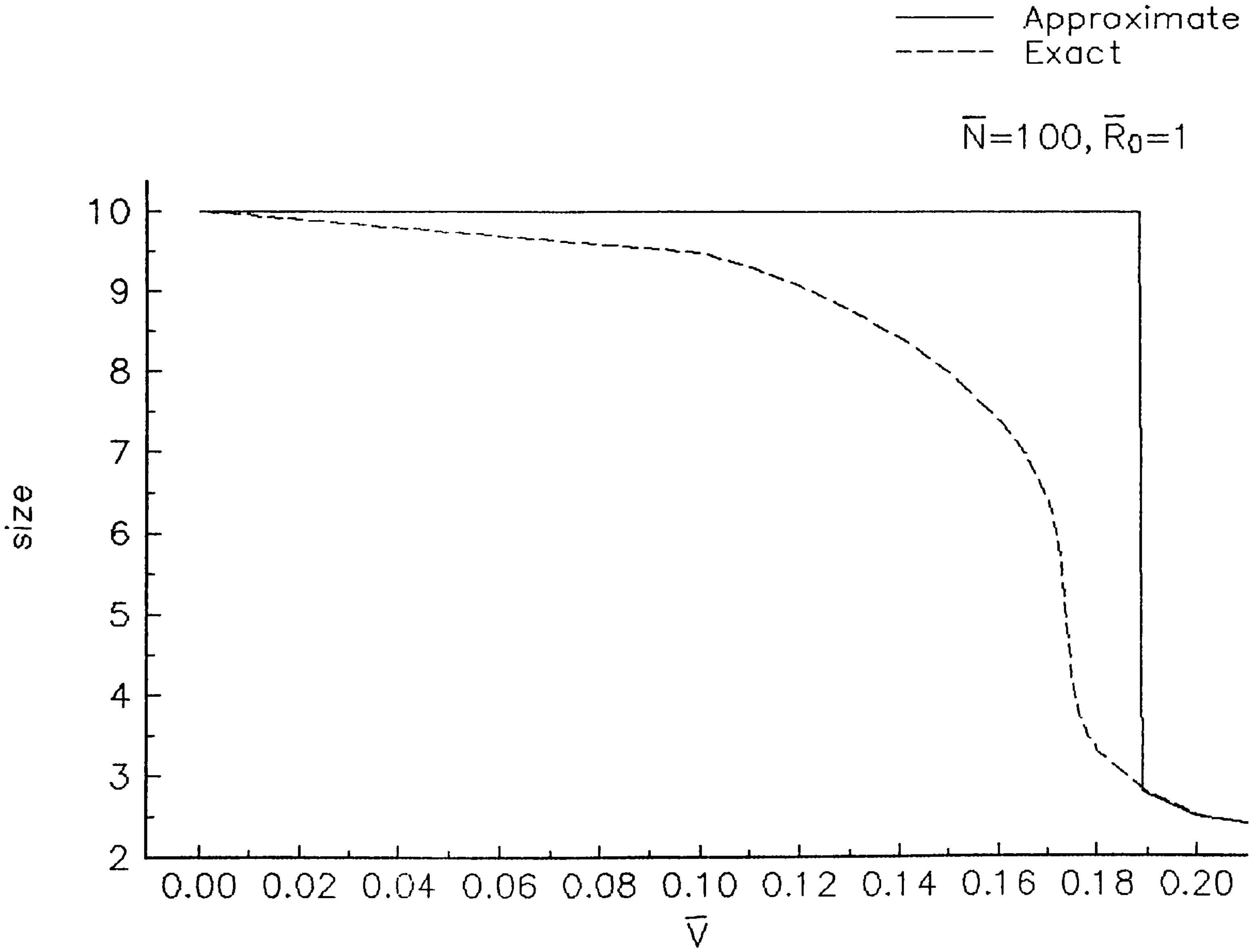

Fig. III.6. Plot of size as a function of $\overline{q}$

Appendix A1

Simplification of e^{-S_t}

$S_t[\vec{r}(s)]$ is given by Eq. 32 as,

$$S_t[\vec{r}(s)] = \frac{3}{2\ell}\int_0^N ds \left[\frac{d\vec{r}(s)}{ds}\right]^2 + (q^2/12\ell N)\int_0^N ds \int_0^N dt \quad [\vec{r}(s)-\vec{r}(t)]^2. \tag{A1.1}$$

We note that

$$\exp\left[-(q^2/12\ell N)\int_0^N ds \int_0^N dt \; [\vec{r}(s)-\vec{r}(t)]^2\right]$$

$$= \exp\left[-(q^2/6\ell)\int_0^N dt \; [\vec{r}(t)]^2 + (q^2/6\ell N)\left[\int_0^N dt \; \vec{r}(t)\right]^2\right]. \tag{A1.2}$$

$\exp\left[(q^2/6\ell N)\left[\int_0^N dt \quad \vec{r}(t)\right]^2\right]$ in Eq. (A1.2) could be written as,

$$(3\ell N/2\pi q^2)^{3/2}\int_{-\infty}^{\infty} d\vec{y}_1 \; \exp\left[-[3\ell N\vec{y}_1^{\,2}/2q^2] + \int_0^N dt \; \vec{r}(t).\vec{y}_1\right] \tag{A1.3}$$

where $\vec{y}_1$ is a three dimensional vector. Therefore,

$$\exp\left[-(q^2/12\ell N)\int_0^N ds\int_0^N dt \; [\vec{r}(s)-\vec{r}(t)]^2\right] = \exp\left[-(q^2/6\ell)\int_0^N dt \; [\vec{r}(t)]^2\right]$$

$$(3\ell N/2\pi q^2)^{3/2}\int_{-\infty}^{\infty} d\vec{y}_1 \; \exp\left[-[3\ell N\vec{y}_1^{\,2}/2q^2] + \int_0^N dt \; \vec{r}(t).\vec{y}_1\right]. \tag{A1.4}$$

Hence $\exp(-S_t)$ can be written as

$$(3\ell N/2\pi q^2)^{3/2}\int_{-\infty}^{\infty} \exp\,[-3\ell N\vec{y}_1^{\,2}/2q^2]\; \exp\left[-\int_0^N \left[\frac{3}{2\ell}\left(\frac{d\vec{r}(t)}{dt}\right)^2 + \right.\right.$$

$$(q^2/6\ell)\ \vec{r}(t)^2 - \vec{y}_1.\vec{r}(t)\ \Big]\ dt\ \Big]\ d\vec{y}_1. \tag{A1.5}$$

Now we make a change of variables in Eq. (A1.5) by defining, $\vec{y} = (3\ell\vec{y}_1/q^2)$. Then Eq. (A1.5) becomes,

$$\exp(-S_t) = (N/6\pi\ell)^{3/2}\ q^3 \int_{-\infty}^{\infty} \exp\left[-\int_0^N \left[\frac{3}{2\ell}\left(\frac{d\vec{r}(t)}{dt}\right)^2\right.\right.$$

$$\left.\left. + (q^2/6\ell)\ \vec{r}(t)^2 - (q^2/6\ell)\vec{y}^2 - (q^2/3\ell)\ \vec{y}.\vec{r}(t)\ \right] dt\ \right] d\vec{y} \tag{A1.6}$$

Eq. (A1.6) can be rearranged to get Eq. (35).

APPENDIX A2

Calculation of the propagator

Following Eq. (41), we can write,

$$G_{ho}^{\vec{y}}\ (\vec{R},N;\vec{0},0) = [q/2\pi\ell\ \sinh\ (qN/3)]^{3/2}$$

$$\exp\left[-\frac{q}{2\ell\sinh(qN/3)}[\cosh(qN/3)(\vec{R}+\vec{y})^2+\vec{y}^2)-2\vec{R}\vec{y}]\right]. \qquad (A2.1)$$

Integrating over $\vec{y}$, we get,

$$\int d\vec{y}\ G_{ho}(\vec{R}+\vec{y},N;\vec{y},0) = [1/2(\cosh(qN/3)-1)]^{3/2}$$

$$\exp\left\{-\left[\frac{q\ \coth(qN/6)}{4\ell}\right]R^2\right\} \qquad (A2.2)$$

$$\int d\vec{R}\int d\vec{y}\ G_{ho}(\vec{R}+\vec{y},N;\vec{y},0) = [2\pi\ell/q\ \sinh\ (qN/3)]^{3/2}\ . \qquad (A2.3)$$

Taking the ratio of Eq. (A2.2) and (A2.3), we get

$$G^{t}(\vec{R},N;\vec{0},0) = \frac{\int d\vec{y}\ G_{ho}(\vec{R}+\vec{y},N;\vec{y},0)}{\int d\vec{R}\int d\vec{y}\ G_{ho}(\vec{R}+\vec{y},N;\vec{y},0)} \qquad (A2.4)$$

$$= \left[\frac{q\coth(qN/6)}{4\pi\ell}\right]^{3/2}\ \exp\left[-\frac{q\vec{R}^2\ \coth(qN/6)}{4\ell}\right]. \qquad (A2.5)$$

which is Eqn. (44). We have,

$$Z = [q^3(N/6\pi\ell)^{3/2}]\int_{-\infty}^{\infty}d\vec{y}\int d\vec{R}\ G_{ho}(\vec{R}+\vec{y},N;\vec{y},0). \qquad (A2.6)$$

Substituting Eq. (A2.3) in (A2.6), we get,

$$Z = \left[\frac{qN/3}{\sinh\,(qN/3)} \right]^{3/2}$$ which is Eq. (55).

