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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

Towards a Theory for the Orientation Dependent Packing Entropy of Inhomogeneous Polymer Systems

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SUMMARY

This report can be thought of as consisting of three parts. In the first part a review is given of Di Marzio's site fraction concept to calculate the configurational entropy of polymers in a homogeneous system. The second part is concerned with Monte Carlo calculations, performed to check the validity of this concept. Results are presented of the packing of rigid, rodlike polymer chains on a square lattice, in the spirit of earlier work by McCrackin. Using a slightly adapted algorithm we also present results of calculations done on a refined lattice. It is shown that (a) the concept gives quite satisfactory results in the volume fraction range of 0.05 (the lowest volume fraction tested) to approximately 0.6, but (b) that one should be suspicious of the theory's validity at volume fractions approaching 1.0; it is furthermore shown that (c) the theory works better for small rods than for larger ones. This last point is partly ascribed to a Markovian approximation used in the theory. The third and last part of this report deals with the application of the site fraction treatment to the calculation of the configurational entropy of a polymeric system having a density gradient in one direction.

CHAPTER 1

INTRODUCTION

Over the past many years various theories have been presented that model inhomogeneous polymer systems, like polymers adsorbing on a plane wall (1,2,3) or polymer-polymer interfaces (4,5). One of these theories, the so called Scheutjens-Fleer (3) theory of polymer adsorption, is particularly promising. There are several reasons why one may say so. The theory does not, to give an example, assume the chains to be of infinite length, like so many other theories do. It also not only enables us to obtain detailed structural information of the solution near the adsorbing wall, but also provides us with quite extensive thermodynamic information. Furthermore, the theory is proven to be very flexible in the sense that extensions to other polymeric systems, like bilayer membranes (6) and semi-crystalline bulk polymer (7), appear to be relatively straightforward.

The Scheutjens-Fleer theory (SF-theory) is a lattice theory, and in essence a sophisticated "hybrid" of Flory's theory on polymer solutions (8), and Di Marzio's (and Rubin's) theory of polymer between plates (1). Without going to deeply into the subject, this "hybrid" combines Flory's volume fraction concept to calculate entropy and energetics of the polymer system, and Di Marzio's matrix method to carry out the step weighted random walk representing the configuration of a polymer molecule.

Using Flory's volume fraction concept to calculate the entropy of polymer chains may give a reasonable approximation in the case of a non-oriented, semi-dilute system, but is less appropriate for oriented, more concentrated systems. It is the goal of this study to investigate the possibilities of introducing the more accurate orientation dependent site fraction concept, developed by Di Marzio (9), to describe systems having a gradient in the polymer density. Such systems include adsorbing polymers, bilayer membranes etc. To achieve this goal, we will first describe Di Marzio's method for the case of rigid molecules (chapter 2). We shall then check the site fraction concept by means of Monte Carlo calculations (chapter 3), and finally concern ourselves with the problem of deriving an expression for the configurational entropy of a polymer solution near a wall, or more correctly, of a polymer solution which has a density gradient in one of the directions (chapter 4). Unfortunately, we are at the moment only able to give a general formalism describing how to solve the problem.

CHAPTER 2

THE ENTROPY OF CHAIN MOLECULES

2.1 INTRODUCTION

The (configurational) entropy of polymer molecules, be it in bulk polymer, in polymer solutions or in more complicated systems like interphases, consists of three contributions. First of all, there is the contribution from the many "shapes" (conformations) of the molecules. Second, the position of the centers of mass of the molecules also contribute to the entropy of the system. Note that this contribution depends on how we define the conformation of the polymer chain, i.e. whether a different spatial position of a certain "shape" of a molecule be counted a different conformation. Last, but not least, we have to account for the entropy that arises from the competition of the molecules for space. This contribution to the (configurational) entropy of a polymer system accounts for the effect that volume restrictions have on the average "shape" of the chains due to spatial interference.

Thus, we can write the configurational entropy S of a polymer system as

$$(1)\quad S=S(conf)+S(cm)+S(int)$$

where S(conf) is the conformational part of the entropy, S(cm) the part due to the freedom of the centers of mass of the molecules and S(int) that part that arises from the interference of the chains. Obviously, both S(conf) and S(cm) contribute positively to the entropy, whereas S(int) contributes negatively to the entropy of the system. That is to say that $S(conf) \geq 0$, $S(cm) \geq 0$ and $S(int) \leq 0$ (10). One can easily see that $S(int) \leq 0$ because interference of chains reduces the freedom of chains with respect to unhindered chains.

The entropy due to the conformations and centers of mass of the (unhindered) polymer molecules can be determined with relative ease, depending on how accurate the calculation has to be. It is predominantly the interference part of the entropy that tends to give headaches to all those who are involved in the statistical mechanics of chain molecules.

To illustrate the importance of the interference of the molecules to the total entropy, we shall at first restrict ourselves to stiff, rodlike molecules. By doing so we can concentrate on the competition of the molecules for space, and the cooperative effect it has on the overall orientation (and by definition on the conformation) of the chains. The rigid rod problem has in itself importance because of the fact that rigid rods are used to model liquid crystals of asymmetric molecules (see for instance (11) and (12)). We end the chapter by applying the general ideas developed for the rigid rods to polymers of arbitrary shape in a homogeneous system.

2.2 RIGID RODS

We want to calculate the entropy of a system consisting of stiff, rodlike polymer molecules, (rigid rods). There are several approaches to this problem, each with their own advantages and disadvantages.

The first approach, those of the continuum models, is the most realistic. It allows both chains and their constituent segments to occupy all positions of a certain volume in space (and phase space). All within the physical limits determined by for instance excluded volume and, in the case of flexible polymers, bond angles of course. One need not say that these models tend to be rather complicated, and in many cases almost impossibly complicated. Despite the fact that one can model the physical reality with the highest possible accuracy, at least in theory, usually the analysis becomes too complicated, and one has to take recourse to mathematically involved approximations or restrict the validity of the analysis to special, very limited cases. To avoid this, "coarse grained" methods have been developed.

The lattice treatment, the second way of approaching the problem we mentioned, is such a "coarse grained" method. The lattice theories represent the space to be filled partially or completely by polymer molecules by a lattice. The lattice sites are then thought to be occupied by polymer segments and, say, solvent molecules or "holes" (free volume). This is done in such a way that each site is either filled by a segment or a solvent molecule (or empty in the case of "holes"). Figure (2.1) visualizes this concept. One can easily understand that the achieved discretization of the space to be occupied by the molecules of our system reduces the set of configurations from an uncountable, in principle infinite set to at least a countable set. This simplifies the problem considerably, be it at the cost of accuracy.

We shall restrict ourselves to the lattice approach, obviously because of the convenience of the concept, but also because of the fact that at least qualitative behavior of the molecules have been predicted reasonably well for many different polymeric systems. Examples can be given form the field of polymer solutions, bulk polymer, amorphous and semi-crystalline, interphases of copolymers and so forth. In the next section we shall deal with the lattice theory of rigid rods as proposed by Di Marzio (9).