APPENDIX A3

Calculation of $I_{\alpha\alpha}$ and $I_{\alpha\beta}$

$I_{\alpha\alpha}$ can be written as

$$I_{\alpha\alpha} = \frac{\dfrac{v^2}{2} \displaystyle\int_0^N dt \int_0^N ds \int d\vec{y} \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{R}} D\vec{r}(t) e^{-S_t} \exp\left[-[\vec{r}_\alpha(t)-\vec{r}_\beta(s)]^2/R_o{}^2 \right]}{\displaystyle\int d\vec{y} \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{R}} D\vec{r}(t) e^{-S_t}} \qquad (A3.1)$$

where $\vec{y}$ is three dimensional and S_t is given by Eq. (32) of Chapter III.

$$\int d\vec{y} \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{R}} D\vec{r}(t) e^{-S_t^{\vec{y}}} = \exp[-qN/2]$$ in the limit $(qN/3) >> 1$ limit

(ground state dominance approximation).

The numerator in Eq. (A3.1) can be written as

$$= (v^2/2) \int_0^N dt_\alpha \int_0^N dt_\beta \int d\vec{r}_2 \int d\vec{r}_1 \exp\left[-[\vec{r}_1-\vec{r}_2]^2/R_o{}^2 \right] \int d\vec{y} \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{R}} D\vec{r}(t)\ e^{-S_t^{\vec{y}}}$$

$$\delta(\vec{r}_1-\vec{r}_\alpha(t_\alpha))\ \delta(\vec{r}_2-\vec{r}_\beta(t_\beta)). \qquad (A3.2)$$

Eq. (A3.2) may be written as a product of three propagators,

$$= (v^2/2) \int_0^N dt_\alpha \int_0^N dt_\beta \int d\vec{r}_2 \int d\vec{r}_1 \exp\left[-[\vec{r}_1-\vec{r}_2]^2/R_o{}^2 \right] \int d\vec{y}\ G_{ho}^{\vec{y}}(\vec{R},N|\vec{r}_2,t_\beta)$$

$$\times\ G_{ho}^{\vec{y}}(\vec{r}_2,t_\beta|\vec{r}_1,t_\alpha)\ G_{ho}^{\vec{y}}(\vec{r}_1,t_\alpha|\vec{0},0) \qquad (A3.3)$$

$$= (V^2/2) \int_0^N dt_\alpha \int_0^N dt_\beta \int d\vec{r}_2 \int d\vec{r}_1 \exp [-[\vec{r}_1-\vec{r}_2]^2/R_o^2$$

$$\int d\vec{y}\; G_{ho}(\vec{R}+\vec{y},N|\vec{r}_2+\vec{y},t_\beta)\; G_{ho}(\vec{r}_2+\vec{y},t_\beta|\vec{r}_1+\vec{y},t_\alpha)\; G_{ho}(\vec{r}_1+\vec{y},t_\alpha|\vec{y},0). \qquad (A3.4)$$

The propagators in Eq. (A3.4) correspond to harmonic oscillators and are given by Eq. (41) of Chapter III. In the ground state dominance approximation, the expression for the propagator reduces to a simpler form and can be written as,

$$G_{ho}(\vec{r},N;\vec{r}'\,0) \approx \exp [-q \{\vec{r}^2 + \vec{r}'^2\}/2\ell - qN/2] \; [q/\pi\ell]^{3/2}. \qquad (A3.5)$$

We introduce Eq. (A3.5) in (A3.4), analytically evaluate the integrals in the (qN/3) >> 1 limit to get

$$I_{\alpha\beta} \simeq (NV)^2/ \; [[1+2\ell/(qR_o^2)]^{3/2}] \qquad (A3.6)$$

In order to evaluate $I_{\alpha\alpha}$ exactly, we have introduced the exact expressions for the propagator in Eq. (A3.4). We have the integral

$$I_{\alpha\alpha} = (V^2/2) \int_0^N I(t)\; dt \qquad (A3.7)$$

where

$$I = \int d\vec{r}_1 \int d\vec{r}_2\; G_{ho}(\vec{r}_2,\vec{r}_1;t)\; G_{ho}(\vec{r}_1,\vec{r}_2;N-t) \exp [-[\vec{r}_1-\vec{r}_2]^2/R_o^2 . \qquad (A.3.8)$$

Substituting the expressions for the propagators in Eq. (A3.8) and after simplification, we get

$$I = \left[1+(4/\bar{q}\;\; \bar{R}_o^2) \frac{\sinh(\bar{q}t/3)\; \sinh(\bar{q}(\bar{N}-t)/3)}{\sinh\,(\bar{q}\; \bar{N}/6)} \right]^{-1/2} . \qquad (A3.9)$$

Therefore, we will have

$$I_{\alpha\alpha} = (V^2/2) \int_0^N t\,dt \left[1+(4/\bar{q}\ \ \bar{R}_o{}^2) \frac{\sinh(\bar{q}t/3)\ \sinh(\bar{q}(\bar{N}-t)/3)}{\sinh\ (\bar{q}\ \bar{N}/6)} \right]^{-3/2} \tag{A3.10}$$

In the case of $I_{\alpha\beta}$, instead of Eq.(A3.5), we will have a product of four propagators,

$$= (V^2/2) \int_0^N dt_\alpha \int_0^N dt_\beta \int d\vec{r}_2 \int d\vec{r}_1 \exp\ [\,-[\vec{r}_1-\vec{r}_2]^2/R_o{}^2$$

$$\int d\vec{y}_\alpha \int d\vec{y}_\beta\ G_{ho}(\vec{R}+\vec{y},N|\vec{r}_1+\vec{y}_\alpha,t_\alpha)\ G_{ho}(\vec{r}_1+\vec{y}_\alpha,t_\alpha|\vec{y}_\alpha,0)$$

$$G_{ho}(R+\vec{y}_\beta,N|\vec{r}_2+\vec{y}_\beta,t_\beta)\ G_{ho}(\vec{r}_2+\vec{y}_\beta,t_\beta|\vec{y}_\alpha,0). \tag{A3.11}$$

Eq. (A3.11) can be evaluated in the ground state dominance approximation to get

$$I_{\alpha\beta} \simeq (NV)^2/\ [\,[1+6\ell/(qR_o{}^2)]^{3/2}] \tag{A3.12}$$

To evaluate $I_{\alpha\alpha}$ and $I_{\alpha\beta}$ exactly, we introduce the expressions for the propagators in Eq. (A3.10) to get

$$I_{\alpha\beta} = (V^2/2) \int_0^N dt \int_0^N ds \int d\vec{r}_2 \int d\vec{r}_1$$

$$\frac{1}{\mathrm{ch}(qs/3)\mathrm{sh}(qt/3)[\mathrm{th}(qs/3)+[\mathrm{th}(qs/3)+2\mathrm{th}(qt/6)]^{1/2}}$$

$$\frac{1}{\mathrm{ch}(qt/3)\mathrm{sh}(qs/3)[\mathrm{th}(qt/3)+[\mathrm{th}(qt/3)+2\mathrm{th}(qs/6)]^{1/2}}$$

$$\exp\left\{-\frac{q}{2\ell}\left[\coth(qt/3)\ -\ \frac{\mathrm{th}^2(qt/6)}{[\mathrm{th}(qs/3)+2\mathrm{th}(qt/6)]}\right]\vec{r}_1{}^2\right\}$$

$$\exp\left\{-\frac{q}{2\ell}\left[\coth(qs/3)\ -\ \frac{\mathrm{th}^2(qs/6)}{[\mathrm{th}(qt/3)+2\mathrm{th}(qs/6)]}\right]\vec{r}_2{}^2\right\} \tag{A3.13}$$

In Eq. (A3.12), the integrals involving $\vec{r}_1$ and $\vec{r}_2$ are Gaussian, which can be easily performed resulting in a double integral over t and s. This can be evaluated numerically using standard procedures.

APPENDIX A4

The size of the polymer chain

The size of the polymer is given by,

$$\langle (R(N)-R(0))^2 \rangle = \int d\vec{R}\, \vec{R}^2 \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{R}} D\vec{r}(t)\; e^{-S_t} \left[\int d\vec{R} \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{R}} D\vec{r}(t)\; e^{-S_t} \right]^{-1} . \tag{A4.1}$$

$$= \int d\vec{R}\, \vec{R}^2\, P(\vec{R}) \tag{A4.2}$$

where

$$P(\vec{R}) = \frac{\int d\vec{R} \int d\vec{y}\; G_{ho}(\vec{R}+\vec{y},N;\vec{y},0)\; \vec{R}^2}{\int d\vec{R} \int d\vec{y}\; G_{ho}(\vec{R}+\vec{y},N;\vec{y},0)} . \tag{A4.3}$$

This quantity has been evaluated to get Eq. (44) of Chapter III. i.e.,

$$= \left[\frac{q\coth(qN/6)}{4\pi \ell} \right]^{3/2} \exp\left[- \frac{q\vec{R}^2 \coth(qN/6)}{4\ell} \right] . \tag{A4.4}$$

Substituting this in Eq. (A4.2), we get,

$$\langle \vec{R}^2 \rangle = 6\ell \tanh[(qN/6)]/q . \tag{A4.5}$$

This on introducing dimensionless variables and defining $u = \bar{q}\, R_o^{\,2}$ we get Eq. (68) of Chapter III.

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CHAPTER - IV

THE ADSORPTION OF POLYMERS ON A CHEMICALLY RANDOM SURFACE

IV.1. INTRODUCTION

The adsorption of polymers on surfaces has been a subject of extensive experimental and theoretical investigations [1-3, 9-15]. In spite of this interest and of a vast body of experiments [2], the processes involved are only poorly understood. Since such processes are important in both technology and biophysics, a systematic theoretical investigation of the same are desirable. Furthermore, since the adsorption of atoms and molecules on solid surfaces has revealed a variety of interesting phenomena [3], the study of adsorption of macromolecules also merits further attention. Finally, since the statistical mechanics of polymer conformations in the bulk of dilute, semi dilute and concentrated polymer solutions has become well understood [4-8] and a large number of experimental observations on such bulk properties could be explained, it is of interest to consider the effect of an interface.

The statistical mechanics of such an adsorbed polymer chain presents a variety of novel and interesting aspects, and has received considerable attention in the recent past [15]. Unfortunately, most theoretical attempts have been focused on planar, uniform surfaces [9-11], which can only rarely be attained in practice.

In nature, adsorption of polymers takes place not only at planar, regular surfaces but also at other kinds of surfaces, viz., spherical and cylindrical surfaces, which are rough, with differing extents of roughness. For eg., it is quite well known that colloidal particles, which are mostly spherical in shape in non polar solvents, are often maintained dispersed by means of adsorbed polymers [16] and adsorption can also take place on micelles [17], which can have any shape. Recently, attempts were made to understand the effect of local curvature on the adsorption characteristics [18-20].

In practice, the surface roughness is random unless great care is taken to develop a planar, perfect surface. The randomness on a surface can arise from either physical or chemical origins. In the case of physical roughness, the local curvature of the surface is a random variable. Such a surface can be modeled as consisting of 'hills' and 'valleys', made up of protrusions of spheres or cylinders of appropriate curvatures at different spatial localizations. In the case of chemical roughness, certain regions of the surface (either planar or physically rough) have different affinities for the polymers compared to the rest of the surface.

There have not yet been any controlled experiments to study the effect of surface roughness, even though the adsorption on rough surfaces can reveal a lot of information on the nature of the surface. There have been a few theoretical investigations focusing on the adsorption on a periodically rough surfaces and also on a fractal surface [21]. There have also been some investigations on the adsorption on both chemically and physically random surfaces [15].

Adsorption of polymer chains on a surface is governed by the competition between two conflicting effects viz., the gain in potential energy obtained by the monomers by adsorbing to the attractive surface and the loss in chain entropy associated with the reduction in the number of possible chain conformations of the adsorbed chains, when compared with that of free chains.

This chapter investigates a model for adsorption on a planar, but chemically random surface. The chemical randomness may be caused by impurities on the surface or because the adsorption is on the surface of an alloy, which has a random distribution of its components on the surface. Among the many mathematical formulations of the adsorption of polymer chains to a surface, the simplest is the *propagator method* introduced by Edwards and later reviewed by de Gennes [5] and Wiegel [22].

IV.2. ADSORPTION ON A REGULAR SURFACE

We first discuss the de Gennes' approach [9] to the adsorption of the polymers on a flat, uniform surface. His approach is the following ;

$G(\vec{r},\vec{r}\,';N)$ is the probability distribution function, for a chain of length N, whose one end is at $\vec{r}\,'$. $G(\vec{r},\vec{r}\,';N)$ obeys the diffusion equation,

$$\{\partial/\partial N - (\ell^2/6)\nabla_{\vec{r}}^{\,2}\}\; G(\vec{r},\vec{r}\,';N) = \delta(N)\delta(\vec{r}-\vec{r}\,') \; . \tag{1}$$

We imagine that there is a surface at z=0. We adopt the notation

$$\vec{r} = (\vec{x},z) \; . \tag{2}$$

The presence of the wall (surface), can lead to the attraction or repulsion of the polymer segments to it. This, according to de Gennes, is modeled by putting

$$\left[\frac{\partial \ln G(\vec{r},\vec{r}\,';N)}{\partial z}\right]_{z=0} = -c_o \; . \tag{3}$$

The sign of the constant c_o depends on the temperature. At low temperatures, the attractive interaction between the polymer and the surface dominates, resulting in adsorption. In such cases, c_o is positive whereas at higher temperatures when the repulsive interaction increases, c_o will have a negative sign. It is convenient to expand G in terms of the eigen functions of $\psi_m(\vec{r})$ of the problem. Equation (1) has solution of the form,

$$G(\vec{r},\vec{r}\,';N) = \sum_m \psi_m(\vec{r})\; \psi_m(\vec{r}\,')\; e^{-E_m N} \tag{4}$$

where $\psi_m(\vec{r})$ obeys,

$$\left[\frac{\partial \ln \psi(\vec{r},\vec{r}\,';N)}{\partial z}\right]_{z=0} = -c_o. \tag{5}$$

and are normalized according to,

$$\int_{z>0} \psi_m(\vec{r})\; \psi_m^*(\vec{r})\; d\vec{r} = 1. \tag{6}$$

de Gennes' prescription can easily be converted into a path integral one, in which the paths are not forbidden to the region z < 0 and hence are unconstrained.

IV.3. MODELING ADSORPTION ON A RANDOM SURFACE

To model adsorption on a planar, but random surface, we generalize Eq. (3) to

$$\left[\frac{\partial \ln G(\vec{r},\vec{r}\,';N)}{\partial z}\right]_{z=0} = -c_o - \nu(\vec{x}) \tag{7}$$

where $\nu(\vec{x})$ is a random function of $\vec{x}$.

IV.3.i. A path integral representation for $G(\vec{r},\vec{r}\,';N)$

A path integral expression for $G(\vec{r},\vec{r}\,';N)$ is very convenient to use, in our analysis below. To arrive at such a representation, we consider $\mathcal{G}(\vec{r},\vec{r}\,';N)$ defined by

$$\{\partial/\partial N - (\ell/6)\nabla_{\vec{r}}^{2} - \ell(c_o+\nu(\vec{x}))\delta(z)/3\}\ \mathcal{G}(\vec{r},\vec{r}\,';N) = \delta(N)\delta(\vec{r}-\vec{r}\,'). \tag{8}$$

$\mathcal{G}(\vec{r},\vec{r}\,';N)$ has the path integral representation ,

$$\mathcal{G}(\vec{r},\vec{r}\,';N) = \int_{\vec{r}(0)=\vec{r}\,'}^{\vec{r}(N)=\vec{r}} D\vec{r}(s)\ \exp\left\{-\frac{3}{2\ell}\int_0^N \dot{\vec{r}}(t)^2\,dt - (1/3)\int_0^N \ell(c_o+\nu(\vec{x}))\ \delta(z(t))\,dt\right\} . \tag{9}$$

Now consider

$$Q(\vec{r},\vec{r}';N) = \mathcal{G}(\vec{r},\vec{r}';N) + \mathcal{G}(\vec{r},P\vec{r}';N) \tag{10}$$

where $P\vec{r} = (\vec{x},-z)$. Clearly $Q(\vec{r},\vec{r}';N)$ is an even function of z.

Now

$$\left[\frac{\partial\, Q(\vec{r},\vec{r}';N)}{\partial z}\right]_{z=+0} = \left[\frac{\partial\, \mathcal{G}(\vec{r},\vec{r}';N)}{\partial z}\right]_{z=+0} - \left[\frac{\partial\, \mathcal{G}(\vec{r},\vec{r}';N)}{\partial z}\right]_{z=-0} . \tag{11}$$

From Eq. (8) we get

$$(\partial/\partial z)\, \mathcal{G}(\vec{r},\vec{r}';N)\Big|_{z=-0}^{z=+0} = -2\{c_o + \nu(\vec{x})\}\, \mathcal{G}(\vec{r},\vec{r}';N)\Big|_{z=0} . \tag{12}$$

But from Eq. (10)

$$Q(\vec{r},\vec{r}';N)\Big|_{z=0} = 2\, \mathcal{G}(\vec{r},\vec{r}';N)\Big|_{z=0} . \tag{13}$$

Combining Eq. (11), (12) and (13) we get,

$$\left(\frac{\partial Q(\vec{r},\vec{r}';N)}{\partial\, z}\right)_{z=+0} = -\Big\{c_o + \nu(\vec{x})\Big\} Q(\vec{r},\vec{r}';N)\Big|_{z=+0} \tag{14}$$

or

$$\left(\frac{\partial \ln Q}{\partial z}\right)_{z=+0} = -\{c_o + \nu(\vec{x})\} \tag{15}$$

Further, it is easily seen that $Q(\vec{r},\vec{r}';N)$ obeys the equation,

$$\{\partial/\partial N - (\ell^2/6)\nabla_{\vec{r}}^{\,2}\}\; Q(\vec{r},\vec{r}';N) = \delta(N)\delta(\vec{r}-\vec{r}'), \tag{16}$$

for $z > 0$. Therefore, we conclude that $G(\vec{r},\vec{r}';N)$ and $Q(\vec{r},\vec{r}';N)$ are identical.

Therefore,

$$G(\vec{r},\vec{r}\,';N) = \mathcal{G}(\vec{r},\vec{r}\,';N) + \mathcal{G}(\mathcal{P}r,\vec{r}\,';N). \qquad (17)$$

We write Eq. (9) as

$$\mathcal{G}(\vec{r},\vec{r}\,';N) = \int_{\vec{r}(0)=\vec{r}\,'}^{\vec{r}(N)=\vec{r}} D\vec{r}(s)\exp\{\, -S_{ran}[\vec{r}(s)] \,\}/\mathcal{N} \qquad (18)$$

where $\mathcal{N}$ is given by

$$\mathcal{N} = \int d\vec{r} \int_{\vec{r}(0)=\vec{r}\,'}^{\vec{r}(N)=\vec{r}} D\vec{r}(s)\exp\ \{-S_{ran}[\vec{r}(s)]\}\ . \qquad (19)$$

with

$$S_{ran}[\vec{r}(s)] = S_{\delta}[\vec{r}(s)] - (\ell/3)\int_0^N ds\, v(\vec{x}(s)\delta[z(s) \qquad (20)$$

$S_{\delta}\ [\vec{r}(s)]$ is defined by

$$S_{\delta}\ [\vec{r}(s)] = S_o[\vec{r}(s)] - (\ell/3)\int_0^N c_o\ \delta[z(s)]ds \qquad (21)$$

and

$$S_o[\vec{r}(s)] = \frac{3}{2\ell}\int_0^N ds \left[\frac{d\vec{r}(s)}{ds}\right]^2 . \qquad (22)$$

It is quite interesting to note that the path integral in Eq. (18) can enter the region $z < 0$ too.