2.1.1 A Lattice Approach

Consider a simple cubic lattice of N lattice sites. On this lattice we place N_r rigid rods each r segments long in the directions of the three orthogonal base vectors. Our population of rods consists consequently of three species: one for every direction. Thus

$$(2)\quad N_r = \sum_{i=1}^{3} N(i)$$

where $N(i) \geq 0$ the number of rods pointing in the i direction (i=1,2,3). The rods are placed in such a way that each segment occupies only one lattice site and that all the sites are at the most singly occupied. Thus, each rod occupies r consecutive lattice sites in a certain direction (fig.(2.2)). Obviously, $N=N_r*r+N_o$, if $N(0)\geq 0$ is the number of unoccupied sites ("holes"). To calculate the entropy of such a system, we have to find out how many ways we can place the population {N(i)} of rods on the lattice.

It turns out to be handy to calculate the number of ways we can place a single rod in the i direction, given the presence of a number of rods on the lattice. Let us assume that there are j(1), j(2) and j(3) rods on the lattice, where j(k) (k=1,2,3) is the number of rods on the lattice in the kth direction. If we want to know the number of ways to place the (j(i)+1)th molecule we must know how many of the remaining $N-r*(j(1)+j(2)+j(3))$ empty sites have r-1 contiguous sites in the i direction that are empty. Let us define $\underline{r}$ (k) to be the position on the cubic lattice of the k-th segment of a chain we intend to put on the lattice. This site has to be empty because we do not allow for double occupancy of lattice sites. Since we are dealing with rigid, rodlike polymers we know that

$$(3)\quad |\underline{r}(i) - \underline{r}(i-1)| = b.\underline{e}(k) \qquad (i=2,\dots,r)$$

where b is the bond length, $\underline{e}(i)$ the i-th base vector and k a constant for all i. The probability that, having chosen an empty site for the first segment, there are (r-1) contiguous empty sites in the i direction can now be written as

$$(4)\quad p\Big(\prod_{i=2}^{r} \underline{r}(i) \;\Big|\; \underline{r}(1)\Big) = \mathop{\pi}_{i=2}^{r} p\Big(\underline{r}(i) \;\Big|\; \prod_{k=1}^{i-1} \underline{r}(k)\Big)$$

where we have used standard probability theory notations and Bayes' theorem (17). This equation is hard to solve for r>1 let alone for r>3 (16). We can however use a Markovian approximation, where we forget about long range correlations along the chain, and write

$$(5)\quad p\Big(\prod_{i=2}^{r} \underline{r}(i) \;\Big|\; \underline{r}(1)\Big) \simeq \mathop{\pi}_{i=2}^{r} p\big(\underline{r}(i) \;\big|\; \underline{r}(i-1)\big) \simeq \big(p(\underline{r}(2) \;|\; \underline{r}(1)\big)^{r-1}$$

Physically equation (5) means that we start at an empty site, calculate the probability that (r-1) steps in the i direction are successful, i.e. that they each end at a empty site, and assume that the step probability is independent of the ranking number of the segment we want to place.

The step probability can be calculated from the number of neighbors to segments that are potentially empty and the number of potentially empty neighbors to holes in the direction anti-parallel to the i direction (the (-i) direction), that is to say anti-parallel to the direction of the i-th base vector (9). The ratio of these numbers is equal to the ratio of the conditional probabilities of respectively finding a neighbor to a segment in the (-i) direction and finding a neighbor to a hole in the (-i) direction. We write for this ratio of probabilities the following expression:

$$(6) \qquad ((1-r)*j(i) + r * \sum_{k=1}^{3} j(k))/(N-r * \sum_{k=1}^{3} j(k))$$

We can easily derive (6) by keeping in mind that when stepping in the i direction one can "see" all r segments from each rod in the perpendicular ($j \neq i$) directions, but just 1 segment from each rod in the ($j=i$) direction: the other r-1 segments are shielded by the first segment. Because the sum of the conditional probabilities equals 1, we find for the probability that a step in the i direction ends on an empty site, given the presence of j(i) (i=1,2,3) rods,

$$(7) \quad p(i;j(1), j(2), j(3)) = (N-r* \sum_{k=1}^{3} j(k))/(N+(1-r)*j(i))$$

Obviously, to place the (j(i)+1)th rod, we have to make (r-1) steps, starting at an empty site. Thus, placing the (j(i)+1)th rod can be done in

$$(8) \quad (N-r* \sum_{k=1}^{3} j(k))* (p(i;j(1), j(2), j(3)))^{r-1}$$

different ways.

What we are going to do now is first place N(1) rods, one by one, and calculate the number of ways we can do that. Then, we put the N(2) molecules on the lattice, again one by one, and calculate the number of ways we can do that given the presence of the N(1) molecules in direction 1. Finally, we place N(3) rods of direction 3 and determine the number of ways to put them on the lattice, given the presence of the N(1) and N(2) rods of respectively type 1 and 2.

For placing the N(1) rods in the 1-direction, we get

$$(9)\quad \prod_{j(1)=0}^{N(1)-1} (N-r * j(1))* (p(1;j(1),\ 0,\ 0))^{r-1} \ / \ N(1)!$$

where the factor N(1)! accounts for the indistinguisability of the rods in the 1 direction. Next we put the N(2) rods in the 2 direction on the lattice. This is possible in

$$(10)\quad \prod_{j(2)=0}^{N(2)-1} (N-r*N(1)-r*j(2))*(p(2;N(1),\ j(2),0))^{r-1} \ /N(2)!$$

ways. Finally, we place the rods in the 3 direction, giving

$$(11)\quad \prod_{j(3)=0}^{N(3)-1} (N-r*N(1)-r*j(2))*(p(3;N(1),N(2),j(3))^{r-1} \ /N(3)!$$

for the number of ways to pack. The product of (6), (7) and (8) gives the number of ways g({N(i)},N(0)) we can pack Nr=N(1)+N(2)+N(3) rigid molecules on a square lattice. Using the approximation

$$(12)\quad y^x \simeq y!/(y-x)!$$

for x<<y, one can show that

$$(13)\quad g(\{N(i)\},\ N(0)) = \prod_{i=1}^{3}(N-(r-1)*N(i))!/\{N(0)!(N!)^2\prod_{i=1}^{3}N(i)!\}$$

Note that we have implicitly taken care of the degeneracy of the rods in the +i and the -i direction (i=1,2,3). One can futhermore prove that the result (equation (13)) is not dependent on the order in which we lay down the rods on the lattice, to calculate g({N(i)},N(0)). Herzfeld for instance obtains the same result by first placing N_r monomers on the lattice and then subsequently "extending" N(1) monomers in the 1 direction, N(2) in the 2 direction and N(3) rods in the 3 direction (13).

The entropy of a system of {N(i)} rigid rods on a cubic lattice of N sites can be calculated from (9) and is equal to

$$(14)\quad S/k = \ell n\ (g(\{N(i)\},\ N(o)))$$

where k is Bolzmann's constant. For large enough N, using the Stirling approximation, this can be written into the following form

$$(15)\quad S/k\cdot r\cdot Nr = Vr^{-1}\{\sum_{i=1}^{3}((1-v(i) + v(i)/r)\ell n(1-v(i)+v(i)/r) \\ -(v(i)/r)\ell nv(i)/r))-v(o)\ell nv/(o)\}$$

giving the entropy per segment, where V(i)=N(i)*r/N the volume fraction of rods of species i, V(0)=N(0)/N the volume fraction solvent or "holes" and V_r the overall volume fraction of rods. Choosing an appropriate reference state we can calculate ΔS=S-S(ref), being the entropy of our system with respect to this reference state (see below).

2.2.2. Results of Calculations

As we said before, rigid rods on a lattice can be used as a model for liquid crystals, for which the constituent molecules are known to be asymmetric. Now, liquid crystals have shown to give transitions from the disordered, isotropic state to more ordered states like the nematic state, where on the average the molecules point their longest axis in a certain preferred direction, or the cholesteric state where (to put it simply) the unique direction is perpendicular to the longest axis of the molecules. (see footnote at the end of this section) (for instance (14)). In terms of rigid rods on a lattice (and neglecting fluctuations), one can expect transitions from a system where N(1)=N(2)=N(3) (the isotropic phase) to a system where N(1)≥N(2),N(3) (the nematic phase) or where N(1)=0 and N(2)=N(3) (the quasi cholesteric phase). Permutations of the three directions in the definitions of the different phases do not change the definitions, of course.

We shall now show that these transitions can at least partly be due to the packing effects of asymmetric molecules. In other words, we shall show that a system can have a lower free energy dF=dU-TdS in a ordered state than in a disordered, even when dU=0. To do this we use equation (15) to calculate the free energy dF=-TdS=-T*(S-S(ref)), and we define the isotropic state to be the reference state. The orientation of the molecules is defined by the order parameter S(i), the fraction of molecules pointing in the i direction. Of course, S(1)+S(2)+S(3)=1. S(i) is not to be confused with the entropy S.

Figure (2.3) shows the free energy per segment as a function of the fraction rods of length 10 in the 1 direction [S(1)] for various volume fractions V_r. The 2 and 3 direction are thought to be symmetric with respect to one another, i.e. S(2)=S(3). $S(1)\to 0$ corresponds to the quasi cholesteric phase, S(1)=1/3 to the isotropic phase and $S(1)\to 1$ to the nematic phase. We see that for a dilute system, V_r low, the lowest free energy is obtained for S(1)=1/3, namely dF=0 (remember that the reference is the isotropic state). This is of course to be expected. For higher values of Vr, one can clearly see that the free energy for both the nematic and the cholesteric states becomes lower than that of the corresponding isotropic state. This means that for these rigid molecules by increasing the density a change in the average orientation can be observed, from isotropic to nematic (stable) or cholesteric (metastable). See also figure (2.4) and (2.5), where we have plotted for the three cases S(1)=0, S(1)=1/3 and S(1)=1 the free energy per segment as a function of the volume fraction V_r rods. Figure (2.5), determined from figure (2.4), suggests the most probable curve for the free energy as a function of the volume fraction. We observe a transition from isotropic to nematic, at least for this molecule, at a volume fraction of Vr=0.4. To reach the cholesteric phase a energy term would be needed to assist, i.e. to lower the free energy curve (9). We have also plotted the free energy for S(1)=0, S(1)=1/3 and S(1)=1 as a function of the length of the molecule. Figure (2.5) gives the result for a closely packed system, V_r=0.99, and figure (2.7) for a less densely packed system, Vr=0.6. We can see that even for a closely packed system, there is a minimum chain length before nematic packing becomes more favorable (approximately 4), and we start seeing long range orientational order (cf.13). For lower volume fractions this minimum chain length increases to higher values.

Footnote. A true cholesteric state is a little more complicated. One can view it as stacked two-dimensional nematic phases, where the direction of the molecules in each 2-D nematic phase is shifted a little with respect to the direction of the molecules of the lower neighbor. The essence of this phase is the absence of the molecules who have their longest axis in direction perpendicular to the planes in which the 2-D nematic phases lie. The cholesteric state we describe with the model is simpler than a true cholesteric state, only the just described basic feature of not having molecules pointing toward a certain direction is modelled. We shall therefore refer to this simplified cholesteric state with "quasi cholesteric state".

2.2.3 Limitations of the Lattice Approach

We learned from figure (2.3) that at high enough a volume fraction the state with the lowest free energy would be the nematic state, for which $S(1)\to 1$. This means that virtually all rods point in the preferred direction of the liquid crystal. We define the orientational order parameter $P(1)=(3*\langle\cos(a(i))\rangle-1)/2$, where $\langle.\rangle$ indicates an ensemble average over all molecules with angle $a(i)$ between the long axis of the molecule and the preferred direction. In a cubic lattice, with only three orientations, this expression reads $p(1)=(3*S(1)-1)/2$. We see that whenever $S(1)$ equals 1, $P(1)$ also equals 1. Experiments usually provide us with values of approximately $P(1)\leq 0.6$ for the nematic state (14). The discrepancy between experimental and theoretical results is of course due to the fact that in a cubic lattice we only allow the rods to be pointing in the 3 orthogonal directions. Another factor is likely to be the fact that we confine the rods to the lattice sites, i.e. the discretization of real space. Both adequacies can be corrected, at least in an approximate way. Let us start with allowing the rods to have more orientations on the lattice than the those of the three orthogonal base vectors. This can be done by placing the first segment of a rod on the lattice in the ordinary way, and then placing the remaining consecutive segments in a given direction, where these segments need not occupy a single lattice site. Figure (2.6) shows this.

Say we allow for n different rod angles (with respect to the 1 direction), and which we shall refer to as angles $i=1,2,...,n$. The excluded volume a rod experiences from another rod is now a function of the angle between the orientations of both rods. This means that $p(i;j(1),j(2),...,j(n))$ is not only a function of the number of rods, but also of the angles between the rods (recall equation (4), $j(i)$ now denotes the number of rods at an angle i). We know from previous results that two rigid rods i and j at an angle $e(i,j)=0$ experience the mole fraction type of interference, while two rods at an angle of $e(i,j)=\pi/2$ interfere in the volume fraction type of way (i.e. all r segments are "felt", see section 2.2.1). For rods i and j at an angle $0 \leq e(i,j) \leq \pi/2$ we would expect a behavior that lies between the mole fraction and volume fraction type of behavior. Imagine that we place a rod of length r on a lattice that already contains a number of parallel rods, also of length r. We place this new rod at an angle e with respect to the already present rods. The interference effect these rods have on the configurational entropy of our "new" rod is thought to be equal to a system where a rod is placed perpendicularly to a field a parallel rods of a projected length. The projection is perpendicular to direction of the newly placed rod, and equal to approximately 1+(r-1)*sin(e) if one takes into account the finite thickness of the rigid molecules (9). See figure (2.9). This means that

$$(16)\quad p(i;j(1),\ldots,j(n)) = \frac{(N-r*\sum_{k=1}^{3} j(k))}{\{N-r*\sum_{k=1}^{3} j(k)+\sum_{k=1}^{3}(1+(r-1)*\sin(e(i,k)))*j(k)\}}$$

Note that if we restrict ourselves to the original three perpendicular orientations we obtain equation (4).