We can take the random function to be Gaussian with vanishing average and to have the correlation function $\langle v(\vec{x})v(\vec{x}\,')\rangle = B(\vec{x}-\vec{x}\,')$, where $\langle \ldots \rangle$ denotes averaging with respect to the random function. In the following we consider randomness with a correlation length R_o and take $B(\vec{x}) = V^2 \exp[-\vec{x}^2/R_o{}^2]$, where V is the parameter describing the randomness. $G(\vec{r},\vec{r}\,';N)$ is now a functional of $v(\vec{x})$ and is still given by the equation (17). Here we again employ the *replica formalism* [26-28]. Introducing n replicas, labelled with $\alpha = 1,2,\ldots n$, one can write

$$\mathcal{G}(\vec{r},\vec{r}\,';N) = \lim_{n\to 0} \prod_{\alpha=1}^{n} \int_{\vec{r}_\alpha(0)=\vec{r}\,'} D\vec{r}_\alpha(s_\alpha)\exp\left[-S_{ran}[\vec{r}_\alpha(s_\alpha)]\right]$$

$$\delta[\vec{r}_1(N)-\vec{r}]. \tag{23}$$

On performing the average over the random function $v(\vec{x})$, we get,

$$\langle\mathcal{G}(\vec{r},\vec{r}\,';N)\rangle = \lim_{n\to 0} \left[\prod_{\alpha=1}^{n} \int_{\vec{r}_\alpha(0)=\vec{r}\,'} D\vec{r}_\alpha(s_\alpha)\right]\exp\{-S\}\ \delta[\vec{r}_1(N)-\vec{r}] \tag{24}$$

where

$$S = \sum_\alpha S_o[\vec{r}_\alpha(s_\alpha)] - S_1 \tag{25}$$

with

$$S_1 = \frac{1}{2}\left[-\frac{\ell}{3}\right]^2 \sum_{\alpha,\beta=1}^{n} \int_0^N ds\int_0^N dt\ B(\vec{x}_\alpha(s)-\vec{x}_\beta(t))\delta(z_\beta(t))\delta(z_\alpha(s)). \tag{26}$$

Our interest is only in the adsorbed molecules, for which we would like to calculate the size $\langle[\vec{r}(N)-\vec{r}(0)]^2\rangle$. The integral in Eqn.(24) can not be evaluated analytically. So, as in Chapter III, we adopt the variational formulation of Feynman's path integral technique, with the trial action,

$$S_T[\vec{r}(s)] = \sum_\alpha S_t[\vec{r}_\alpha(s_\alpha)] \tag{27}$$

where

$$S_t[\vec{r}(s)] = S_o[\vec{r}(s)] - (\ell c/3)\int_0^N \delta[z(s)]ds$$

$$+ \quad (q^2/12\ell N)\int_0^N ds\int_0^N dt\ [\vec{x}(s)-\vec{x}(t)]^2. \tag{28}$$

In the above, c and q are trial parameters. Note that the action in Eqn. (28) has a δ-function attractive part as well as a harmonic oscillator like non-local part (last term in Eq. (28)). As in Chapter III we prefer to use this non-local action rather than the one used in reference [56], as this action is unchanged by translations parallel to the surface, whereas the one in reference [29] is not. With this trial action, all the path integrals that are needed for the calculation of the size of the polymer can be evaluated as earlier. For example, consider the propagator for the trial action, defined by

$$G_t(\vec{r},\vec{r}\,';N) = \frac{I(\vec{r},\vec{r}\,';N)}{\int d\vec{r}\ I(\vec{r},\vec{r}\,';N)} \tag{29}$$

with

$$I(\vec{r},\vec{r}\,';N) = \int_{\vec{r}(0)=\vec{r}\,'} D\vec{r}(s)\exp\{-[S_t[\vec{r}(s)]]\}\ \delta[\vec{r}(N)-\vec{r}]. \tag{30}$$

It is possible to write the above as

$$G_t(\vec{r},\vec{r}\,';N) = \frac{\int d\vec{y}\int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{0}} D\vec{r}(s)\exp(\,-\,S_t^{\vec{y}})}{\left[\int d\vec{r}\int d\vec{y}\int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{r}} D\vec{r}(s)\exp(-S_t^{\vec{y}}[\vec{r}(s)])\right]} \tag{31}$$

where

$$S_t^{\vec{y}}[\vec{r}(s)] = S_o[\vec{r}(s)]-(\ell c/3)\int_0^N \delta[z(s)]ds + (q^2/6\ell)\int_0^N ds\ \ [\vec{x}(s)-\vec{y}]^2. \tag{32}$$

The denominator in Eq. (31) is simply a normalization factor which ensures that the propagator $G_t(\vec{r},\vec{r}';N)$ is normalized. In the above equations, $\vec{y}=(y_1,y_2)$ is a two dimensional vector. As the $\vec{x}$ and z are not coupled in the equations (31) and(32), one gets,

$$G_t(\vec{r},\vec{r}';N) = \frac{I_1(\vec{r},\vec{r}';N)}{\int d\vec{r}\ I_1(\vec{r},\vec{r}';N)} \tag{33}$$

with

$$I_1(\vec{r},\vec{r}';N) = G_\delta(z,z';N) \int d\vec{y}\ G^{\vec{y}}(\vec{x},\vec{x}';N). \tag{34}$$

$G_\delta(z,z';N)$ is the propagator for Brownian motion in the presence of a delta function sink and obeys the differential equation,

$$\{\partial/\partial N - (\ell/6)\partial^2/\partial z^2 - \ell c\delta(z)/3\}\ G_\delta(z,z';N) = \delta(N)\delta(z-z'). \tag{35}$$

$G^{\vec{y}}_{ho}(\vec{x},\vec{x}';N)$ is the propagator for Brownian motion in the presence of a parabolic sink, having origin at $\vec{y}$ and satisfies,

$$\{\partial/\partial N - (\ell/6)\nabla^2_{\vec{x}} - (q^2/6\ell)(\vec{x}-\vec{y})^2\}G^{\vec{y}}_{ho}(\vec{x},\vec{x}';N) = \delta(N)\delta(\vec{x}-\vec{x}'). \tag{36}$$

Explicit expressions for both $G_\delta(z,z';N)$ and $G^{\vec{y}}_{ho}(\vec{x},\vec{x}';N)$ are available. Hence the propagator $G_t(\vec{r},\vec{r}';N)$ is known. If $c > 0$, then the operator $-(\ell/6)\partial^2/\partial z^2 - \ell c\delta(z)/3$ has one negative eigen value, given by $\epsilon_b = -\ell c^2/6$, with the associated eigen function $\psi_b(z) = \sqrt{c}\ \exp(-c\ z)$. This corresponds to the adsorbed (bound) state of the polymer. As the paths are not restricted to the region $z > 0$, the normalization that we can use is $\int_{-\infty}^{\infty} dz\ \psi_b(z)^2 = 1$. In the limit where N becomes very large, the two propagators $G_\delta(z,z';N)$ and $G^{\vec{y}}_{ho}(\vec{x},\vec{x}';N)$are dominated by the lowest possible eigen functions (ground state dominance) and hence one has

$$G_\delta(z,z';N) \approx c\exp\{-c(|z|+|z'|) - \epsilon_b N\} \tag{37}$$

and

$$G^{\vec{y}}_{ho}(\vec{x},\vec{x}';N) \approx \exp[-\{q((\vec{x}-\vec{y})^2+(\vec{x}'-\vec{y})^2)/(2\ell)\} - q\ell N/3]\ q/(\pi\ell) \tag{38}$$

Remembering that the variational parameters c and q have to be determined so as to best suit the description of adsorbed polymers, we make use of the Feynman's variational procedure (See references [30] and [31]), for their determination. Thus, we expect the integral

$$I(n) = \prod_{\alpha=1}^{n} \left[\int_{\vec{r}_\alpha(0)=\vec{0}}^{\vec{r}_\alpha(N)=\vec{0}} D\vec{r}_\alpha(s_\alpha) \right] \exp[-S] \tag{39}$$

to behave like $\exp[-nF_1(N)]$ for $n \to 0$ and large N. We estimate $F_1(N)$ variationally, in the limit $n \to 0$ and choose c and q so as to get the best approximation for it. These parameters are then used to calculate $\langle[\vec{r}(N)-\vec{r}(0)]^2\rangle$. Thus

$$I(n) = \left[\prod_{\alpha=1}^{n} \int_{\vec{r}_\alpha(0)=\vec{0}}^{\vec{r}_\alpha(N)=\vec{0}} D\vec{r}_\alpha(s_\alpha) \right] \exp[-S_T]\ \langle \exp-(S-S_T)\rangle_T$$

$$\geq Z_t^n \exp\langle-(S-S_T)\rangle_T \tag{40}$$

where $\langle....\rangle_T$ denotes averaging with respect to the trial action S_T and

$$Z_t = \left[\prod_{\alpha=1}^{n} \int_{\vec{r}_\alpha(0)=\vec{0}}^{\vec{r}_\alpha(N)=\vec{0}} D\vec{r}_\alpha(s_\alpha) \right] \exp[-S_t[\vec{r}(s)]]$$

$$= [q^2N/(6\pi\ell)]\int d\vec{Y} \int_{\vec{r}_\alpha(0)=\vec{0}}^{\vec{r}_\alpha(N)=\vec{0}} D\vec{r}_\alpha(s_\alpha)\ \exp\{-S_t^{\vec{Y}}[\vec{r}(s)]\}$$

$$= N_o\ G_\delta(0,0;N) \int d\vec{y}\ G_{ho}^{\vec{y}}(\vec{0},\vec{0};N)$$

$$= N_o\ G_\delta(0,0;N)/[2\sinh(qN/6)]^2 \qquad (41)$$

(See Appendix B1 for details of calculation of Eq. (41).)

with $N_o = q^2N/(6\pi\ell)$. As our interest is in the description of the adsorbed state, we take only the corresponding part from $G_\delta(0,0;N)$, which is equal to $\psi_b(0)^2\ \exp(-\epsilon_b N)$. In the limit of large N, one gets

$$Z_t \approx q^2N\psi_b(0)^2\ \exp(-qN/3-\epsilon_b N)/(6\pi\ell) \qquad (42)$$

from Eq. (41). The other integrals that occur in $\langle S-S_T\rangle$ are,

(i) $(q^2/12\ell N)\int_0^N ds\int_0^N dt\ \langle[\vec{x}(s)-\vec{x}(t)]^2\rangle_T$

$$= -(q/2)\ \frac{\partial}{\partial q}\left[\ \ln\left[\prod_{\alpha=1}^{n}\ \int_{\vec{r}_\alpha(0)=\vec{0}}^{\vec{r}_\alpha(N)=0} D\vec{r}_\alpha(s_\alpha)\right]\exp\ [-S_T]\right]$$

$$= nq\ \frac{\partial}{\partial q}\ [\ln\sinh(qN/6)]$$

$$= (nqN/6)\coth(qN/6)$$

$$\approx nqN/6, \text{ in the } qN/3 \gg 1 \text{ limit.} \qquad (43)$$

(ii) $\langle\ell(c_o-c)/3\int_o^N \delta(z_\alpha(s))ds\rangle_T$, which can be evaluated similarly to be $\ell(c_o-c)cN/3$.