Eliminating the lattice as far as confinement of segments to the discrete lattice sites is concerned, is possible by refining the lattice. In order to do that a generalization of Di Marzio's treatment of the packing of "thick" rods, i.e. rods R(x) sites long and R(y) sites wide in the case of a two dimensional lattice, is necessary. Such a generalization has been proposed by Herzfeld (13). The connection between the discrete lattice and a continuous "lattice" becomes clear in the following. We start with a (for reasons of simplicity) square lattice of N sites, on which we have placed a number of rods R(x) sites long and R(y) sites wide. Having a generalized theory we can now calculate the packing entropy S=k*ln(g({N(i)},N(0))) of this system. We then replace the lattice by a refined lattice, where each site is subdivided in l^2 sites. The number of lattice sites increases from N to $N*l^2$, whereas the length of the rods in units of lattice sites increases from R(x) to R(x)*l. The width of the rods increases of course also from R(y) to R(y)*l. Having done so, the expression for the entropy becomes a function of l: S=k*ln(g({N(i)},N(0),l)). If we let l go to infinity the "lattice" becomes continuous and we got rid of the discrete nature of the lattice. Herzfeld has done this and analyzed the effect the discretization has on the properties of the system.

In the next chapter we will test the Herzfeld formulae by comparing the results with Monte Carlo calculations, to get an idea how well the generalization of the site fraction treatment works.

2.3 RIGID CHAINS OF ARBITRARY SHAPE

The lattice treatment we used to determine the entropy due to orientation dependent packing of linear, rodlike molecules can be extended for the case of polymer molecules of arbitrary shape. Central in the described method is the expectancy p(i) that a lattice site is empty, given that an adjacent site in the (-i) direction is potentially empty. We calculated this expectancy by observing the following. Say we step form an empty site in the i direction to an adjacent site. The step is considered to be successful whenever this site is empty. In other words, if the original site from which we are stepping adjoins a hole in the (-i) direction, then the step is successful. The number of times that this happens is proportional to N(0), the number of such neighbors to holes (equal in all directions). If we step from an empty site in the i direction to a neighboring site, and this site happens to be occupied, than the step is considered to be unsuccessful. The probability that this happens is proportional to the number of (potentially vacant) sites adjoining polymer chains in the (-i) direction B(-i). This means that p(i)=N(i)/(N(i)+B(-i)) since the sum of both probabilities equals 1. B(-i) equals the number of sites adjacent to polymer segments minus the number of bonds in the i direction, because this is the number of sites not accessible to new polymer segments. See figure (2.10).

2.3.1. Cylindrically Symmetric Molecules

We shall restrict ourselves in this section to chains which are cylindrically symmetric along one of the axis of the configuration. Let 1', 2' and 3' be the three local base vectors of the polymer configuration, and let 1, 2 and 3 be the base vectors of the cubic lattice. Any polymer molecule on the lattice occupies r lattice sites, being the degree of polymerization, and each lattice site can be occupied by at most 1 segment (on the average). We assume that a fraction a(i) of the bonds of the molecules point in the i=-3',-2',-1',1',2',3' directions of the local base, where negative values indicate directions anti-parallel to the respective base vectors. To calculate the entropy due to the packing of a number of these chains on the cubic lattice, i.e. the center of mass part and the interference part of the entropy, we only need to take into account the fractions a(x):=a(1')+a(-1'), a(y):=a(2')+a(-2') and a(z):=a(3')+a(-3') because of symmetry considerations. Cylindrical symmetry implies that, say, a(x)=a(y) where we define the z-axis to be the main axis of the configuration. Since the local z-axis can point in either three directions of the lattice base, we can distinguish between three possible orientations of the molecules (provided that they're not spherical). Let N(i) be the number of molecules of which the local z-axis points in the i direction. We calculate the packing entropy of the distribution {N(i)} of chains in a similar way as we did in the case of the linear molecules, namely by adding one molecule at the time to the lattice.

Let us for starters assume that there are j(k) (k=1,2,3) molecules of type k on our cubic lattice of N sites. We can place the (j(k)+1)th chain of type k in at most

$$(17)\quad N(0) = N - r\cdot\sum_{k=1}^{3} j(k)$$

different ways, being the number of empty lattice sites. We have to correct this number for the fact that not all of these sites can harbour a first segment of a chain because of interfering segments of other polymer molecules elsewhere along this chain. In order to find the correction factor we will carry out an analogue of the step by step procedure followed in the rigid rod case, i.e. we will take a(x)*(r-1) steps in the x direction, a(y)*(r-1) in the y direction and a(z)*(r-1) steps in the z direction and for each step determine the probability that the step is successful.

The conditional probability p(i;j(1),j(2),j(3)) that a step in the i direction is successful, given the presence of j(k) (k=1,2,3) molecules, equals

$$(18)\quad p(i;j(1),\ j(2),j(3)) = N(o)/(N(o)+r\cdot\sum_{k=1}^{3} j(k)-(r-1)\cdot\{a(z)\cdot j(i)-a(x)\cdot j(i)+\sum_{k=1}^{3} a(x)\cdot j(k)\})$$

where $N(0) = (N-r*\sum_{k=1}^{3} j(k))$

This means that we can place the (j(i)+1)th chain in

$$(19)\quad \underbrace{\left(N-r\cdot\sum_{k=1}^{3} j(k)\right)}_{(I)}\cdot\underbrace{\prod_{k=1}^{3} p(k;j(1),j(2),j(3))^{(a(z)\delta_{k,i}+(1-\delta_{k,i})a(x))\cdot(r-1)}}_{(II)}$$

different ways, where $\delta_{k,i}$ is the Kronecker delta. (I) denotes the uncorrected center of mass part and (II) the interference correction term. If we first place the N(1) type of chains on the lattice, then we can do that in

$$(20)\quad \prod_{j(1)=0}^{N(1)-1} (N-r\cdot j(1))\cdot p(1;j(1),o,o)^{a(z)\cdot(r-1)}\cdot p(2;j(1),o,o)^{a(x)\cdot(r-1)}\cdot p(3;j(1),o,o)^{a(x)\cdot(r-1)} / N(1)!$$

different ways. Next we put the N(2) type of molecules on the lattice, given the presence of the N(1) type of polymers, which is possible in

$$(21)\quad \prod_{j(2)=o}^{N(2)-1} (N-r\cdot N(1)-r\cdot j(2))\cdot p(1;N(1),j(2),o)^{a(x)\cdot(r-1)}\cdot p(2;N(1),j(2),o)^{a(z)\cdot(r-1)}\cdot p(3;N(1),j(2),o)^{a(x)\cdot(r-1)} / N(2)!$$

ways. Finally, we lay down the N(3) type of chains, possible in

$$(22)\ \prod_{j(3)=o}^{N(3)-1} (N-r\cdot N(1)-rN(2)-r\cdot j(3))*p(1;N(1),N(2),j(3))^{a(x)\cdot(r-1)} *$$

$$\cdot p(2;N(1),N(2),j(3)^{a(x)\cdot(r-1)} *$$

$$\cdot p(3;N(1),N(2),j(3))^{a(z)\cdot(r-1)} / N(3)!$$

ways. The product of these three expressions gives us the total number of ways to pack {N(i)} molecules of length r on the lattice, g({N(i)},N(0)). We can write by approximation

$$(23)\ g(\{N(i)\},N(o)) = \frac{1}{\prod_k N(k)! \cdot (N!)^2 \cdot N(o))} *$$

$$(N-(r-1)\cdot(a(z)\cdot N(1)+a(x)\cdot N(2)+a(x)\cdot N(3)))! *$$

$$(N-(r-1)\cdot(a(x)\cdot N(1)+a(z)\cdot N(2)+a(x)\cdot N(3)))! *$$

$$(N-(r-1)\cdot(a(v)\cdot N(1)+a(x)\cdot N(2)+a(z)\cdot N(3)))!$$

Note that this equation is invariant to permutation of the base vectors, a necessary condition. Note furthermore that the expression reduces to the expression derived by Di Marzio for the case N(2)=N(3)=0 (10).

The total entropy of the presented system equals S=k*ln(g({N(i)},N(0)))+Nr*k*ln(g'({a(i)},r)) where Nr=N(1)+N(2)+N(3). The second term represents the configurational entropy of the individual chains, and equals

$$(24)\quad g'(\{\alpha(i)\},r) = \frac{(r-1)!}{\prod_{i}(\alpha(i)\cdot(r-1)!\cdot\prod_{i}(\alpha(-i)\cdot(r-1))!}$$

We refer to the paper by Di Marzio for model calculations, in a application to the theory of rubber elasticity (10).

CHAPTER 3

MONTE CARLO SIMULATION OF THE PACKING OF RODS

In chapter 2 we derived equations for the number of ways to pack oriented rodlike polymer molecules on a cubic lattice. Using the same general principles we were also able to derive analogous equations for arbitrarily shaped chain molecules. The equations only give (mean field) approximations, so we cannot expect them to be accurate under all regimes. To find out how accurate they really are, and under what circumstances major deviations start to occur, we performed Monte Carlo simulations of the random packing of (oriented) rods on a square lattice. We had to restrict ourselves to the 2 dimensional case to keep the required computing time within reasonable bounds. We shall first repeat some of the calculations carried out by McCrackin, comprising the simulation of packing of "thin" rods, i.e. of rods which are r lattice sites long and 1 lattice site wide (15). We will also present results of calculations done on systems consisting of "thick" rods on a square lattice, i.e. of rods R(x) sites long and R(y) sites wide. The results of the calculations will be compared with the results of 2 dimensional versions of the analytical formulae for both thin rods and thick rods.

3.1 THIN RODS

3.1.1. The Algorithm

The algorithm we used to generate N(1) "horizontal" and N(2) "vertical" rods of r segments in such a way on a square lattice of N sites that they are nonoverlapping has been proposed earlier by McCrackin, but we shall nevertheless give a brief description of it.

The general idea of the algorithm is as follows. First we choose randomly an empty, accessible site to place the first segment of the rod (what this means will become clear below). We then consider this site and r-1 sites to the right to be occupied by segments. This is repeated for each of the horizontal rods. Once the horizontal rods have been laid down on the lattice we do exactly the same for the vertical rods, where we choose randomly an accessible site and use this site plus the r-1 consecutive sites below to harbor the segments of the rod. An infinitely large system is simulated by using periodic boundaries.

During the placing of the rods we keep record of how many accessible sites are left each time we put a "new" rod on the lattice. This enables us to calculate (an estimate of) the number of ways to pack N(1) horizontal and N(2) vertical rods. How to do this is easily explained. First we generate a table which gives all empty sites which have r-1 consecutive empty sites to the right. It is clear that when the lattice is empty, all N sites are "accessible" for the placing of a first segment of a new rod. Let G(i) be the number of sites the i-th rod to be placed has available, equal to the number of entries in the just mentioned table. For the first rod we have G(1)=N. Once we've chosen a site to lay down the first segment of the first rod, we remove this site and successive r-1 sites to the right from this table. We have thus removed all sites from the table occupied by segments. But we also have to remove r-1 successive sites to the left of our randomly chosen site, since rods starting at one of these sites imply double occupancy of sites. G(2) is the number of remaining sites. From these G(2) sites we choose randomly a site to place the first segment of the second horizontal rod we are going to put on the lattice. We remove this site and r-1 successive sites the right from our table, these sites are occupied by segments of the second rod. We also eliminate a maximum number of r-1 sites to the left, as far as they have not been removed already. The number of accessible sites is reduced to G(3). We repeat this process till all N(1) are placed on the lattice. Now we have to update the table with accessible sites for the vertical rods. This is done using the following scheme: (1) regenerate the table for the case of an empty lattice, (2) remove all sites occupied by segments of horizontal rods and (3) remove all sites that are at most r-1 sites above occupied sites, as far as not already removed. This gives the first vertical rod G(N(1)+1) lattice sites to start at. Once placed, sites are removed from the table in a similar way as we did for the horizontal rods. This gives G(N(1)+2). We repeat this process until all N(2) vertical rods are put on the lattice.

The product of all G(i)'s, denoted by G, is an estimate of the number of configurations. Repeating the described process n times gives us an average estimate <g>. Thus, if

$$(25)\quad G = \prod_{i=1}^{N(1)+N(2)} G(i)$$

is an estimate for the number of configurations, then

$$(26)\quad \langle g\rangle = \frac{1}{n} * \sum_{i=1}^{n} g(i)$$

is the average of the estimates, where g(i) is the estimate G of the i-th trial and n is the number of trials. McCrackin showed that this is an unbiased estimate of the number of ways to pack rods, given the distribution over horizontal and vertical rods.

Having determined the degeneracy of packing of rods on a square lattice we can also calculate the entropy of the system, using the equation

$$(27)\quad S = k * \ell n(\langle g\rangle/N(1)!N(2)!)$$

where the factorials correct double counting due to indistinguishability of respectively the horizontal and the vertical rods. In the next sections we shall compare the calculated results with the two dimensional version of the analytical result (13), reading

$$(28)\quad g\ (\{N(i)\},N(o)) = \prod_{i=1}^{2} (N-(r-1)\cdot N(i))!/N(o)N!\prod_{i=1}^{2} N(i)!$$

3.1.2 Isotropic Trimers

In this section we shall concentrate on the packing of trimers on a square lattice of 15x15 sites, where we chose the order parameter S(1):=N(1)/(N(1)+N(2)) to be equal to 0.5 (isotropic system). This is to illustrate some of the general characteristics of the calculations and to give a first impression of how well Monte Carlo results match the analytical results.

There are three (rather obvious) points we should keep in mind when engaging in Monte Carlo simulations. First of all, the number of "trials" must be large enough to sample a sufficiently large part of phase space in order to obtain a reasonable estimate of the entropy. In other words we want to repeat the process described in the last section sufficiently often to obtain a small a standard deviation. Remember that the standard deviation decreases with the inverse of the square root of the number of samples. Secondly, we have to keep in mind that, in spite of periodic boundaries, edge effects may infuence the results our calculations. Thus, the lattice has to be large enough that edge effects are negligible. The last point is that we have to optimize both lattice size and number of iterations, and still be able to do the calculations within a reasonable amount of computer time. Because of this, and because of the fact that we made use of a minicomputer (a DEC VAX-11730), we were limited in the extent to which we could study the system.