(ii) $\sum_{\alpha,\beta=1}^{n} I_{\alpha\beta}$ where

$$I_{\alpha\beta} = \int_0^N ds \int_0^N dt \ \langle B(\vec{x}_\alpha(s)-\vec{x}_\beta(t))\delta(z_\beta(t))\delta(z_\alpha(s))\rangle_T . \qquad (44)$$

(See Appendix. B2 for the details of the evaluation of $I_{\alpha\alpha}$ and $I_{\alpha\beta}$).

$I_{\alpha\alpha}$ can be evaluated analytically, and $I_{\alpha\beta}$ $(\alpha \neq \beta)$ numerically. As the results are tedious to analyze, we use the ground state dominance approximation [29] to get the following: $I_{\alpha\alpha} \simeq (NV\ell c/3)^2/ \{2[1+2\ell/(qR_o^2))\}$ and $I_{\alpha\beta} \simeq (NV\ell c/3)^2/ \{2[1+4\ell/(qR_o^2))\}$. where R_o is the correlation length of the potential. Combining the above results, and introducing the dimensionless variables $\bar{N} = N/\ell$, $\bar{c} = c\ell$, $\bar{q} = q\ell$, $\bar{R}_o = R_o/\ell$, $\bar{c}_o = c_o\ell$, $\bar{V} = V\ell$, we get

$$\beta\bar{F}_1(u)/\bar{N} = [\bar{c}^2 - 2\bar{c}\,\bar{c}_o + \bar{q} - \bar{c}^2\,\bar{N}\,f(\bar{q})]/6 \qquad (45)$$

where $f(q) = 2\bar{V}^2\bar{N}\,\overline{qR}_o^{\,2}/[3(2+\bar{q}\,\bar{R}_o^{\,2})(4+\bar{q}\,\bar{R}_o^{\,2})]$. Eqn.(45) can be rearranged to get

$$\beta\bar{F}_1(u)/\bar{N} = [\bar{c}^{\,2} - 2\bar{c}\,\bar{c}_o + u/R_o^{\,2} - \bar{c}^{\,2}f(u)]/6 \qquad (46)$$

where $f(u) = pu/[\,(2+u)\,(4+u)\,]$, $p=2\bar{N}\,\bar{V}^{\,2}/3$ and $u = \bar{q}\,\bar{R}_o^{\,2}$. In Eq. (46), $\bar{c}^2$represents the effect of entropy (in quantum mechanical parlance kinetic energy), trying to spread out the adsorbed chain, increasing its thickness, $-\ 2\bar{c}\ \bar{c}_o$, the lowering of energy resulting from adsorption, $\bar{q}$ effect localizing the chain to dimensions of q^{-1} in directions parallel to the surface and $-\ \bar{c}^{\,2}$ f(u), the effect of the randomness, which results in a net attraction between the chains as is indicated by the negative sign. Note that this term has $-\ \bar{c}^{\,2}$, because of the lowering of energy caused by adsorption. The size of the polymer chain in the adsorbed state can be estimated using the trial action. In the z direction, the thickness of the adsorbed layer is c^{-1}. From the trial action, we find,

$$\langle[\vec{x}(N)-\vec{x}(0)]^2\rangle = 4\ell^2\bar{R}_o{}^2\tanh[u\bar{N}/(6\bar{R}_o{}^2)]/u, \tag{47}$$

using which the size of the chain parallel to the surface can be estimated. (See Appendix A4 of Chapter III for the details of the derivation of Eq. 47). We now find the best values of u and $\bar{c}$, which make $\bar{F}_1(u)$ a minimum.

IV.4. RESULTS

IV.4.i. Ground State dominance Approximation.

Case I : $p < p^o$.

In the above, $p^o = [6+(32)^{1/2}] = 11.656$. Finding the value of c such that $\bar{F}_1(u)$ is a minimum gives $\bar{c} = \bar{c}_o/(1-f(u))$. Note that if $\bar{c}$ is negative, there is no bound (adsorbed) state, which violates our basic assumption in deriving the equation (46). Therefore only $\bar{c} > 0$ are acceptable to us, and this is satisfied if $p < p^o$. Using this value of $\bar{c}$, we get

$$6\beta\bar{F}_1(u)\bar{R}_o{}^2/\bar{N} = -(\bar{c}\,\bar{R}_o)^2 + u - p_1u/[(2+u)(4+u)-pu], \tag{48}$$

where $p_1 = \bar{R}_o{}^2\bar{c}_o^2p$. One can now analyze Eq.(48) to find the following results; If $p_1 < p_1{}^o$ and $p < [6+(32-4p_1)^{1/2}]$, where $p_1{}^o = 8$, then $\bar{F}_1(u)$ has its minimum at u=0. The size of the chain in the parallel direction is $\langle[\vec{x}(N)-\vec{x}(0)]^2\rangle = 2\ell^2\bar{N}/3$, indicating that the chain is unaffected by the randomness. Strictly speaking, this is an artifact of our ground state dominance approximation, which breaks down if $u=0$ (i.e. when $q=0$). Along the curve, $p = [6+ 2\ (8-p_1)^{1/2}]$, the value of u jumps discontinuously, indicating a sudden change in the size of the polymer in the parallel direction. Exact calculations, given below show that the chain size is decreased in both parallel and perpendicular directions by the randomness. If $p_1 > p_1^o$, then the minimum occurs at $u > 0$. As $p_1 \longrightarrow \infty$, the minimum tends to be at $u=(8)^{1/2}$, so that $\langle[\vec{x}(N)-\vec{x}(0)]^2\rangle = 4\ell^2\bar{R}_o^{\,2}\tanh[\sqrt{8}\ \bar{N}/(6\bar{R}_o^{\,2})]/\sqrt{8} \longrightarrow 4\ell^2\bar{R}_o^{\,2}/\sqrt{8} = \sqrt{2}\ R_o$ indicating that the chain occupies only regions of size $\approx R_o$.

Case II : $p > P^o$.

In this case, $f(u)$ is greater than 1 for a range of values of u (or equivalently $\bar{q}$). $\beta F_1(u)$ has its minimum value for $\bar{c} = \infty$, thus indicating that the adsorbed state is collapsed, to a thickness zero in the direction perpendicular to the surface. The chain is now two dimensional. To get its size, we make use of eqn (47). If $\bar{c} \to \infty$ then the important term in the equation is $\bar{c}^2(1-f(u))/6$ and this has its least value when $u = \sqrt{8}$.

The Fig. IV.1 gives a plot of the value of u that minimizes $\beta F_1(u)$, as a function of the variables p and p_1, and the Fig. IV.2 summarizes our discussion above.