Now doing the calculations for relatively dense systems may cause serious difficulties, because of the above mentioned points. A major problem is that many times when we try to lay down the rods randomly (given the distribution) we will find that we cannot do so because there is not enough space. This can happen even when N≥r*Nr because of steric interference of the already placed rods. These "configurations" do count in the averaging (with a g(i)=0), but reduce the number of positive contributions to ⟨g⟩. This means that in a series of runs we may not be able to generate sufficient positive (g(i)≥0) contributions and thereby not sample large enough a part of phase space to get a reasonable estimate of ⟨g⟩. We shall come back to this subject below.

Figure (3.1) shows the average number of configurations of trimers on a square lattice as a function of the number of samples taken, i.e. as a function of the number of runs. The curve is typical for volume fraction less than approximately 0.6, and shows that ⟨g⟩ levels off reasonably well in 10^5 runs (the standard deviation of the sampling is roughly 0.02%). At higher volume fractions however, problems do arise. Figure (3.2) gives ⟨g⟩ as function of the number of runs for trimers on the same square lattice, but now for a volume fraction of 0.6667. We see that the levelling off is rather poor, there are still considerable fluctuations and jumps in the curve (the standard deviation is about 7.9%). That we may expect jumps to occur at higher volume fractions is easily seen when considering the following. Since we place first the horizontal rods, it may very well be that at times the first number of rods are placed in a relatively dense fashion, i.e. close to each other. This leaves as a consequence a relatively large number of sites accessible for the remaining rods, larger at least than when the first rods would have been distributed more evenly over the lattice. This means that at such occasions we would get a large contribution to ⟨g⟩. Because the probability of events like this is expected to be rather low, we see them as "sudden" jumps in the ⟨g⟩ vs. the number of runs curve. This effect is more pronounced in dense systems than in diluted systems. In order to obtain a more acceptable value for the standard deviation we have to do more runs. One should however remember that the standard deviation (s.d.) of the sampling decreases with the inverse square root of the number of samples. This means that in order to get a s.d. of 0.8% we have to increase the number of runs from 10^5 to 10^7. This, however, leads to unacceptably long computing times (remember that all calculations are carried out on a minicomputer).

To illustrate the decrease of the s.d. with an increase of the number of runs, we redid the calculation for 10^6 runs, which should decrease the s.d. with a factor of the square root of ten. The result of this calculation is shown in figure (3.3). We see that the average levels off reasonably well, but the s.d. is still rather high (3.8%). Note that the average of this calculation is well within two times the s.d. of the previous calculation.

That calculations for dense systems are indeed difficult is illustrated in figure (3.4), where we've plotted the fraction of samples in which we were not able to place all rods as a function of the volume fraction. We see that for volume fractions higher than approximately 0.75 the fraction of such rejects begins to come very close to a 100%, making the results of calculations inaccurate.

Comparison of the theoretical predictions by Di Marzio and the Monte Carlo calculations is presented in figure (3.5), for the case of trimers on a square, 15x15 sites lattice. We have also included a calculation based on a Flory type of approach (volume fraction approach as opposed to the site fraction approach). The agreement between Monte Carlo and the theoretical prediction by the Di Marzio treatment seems to be quite good. The Flory type of treatment is less accurate as one can see, except at low volume fractions.

Figure (3.8) gives the relative difference (in percent) of the Monte Carlo calculations and the theoretical results, defined as 100*(Monte Carlo - Theory)/(Monte Carlo). The curve shows that agreement is very good for volume fractions up to approximately $V_r=0.6$, but appears to diverge for denser systems.

Note that the s.d.'s are very small indeed. This is partly due to the fact that we are not showing raw data: remember equation (27). Figure (3.7) shows for three arbitrary cases that although one would think that a 30x30 lattice is huge compared to the size of the trimer, edge effects are not altogether negligible. Figure (3.5) is obviously an upper bound. Although Figure (3.5) is an upperbound, the general trend is preserved using larger lattices, i.e. that the relative error increases with V_r.

3.1.3 More Extensive Calculations

This section deals with more extensive calculations to check the validity of the analytical results. We will present results for a variety of systems and lattice sizes. The variation in lattice size is necessary, as stated before, to see wether results of calculations of relatively small lattices carry over to larger systems (edge effects!). Calculations involving longer rods are necessary to check whether the Markovian approximation breaks down with increasing chain length. A more complete account of the simulation of the packing of thin rods can be found in McCrackin's paper.

The first figure (3.7) gives a comparison between theory and Monte Carlo "experiment" for both a isotropic and a (nearly) nematic system of trimers. Results are given for two lattice sizes. Agreement between the theory and the simulations is remarkable, especially when one concentrates on the larger lattices. The observation that the theory may give erroneous results for volume fractions coming close to 1.0 is however not contradicted (see also McCrackin's paper). The theory gives better results for more oriented systems than for "isotropic" ones (see also Fig. (3.9)). Figure (3.9) gives the relative "errors" of the theoretical predictions as a function of the volume fraction of hexamers. We have chosen for three different orientational states, namely "nematic" (S(1)=1/6), isotropic (S(1)=0.5) and something in between (S(1)=0.25). Although we have only checked volume fractions less or equal than 0.48, we already see that the relative error is much larger than in the case of the trimers (2 to 3 times as large). Figure (3.10) shows the influence of the lattice size on the results, for hexamers in a system where S(1)=0.5

3.2 THICK RODS

3.2.1 Herzfeld's Solution for the Thick Rod Problem

In the previous chapter we referred to the thick rod problem as a way to bridge, at least in part, a lattice approach and a continuum approach. To calculate the entropy of packing of thick rods on a cubic lattice one can make use of a generalization of the Di Marzio theory of thin rods, as described in section (2.2). We shall not give a detailed account of this generalization, due to Herzfeld (13), but instead just point out the strategy used to tackle the problem. We restrict ourselves here to the two dimensional case, for reasons of convenience. In the following section Herzfeld's predictions and Monte Carlo calculations are compared.

Consider a square lattice of N sites. We want to calculate the entropy of a number of rigid rods placed on this lattice, where each of the rods occupy R(x)*R(y) sites. Here R(x) denotes the length of the rods, in units of lattice sites, and R(y) the width. Each lattice site is to be occupied by at most one segment. Say we want N(1) rigid rods to point their longest axis in the 1 direction and N(2) rods in the 2 direction. In order to calculate the number of ways we can place the rods on the lattice we start putting on the lattice N(1)+N(2) single segments. One can easily calculate the number of ways to do that. Once we've done that, we have to correct this number for the excluded volume effect of the thick rods we're going to build around these single segments, in a fashion similar to the way we solved the thin rod problem and the flexible chain problem. That is to say that we make use of a Markovian approximation, where the probability that we can place the rod is replaced by a product of step probabilities. These step probabilities are the conditional probabilities that a site neighbors an empty site in a certain direction.

First we "add" consecutive segments in the, say, 1 direction, segment by segment (see figure (3.11)). This means that we have to add R(x)-1 segments on N(1) and R(y)-1 on N(2) of the placed single segments. Since we are adding in the 1 direction, and there are consequently only rods pointing in the 1 direction, the obstruction the adding of segments may encounter is strictly of the mole fraction type. That means that we only see one segment of the obstructing rods, the knowledge from which we can determine the step probability in the 1 direction. Once this process is finished, we add to the original single segments consecutive segments in the 2 direction. Thus, we place R(y)-1 segments for each N(1)-type rod and R(x)-1 segments for each

N(2)-type rod. Note that we are now dealing with L-shaped molecules. When adding the consecutive segments in the 2 direction, we may find obstruction from N(1)*R(x)+N(2)*R(y) segments (we do not see the others). Finally we fill in the "L"'s. Now only obstructing corner segments can prevent us from entirely filling in the L's, as one can easily see. Using this scheme, one arrives at the conclusion that

$$(29)\quad g(\{N(i)\},N(o))=\frac{(N(o)+N(1)+N(2))!}{N(1)!N(2)!N!N(o)!}\ast$$

$$\frac{(N-(R(x)-1)*N(1)-(R(y)-1)*N(2))!(N-(R(x)-1)*N(2)-(R(y)-1)*N(1))!}{(N-(R(x)+R(y)-2)\cdot(N(1)+N(2))!}$$

where N(0)=N-R(x)*R(y)*(N(1)+N(2)) the number of remaining empty sites. Note that the equation is symmetrical with respect to the interchange of the base vectors, a necessary condition. Note furthermore that for R(x)=r and R(y)=1 equation (29) reduced to equation (28).

Since the probability of finding R(x)*R(y) empty sites in a certain direction is replaced by a Markovian approximation, losing correlations between non-neighboring segments, we have to expect that the theoretical predictions may be less accurate than for the linear polymers.

3.2.2 Results of Calculations

Since extension of the Monte Carlo algorithm for thin rods to an algorithm that is able to handle thick rods is straightforward, we will not waist any paper giving account of it. Instead, results of Monte Carlo calculations are presented involving the placing of rods of dimensions 3x2 3x3 and 6x3 (in units of lattice sites).

Figure (3.12) shows the entropy of "rods" 3 sites long and 3 sites wide as a function of the volume fraction. Agreement between theory and experiment appears to be remarkably good. However, studying the relative differences (fig. (3.12)) shows that it is not as good as for the thin trimers, as one should expect, and that "divergence" occurs at a much lower volume fraction. The shape of the curve strongly suggests that a correction term of quadratic nature could improve the results considerably. Edge effects are quite large, but do not seem to affect the shape of the curve: it just shifts to more negative values (see also fig. (3.14).

Similar, but less pronounced, behavior can be found for rods of 3x2 sites (fig. (3.15)). The influence of the size of the rods on the results can be evaluated with help of figures (3.16) and (3.17). We see that the agreement between theory and M.C. "experiment" is indeed a function of the rod size. The relatively poor results for the thick rods indicate that one should be very careful extrapolating to "continuous" lattices (13).

3.3 SUMMARY AND DISCUSSION

We have shown that the site fraction concept gives quite satisfactory results, at least for rigid, rodlike molecules in the volume fraction range of approximately $0.05 \leq V_r \leq 0.6$. We have not investigated volume fractions of less than 0.05.

Agreement between theory and simulation for the case of "thin" trimers is better than 0.5% for the nematic phase and better than 1.0% for the isotropic phase. This is true for volume fractions less than approximately 0.67. Results for larger "thin" rods seem to be not as good, but are still quite impressive. One finds that in the case of hexamers agreement is better than 2% for the nematic phase and better than 5% (possibly even better than 3%) for the isotropic phase in the volume fraction range of $0.05 \leq Vr \leq 0.5$.

Calculations indicate that the relative difference between theory and Monte Carlo simulations increases rapidly with the volume fraction, casting doubt upon the validity of the theory at volume fractions approaching the value of 1.0.

The generalization of the site fraction concept for refined lattices, where rigid rods have a thickness of more than one lattice site, appears to be less accurate as one would like to see, especially at volume fractions greater than 0.5.

Rods three sites long and two sites wide show a relative discrepancy between theory and "experiment" of less than 2% ,while square rods of 3x3 sites exhibit a relative deviation of less than 4% ($Vr \leq 0.6$). However, these discrepancies seem to increase roughly quadratically with the volume fraction, giving values of respectively ca. 4% and ca. 9% for a volume fraction close to 0.8. Thick rods of six sites length and three sites width also exhibit a similar quadratic behavior of the error as a function of the volume fraction (error less than 8% for $Vr \leq 0.6$ and ca. 16% as $Vr \to 0.8$). Let it be said that the calculations are by no means sacred, i.e. that it is not possible to exclude the possibility of having introduced systematic errors in the calculations. We believe that errors are indeed introduced in the high volume fraction range, because edge effects are more likely to be felt at high volume fractions. However, in spite of this we think that there are enough indications (also from trends at lower volume fractions) that support the statement that one should be skeptical about the theory's validity at high densities ($Vr \to 1.0$). Obviously, this statement does not apply to densities less than approximately 0.6, where theory and simulation agree very well indeed.

Improvement of Di Marzio's site fraction concept is possible by allowing for longer memory of the segments along the chain, i.e. instead of using a Markovian approximation (giving two-segment correlations) including three-segment correlations in the calculation of the interference part of the entropy (see appendix A). This will, however, probably not improve the situation for closely packed systems. As is pointed out elsewhere (11), mean field approximations do not take proper account of long range correlations between rods (like in the case of multi-colored cycles). It is argued that (especially for longer rods) endsegment volume exclusion is neglected to a certain extent.

CHAPTER 4

POLYMER SYSTEMS HAVING A DENSITY GRADIENT

In the next few sections we will give account of an attempt to describe the entropy of a polymer solution having a density gradient in one direction. It is a generalization of the site fraction concept we encountered in the previous chapters. The first section shall deal with the derivation of a general equation for the interference and center of mass part of the configurational entropy. Equations for the "Markovian" step probabilities in terms of site fractions are presented. The second section describes the relationship between the volume fraction step probabilities (zeroth order) and the site fraction step probabilities (first order).

4.1 Configurational Entropy and Step Probabilities

Consider a simple cubic lattice of which the layers are numbered $i=1,2,...m,....$ On the lattice we place polymer molecules and solvent molecules (or "holes") in the usual way. The polymers occupy r sites each. We assume there to be a gradient in the direction perpendicular to the lattice layers (the $+z$ and $-z$ direction) but not in the directions parallel to these layers (the $x,y,-x$ and $-y$ directions). The x,y and z directions represent the directions of the orthogenal base vectors, and $-x,-y$ and $-z$ antiparallel to the orthogonal base vectors.