IV.4.i. Numerical Calculations

We have also done rigorous calculation of the the free

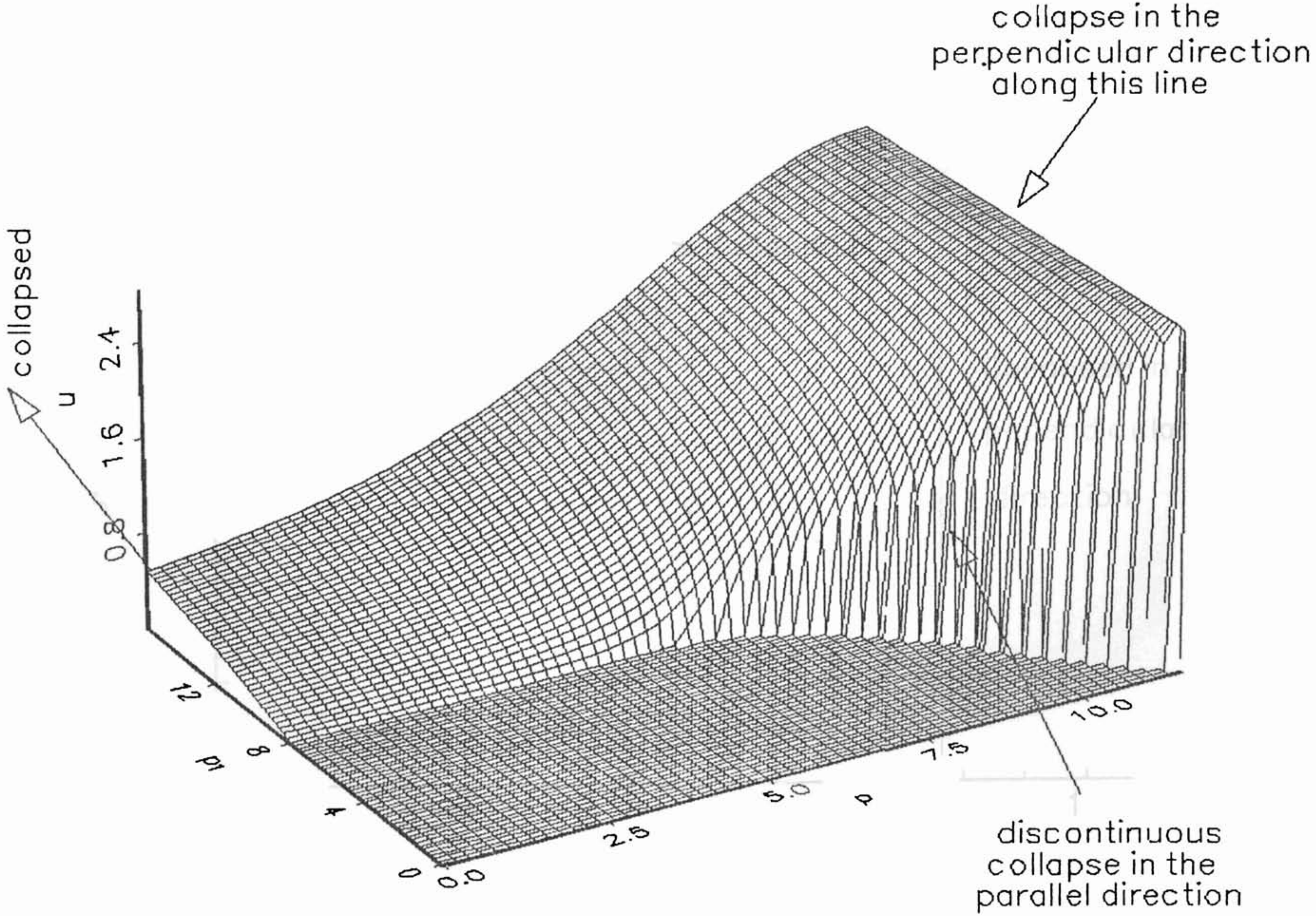

Fig. IV.1. Plot of u as a function of p and p_1

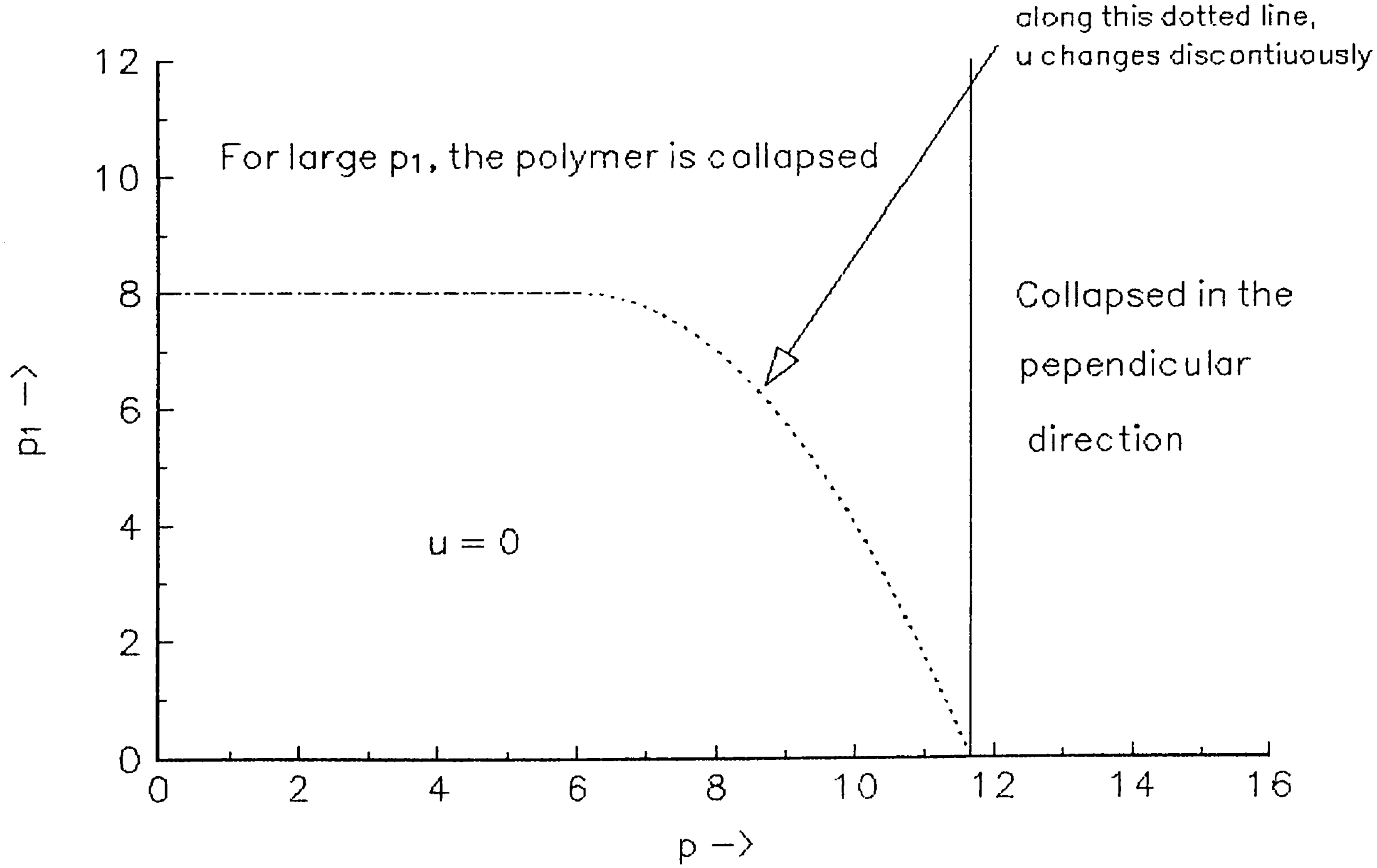

Fig. IV.2. Dependence of u on p and p_1

energy by evaluating $I_{\alpha\beta}$ and $I_{\alpha\alpha}$ on a computer. $I_{\alpha\alpha}$ is given by

$$I_{\alpha\alpha} = (\ell cV)^2 \frac{1}{(a^2-b^2)^{1/2}} \ln \left[\frac{(a+b)+(a^2-b^2)^{1/2} \tanh(\bar{q}\,\bar{N}/6)}{(a+b)-(a^2-b^2)^{1/2} \tanh(\bar{q}\bar{N}/6)} \right] \tag{49}$$

where

$$a = 1 + (2/\bar{q}\,\bar{R}_o^{\,2}) \coth(\bar{q}\,\bar{N}/3) \quad \text{and}$$

$$b = -\,(2/\bar{q}\,\bar{R}_o^{\,2}) \operatorname{cosech}(\bar{q}\,\bar{N}/3).$$

and $I_{\alpha\beta}$ by the integral,

$$(\ell cV)^2 \int_0^1 \frac{ds}{(a_1^{\,2}-b_1^{\,2})^{1/2}} \ln \left[\frac{(a_1+b_1)+(a_1^{\,2}-b_1^{\,2})^{1/2} \tanh(\bar{q}\,\bar{N}/12)}{(a_1+b_1)-(a_1^2-b_1^2)^{1/2} \tanh(\bar{q}\,\bar{N}/12)} \right] \tag{50}$$

where

$$a_1 = 1 + ((2/\bar{q}\,\bar{R}_o^{\,2})/[\sinh(\bar{q}\,\bar{N}/6)]) \; [2\coth(\bar{q}\,\bar{N}/3)-\cosh(\bar{q}\,\bar{N}s/6)$$

and

$$b_1 = -\,(2/\bar{q}\,\bar{R}_o^{\,2})/[\sinh(\bar{q}\,\bar{N}/6)]$$

To verify whether this discontinuous change in u as a function of $\bar{V}$ would occur in the exact case also, we did the following calculation : we took $\bar{N} = 30$, $c_o = 1$ and $R_o = 1$. For this case, $p = p_1 = 20\,\bar{V}^2$ and $u = \bar{q}$. Changing $\bar{V}$ means that one is moving along the line $p = p_1$ in the Fig. IV.2. Simple inspection of the figure shows that there is a discontinuous change in u ($\bar{q}$) from zero to a finite value, along this line. This is seen in the Fig. IV. 3. This means that the polymer size in the parallel direction would decrease suddenly. To find whether this is an

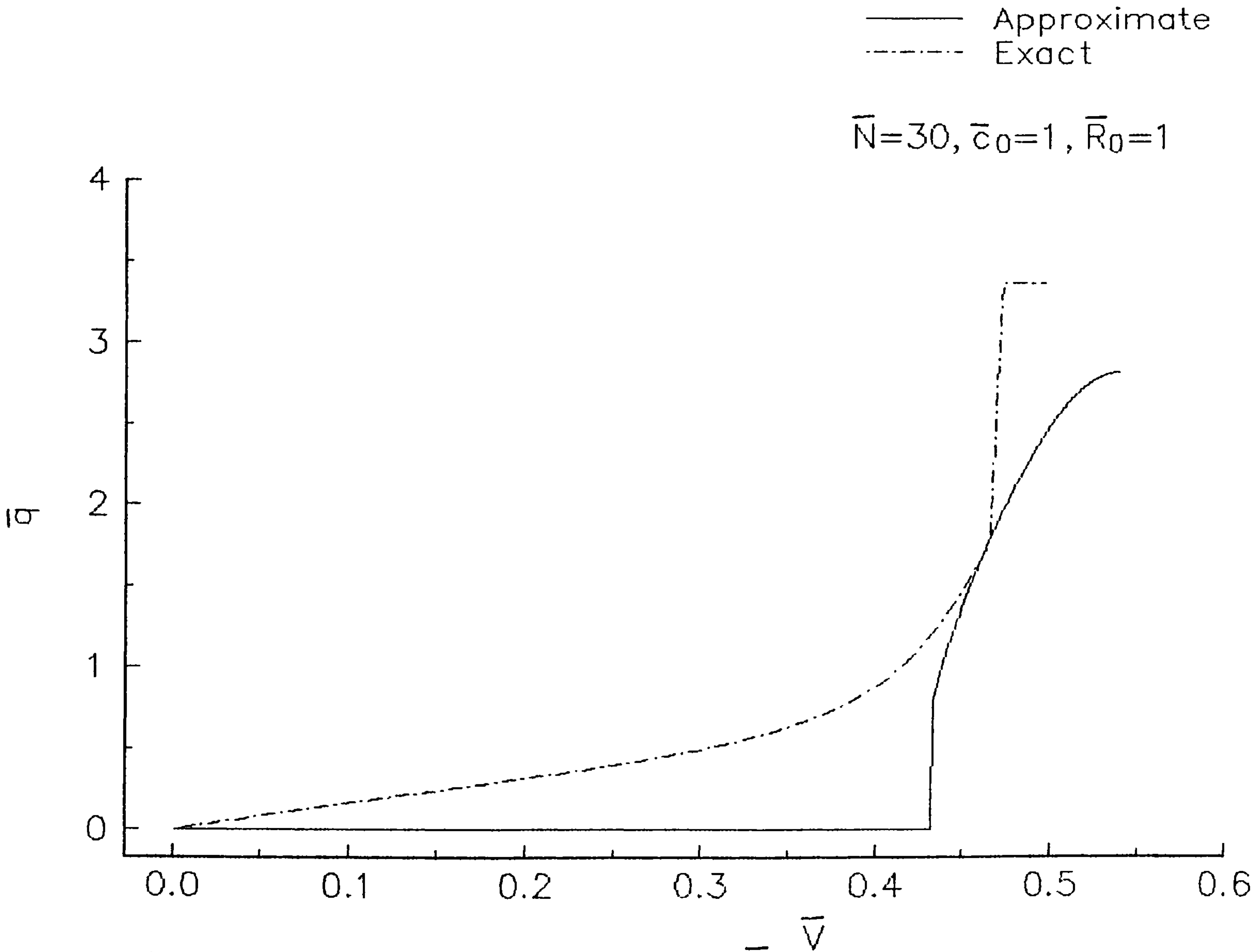

Fig. IV.3. Plot of $\bar{q}$ as a function of $\bar{V}$

artifact of the ground state dominance approximation, we made an exact calculation of $u(\bar{q})$. It is seen that for small randomness, the value of u is not zero but finite. However, the discontinuous change in u is found to persist. This is clear also in plots of the parallel and perpendicular sizes, shown in figures IV.4 and IV.5.

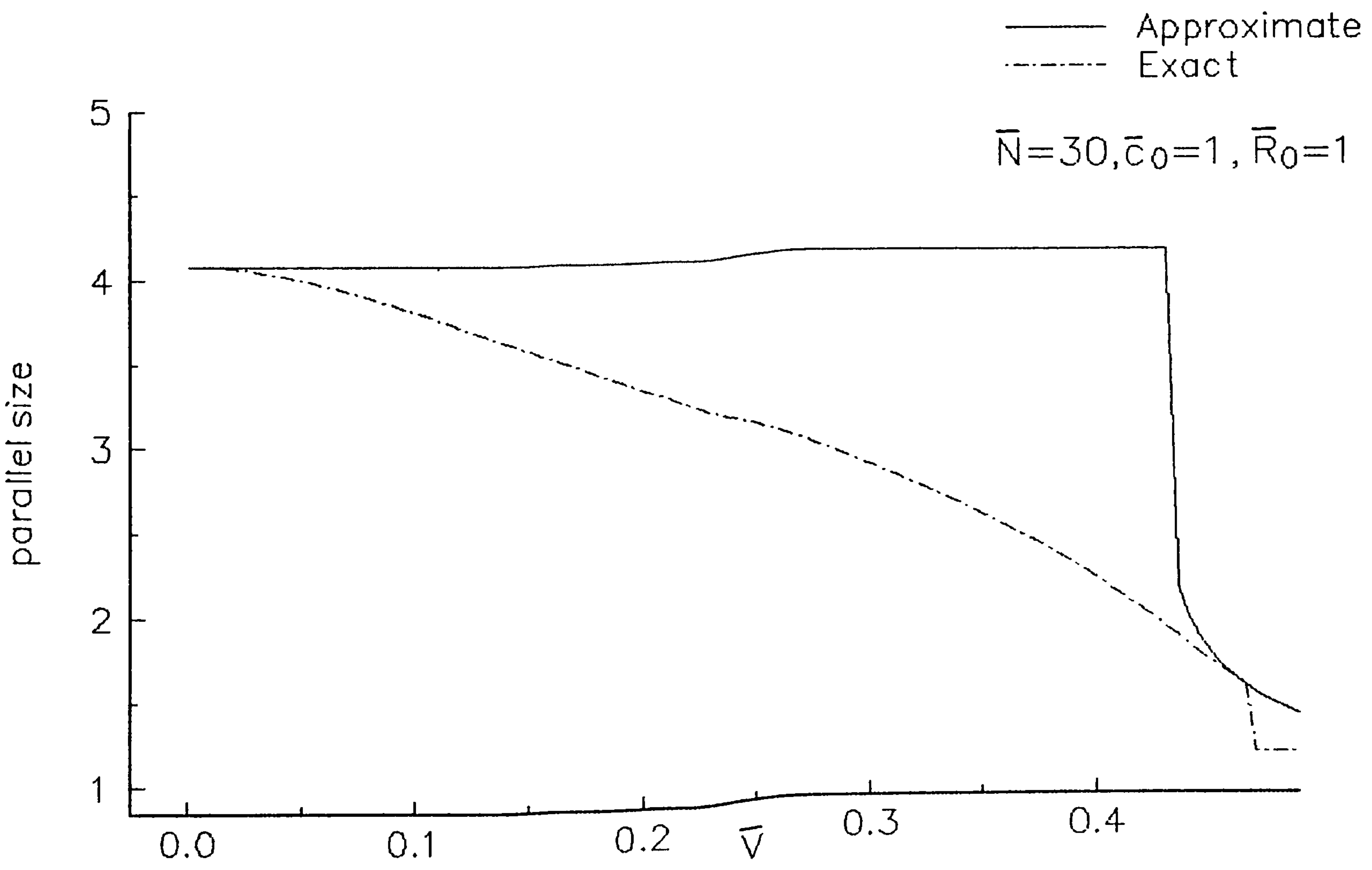

Fig. IV.4. Plot of parallel size as a function of $\overline{V}$

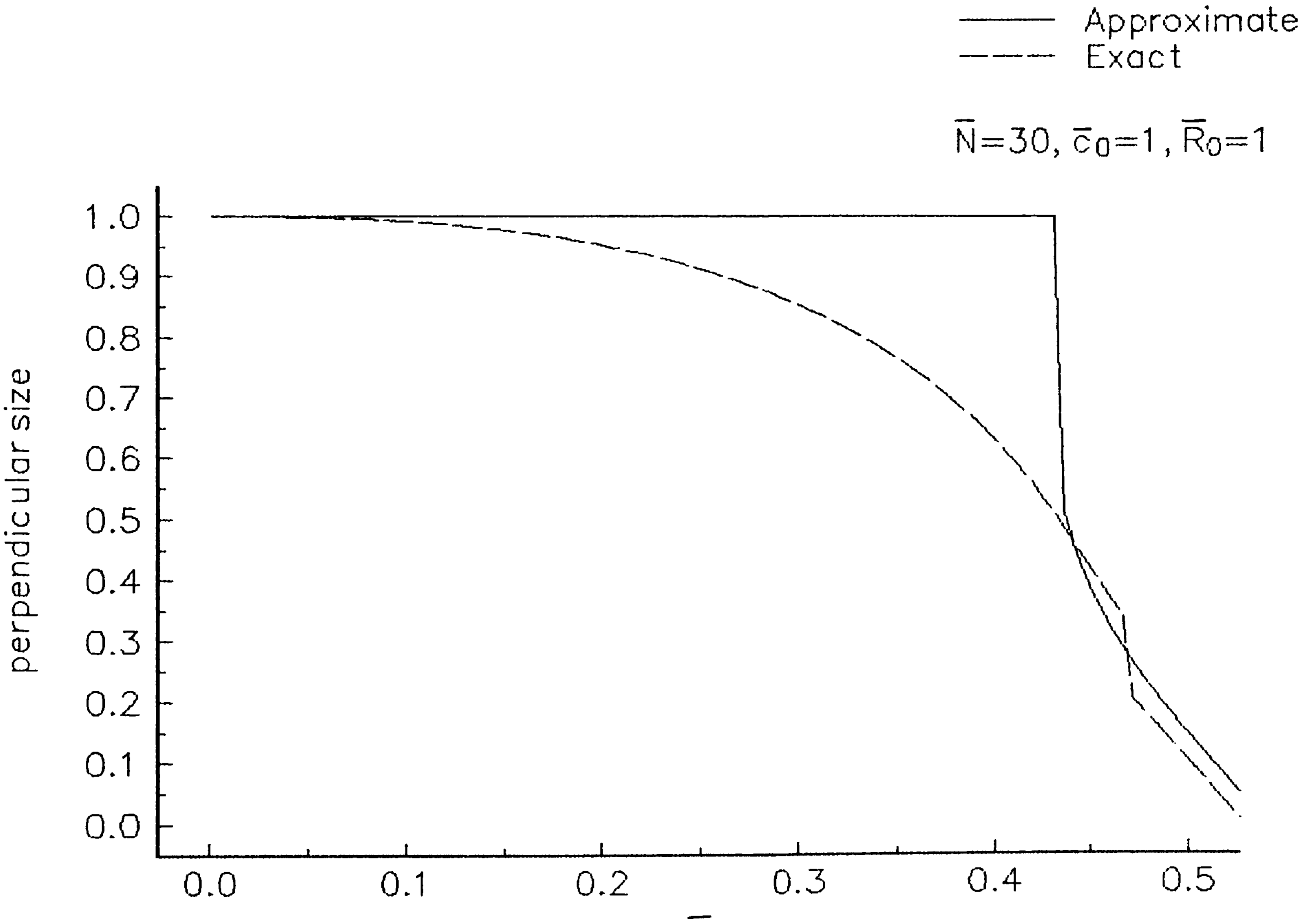

Fig. IV.5. Plot of perpendicular size vs $\bar{V}$

APPENDIX B1

Calculation of Z_t

$$Z_t = N_o\, G_\delta(0,0;N) \int d\vec{y}\; G^{\vec{y}}_{ho}(\vec{0},\vec{0};N) \tag{B1.1}$$

The propagator for a harmonic oscillator is well known in the literature [See Eq. 41 in Chapter III]. Here we have a two dimensional harmonic oscillator whose origin is not at zero, but at some arbitrary point $\vec{y}$. Therefore,

$$G^{\vec{y}}_{ho}(\vec{0},\vec{0};N) = [q/2\pi\ell \,\sinh\,(qN/6)]\, \exp\left[\frac{-q(\cosh(qN/6)-1)\;y^2}{\sinh(qN/6)}\right]. \tag{B1.2}$$

Integration over $\vec{y}$ gives,

$$\int d\vec{y}\; G^{\vec{y}}_{ho}(\vec{0},\vec{0};N) = [1/2(\cosh(qN/6)-1)] = 1/[2\sinh(qN/6)]^2. \tag{B1.3}$$

Now, Eq.(B1.1) could be written as,

$$Z_t = N_o\, G_\delta(0,0;N)/[2\sinh(qN/6)]^2 \tag{B1.4}$$

which in the limit of large N gives Eq.(41).

APPENDIX B2

Calculation of $I_{\alpha\alpha}$ and $I_{\alpha\beta}$

$I_{\alpha\alpha}$ could be written as

$$I_{\alpha\alpha} = \frac{\left[\frac{\ell cV}{3}\right]^2 \int_0^N dt_\beta \int_0^N dt_\alpha \int d\vec{y} \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{0}} D\vec{r}(t) e^{-S_t} \exp\left[-[\vec{r}_\alpha(t)-\vec{r}_\beta(s)]^2/R_o{}^2\right]}{2 \int d\vec{y} \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{0}} D\vec{r}(t) e^{-S_t}} \tag{B2.1}$$

where $\vec{y}$ is two dimensional and S_t is given by Eq. (32) of Chapter IV.

$$\int d\vec{y} \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{0}} D\vec{r}(t) e^{-S_t^{\vec{y}}} = \exp[-qN/3] \text{ in the limit } (qN/3) >> 1 \text{ limit}$$

(ground state dominance approximation).

The numerator in Eq. (B2.1) could be written as

$$= \frac{1}{2}\left[\frac{\ell cV}{3}\right]^2 \int_0^N dt_\alpha \int_0^N dt_\beta \int d\vec{r}_2 \int d\vec{r}_1 \exp\left[-[\vec{r}_1-\vec{r}_2]^2/R_o{}^2 \int d\vec{y} \right.$$

$$\int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{0}} D\vec{r}(t)\ e^{-S_t^{\vec{y}}}\, \delta(\vec{r}_1-\vec{r}_\alpha(t_\alpha))\ \delta(\vec{r}_2-\vec{r}_\beta(t_\beta)). \tag{B2.2}$$

Eq. (B2.2) can be written as a product of three propagators

$$= \frac{1}{2}\left[\frac{\ell cV}{3}\right]^2 \int_0^N dt_\alpha \int_0^N dt_\beta \int d\vec{r}_2 \int d\vec{r}_1 \exp\left[-[\vec{r}_1-\vec{r}_2]^2/R_o{}^2 \right.$$

$$\int d\vec{y}\; G^{\vec{y}}_{ho}(\vec{0},N|\vec{r}_2,t_\beta)\; G^{\vec{y}}_{ho}(\vec{r}_2,t_\beta|\vec{r}_1,t_\alpha)\; G^{\vec{y}}_{ho}(\vec{r}_1,t_\alpha|\vec{0},0)\ . \qquad \text{(B2.3)}$$

As in the case of $I_{\alpha\alpha}$ in Chapter III (See Appendix A3), here also the propagators are that for harmonic oscillators. Here we have two dimensional integrals and the limits of integration are different. It can be evaluated in the ground state dominance approximation , i.e., in the (qN/3) >> 1 limit to get

$$I_{\alpha\alpha} \simeq (NV\ell c)^2/2\;[\,1+2\ell/(qR_o^{\;2})]\ . \qquad \text{(B2.4)}$$

Similarly we evaluate $I_{\alpha\alpha}$ exactly as in the case of polymer in random media to obtain,

$$I_{\alpha\alpha} = (\ell c/3)^2\; 2\bar{V}^{\;2} \int_0^N t\; dt \left[\; 1+(4/\bar{q}\;\;\bar{R}_o^{\;2})\; \frac{\sinh(\bar{q}t/3)\;\sinh(\bar{q}(\bar{N}-t)/3)}{\sinh\;(\bar{q}\;\bar{N}/6)}\right]^{-1} . \qquad \text{(B2.5)}$$

The Eq. (B2.5) can be simplified to get Eq. (49) of Chapter IV. In the case of $I_{\alpha\beta}$, instead of Eq.(B2.3), we will have a product of four propagators,

$$= \frac{1}{2}\left[\frac{\ell cV}{3}\right]^2 \int_0^N dt_\alpha \int_0^N dt_\beta \int d\vec{r}_2 \int d\vec{r}_1\; \exp\,[\,-[\vec{r}_1-\vec{r}_2]^2/R_o^{\;2}$$

$$\int d\vec{y}_\alpha \int d\vec{y}_\beta\; G_{ho}(\vec{y},N|\vec{r}_1+\vec{y}_\alpha,t_\alpha)\; G_{ho}(\vec{r}_1+\vec{y}_\alpha,t_\alpha|\vec{y}_\alpha,0)$$

$$G_{ho}(\vec{y}_\beta,N|\vec{r}_2+\vec{y}_\beta,t_\beta)\; G_{ho}(\vec{r}_2+\vec{y}_\beta,t_\beta|\vec{y}_\alpha,0)\ . \qquad \text{(B2.6)}$$

Eq. (B2.6) can be evaluated in the ground state dominance approximation to get

$$I_{\alpha\beta} \simeq (NV)^2/\;[\,1+4\ell/(qR_o^{\;2})]\ . \qquad \text{(B2.7)}$$

As in the case of polymer in random media, here also we evaluated $I_{\alpha\beta}$ using the exact propagators and obtained the Eq. (50) in Chapter IV.

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CHAPTER V

CONCLUSION

There have been many investigations, both theoretical and experimental, on the behaviour of polymer chains in disordered media and their adsorption on random surfaces.

In the case of a polymer in quenched random media, a simple model which consists of a Gaussian chain in a medium where a certain number of obstacles are frozen at random locations was used. The problem was investigated with the help of Edwards Hamiltonian [1-3] that has been widely used in the theoretical investigations of polymer problems. The quantity of interest is $\langle \bar{R}^2 \rangle$, the mean square end-to-end vector (i.e., the size) of the polymer chain in the presence of quenched disorder.

The analytical treatment of the effect of quenched impurities on chain statistics is difficult due to the necessity of averaging the logarithm of the partition function of the system over the disorder. The replica method employed enables us to perform the averaging correctly. We have adopted the replica formalism [5] and the variational formulation of path integration [4] to calculate the size of polymer chains in random media. We have studied the effect of randomness on the size of the polymer chain in both cases, using a ground state dominance approximation and also exactly.

In the case of a polymer in quenched random medium, we make use of a non-local, quadratic trial action. In the approximate case, we found the following. When the randomness is small, $\langle \vec{R}^2 \rangle = Nl$, which is the value for a free polymer molecule. But as one increases the value of randomness there is a sudden change over from the free polymer like behaviour ($\langle \vec{R}^2 \rangle \propto N$) to one that is not. In the limit where randomness or the length of the chain becomes very large, the size of the polymer chain is found to be given by $\langle \vec{R}^2 \rangle = 6R_o^2/5.248$, a value independent of the length of the polymer molecule.

We have also compared the above predictions with what one would have obtained, if one used the local trial action of Edwards and Muthukumar [1]. In this case, in the ground state dominance approximation, the free energy would not have any contribution from the interactions between the replicas and thus the use of this action does not predict the collapse of the polymer.

We have also done rigorous exact calculation of the free energy when the non-local action is used. The exact calculations revealed that arbitrarily small amounts of randomness will reduce the size of the polymer chain and it will no longer remain a free polymer. We have also found in the exact case that the transition to the collapsed state is smooth, in contrast to the prediction of the ground state dominance approximation. We find that as the length of the polymer chain is increased, the collapse happens at a lesser magnitude of randomness.

We have also investigated adsorption of a flexible polymer chain on a chemically random surface [6]. For this purpose, we have used a generalisation of the de Gennes' boundary condition [7] to a random one, and path integral methods. For weak randomness, it is found that the chain size is unaffected by the randomness. But as one increases the randomness or the chain length, the chain size becomes $\sim R_o$, where R_o is the correlation length of the potential. It is found that when the chain length or the randomness exceeds a certain critical value, the chain first undergoes a sudden collapse in the parallel direction, followed by another sudden collapse in the direction perpendicular to the surface, to a thickness zero, so that it becomes a two dimensional object.

We have also done an exact calculation and found that as randomness is increased, there is a reduction in the size of the polymer chain compared to its value in the absence of randomness. In this case also we have found a sudden, sharp collapse of the polymer chain in the direction parallel to the surface, followed by a collapse in the perpendicular direction.

On the experimental side of the adsorption problem, there are complications because a single chain adsorption is never observed. One always reaches a situation where many chains compete for the same portion of the surface. Furthermore, the single chain problem may be modified by the existence of long range van der Waals forces between the surface and each monomer. The condition required for the adsorption of separate chains are never attained in practice, but they may provide a very useful framework for future investigations of many chain adsorption on surfaces.

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