The configuration of a single polymer chain can be characterized by giving the layer numbers in which we can find the consecutive chain segments (3). An alternative way to describe a configuration is to give the number of bonds a chain has in each direction as a function of the lattice layer number. Thus, one can characterize a chain configuration c by giving a $n(+z,i)c$, being the number of bonds a chain of configuration c has starting in layer i and ending in layer i+1 (defined to be in the +z direction);

b $n(-z,i)c$, ditto for bonds starting in layer i and ending in layer i-1 (-z direction);

c $n(\pm x,i)c$, and $n(\pm y,i)c$, ditto for bonds laying in the plane of the lattice layer (begin and end in layer i).

Obviously, in our definitions of $n(\alpha,i)c$ ($\alpha=\pm x,\pm y,\pm z$) we have implied a numbering of the chain segments in order to determine the direction of a bond. Expressions derived making use of this concept should be insensitive to inversion of the chain numbering. One has furthermore to note that because of assumed homogeneity of the density in the (x,y) plane, we cannot distinguish between bonds in the ±x and ±y directions. We assume therefore that $n(\pm x,i)c = n(\pm y,i)c$.

As stated before, we shall in this section concern ourselves with the packing part of the configurational entropy. Let us assume that there are $j(k)$ chains of configuration $k=1,2,\ldots,c,\ldots$ already on the lattice. We are now going to calculate the number of ways we can place a $(j(c)+1)$th molecule of configuration c. How this can help us in determining the packing entropy of an amount of $N(k)\geq j(k)$ $k=1,2,\ldots,c,\ldots$ polymer chains on a lattice will become clear below.

The number of ways we can place the $(j(c)+1)$th chain assuming that there are $j(k)$ polymer chains on the lattice can formally be written as

$$(30)\quad N_o(j(1),j(2),\ldots j(c),..;i(c))*f(j(1),j(2),\ldots j(c),..)_c$$

where $N_o(j(1),\ldots;i(c))$ equals the number of remaining empty sites on layer $i(c)$, the layer where conformation c has it's first segment; $f(j(1),\ldots)_c$ is a factor that accounts for the interference the (j(c)+1)th chain experiences from the already present chains. $N_o(j(1),\ldots;i)$ equals the total number of sites in a layer i, say L, minus the number of segments in that layer. The factor $f(j(1),\ldots)_c$ is determined using a Markovian approximation similar to the one we used in the case of the rigid rods or the rigid chains of arbitrary shape. Define the following conditional probabilities:

<u>a</u> P_{+z} $(j(1),j(2)\ldots,j(c),\ldots;i)$, being the probability that a site in layer i+1 is empty given that the site it neighbors in layer i is potentially empty;

<u>b</u> P_{-z} $(j(1),j(2),\ldots,j(c)\ldots;i)$, this is the probability that a site in layer i-1 is empty given that the site it neighbors in layer i is potentially empty;

<u>c</u> P_x $(j(2),j(2),\ldots j(c),\ldots;i)$, $p_y(j(1),j(2),\ldots j(c),..;i)$, ditto for two sites in layer i; we do not distinguish between +x and -x, +y and -y because of assumed symmetry in the lattice layers. For clarity we retain the x and y notation, but obviously $p_x=p_y$.

By approximation we may write

$$(31)\quad f(j(1),\ldots j(c)\ldots)_c = \prod_i (P_{+z}(j(1),..;i)^{n(+z,i)_c} \,.\, P_{-z}(j(1)\ldots;i)^{n(-z,i)_c} * \\ P_x(j(1),\ldots;i)^{n(x,i)_c}\; P_y(j(1),\ldots;i)^{n(y,i)_c}$$

We can make use of (30) and (31) to determine the number of ways to place an ensemble of $\{N(k)\}$ (k=1,2,...) polymer molecules on the lattice. A way to do that is first to place all the chains of configuration 1 on an empty lattice giving

$$(32)\quad W(1) = \prod_{j(1)=0}^{N(1)-1} N_o(j(1),o,\ldots,o;i(1)).f(j(1),o,\ldots,o)_1$$

for the number of ways to do that. Subsequently placing $N(2)$ molecules of configuration 2 is possible in

$$(33)\quad W(2) = \prod_{j(2)=0}^{N(2)-1} N_o(N(1),j(2),o,\ldots,o;i(2)).f(N(1),j(2),o,\ldots;o)_2$$

different ways. To pack $N(k)$ chains of configuration k on a lattice on which are already placed $N(1),N(2),\ldots,N(k-1)$ molecules gives

$$(34)\quad W(k) = \prod_{j(k)=0}^{N(k)-1} N_o(N(1),\ldots,N(k-1),j(k),o,\ldots,o;i(k))* \\ f(N(1),\ldots,N(k-1),j(k),o,\ldots,o)_k$$

This means that the packing part of the configurational entropy of an ensemble of $\{N(k)\}$ molecules on a lattice having L sites in each layer equals

$$(35)\quad Sp = k* \ln\,(g(\{N(k)\},L)/\prod_k N(k)!)$$

where

$$(36)\quad g(\{N(k)\};L) = \prod_k W(k)$$

Our concern is now to determine expressions for $N_o(j(1),\ldots;i)$ and $f(j(1),\ldots)_c$, i.e., for N_o and the P's.

N_0 can be determined by bearing in mind that (a) a bond connects two segments, (b) the bond direction determines where the second segment is with respect to the first segment and (c) that therefore counting all bonds that "end" in a layer i gives us the information of how many segments there are in that layer i (not counting the very first segment of the chains). This means that

$$(37)\qquad N_0\,(j(1),j(2),\ldots j(c),\ldots;i) =$$

$$L-\sum_k j(k).(n(+z,i-1)_k+n(x,i)_k+n(y,i)_k+n(-z,i-1)_k+\delta_{i,i(k)})$$

where the Kronecker delta $\delta_{i,i(k)}$ accounts for the very first segment of a chain of configuration k.

We will present expressions for the P's which can be derived using notions described in section (2.2.1). We have to bear in mind that these P's are step probabilities, i.e., probabilities that tell us the chance of finding an empty neighbor to a empty site. Let us take as an example the probability of finding an empty site in layer i+1 to a empty site in layer i, a conditional probability. Since the site in layer i is thought to be empty not all segments in layer i+1 are able to "obstruct our path", namely all those segments connected to bonds coming from or going to layer i. Using this insight one sees immediately that

(38) $p_{+z}\,(j(1),j(2),\ldots;i) =$

$$\frac{N_o\,(j(1),j(2).,,,;i+1)}{N_o\,(j(1),j(2),\ldots;i+1)+\sum_k j(k).\{n(x,i+1)_k+n(y,i+1)_k+n(-z,i+2)_k-n(-z,i+1)_k+\delta_{i,i(k)}\}}$$

or that

(39) $p_{+z}\,(j(1),j(2),\ldots;i) =$

$$\frac{N_o\,(j(1),j(2),\ldots;i+1)}{L-\sum_k j(k).(n(+z,i)_k+n(-z,i+1)_k)}$$

Similarly,

(40) $p_{-z}(j(1),j(2),\ldots;i) =$

$$\frac{N_o\,(j(1),j(2)..;i-1)}{L\;-\sum_k j(K).(n(-z,i)_k+n(+z,i-1)_k)}$$

A step in the plane of a latice layer is a step in a homogeneous system, something we have dealt with before. This provides us with

(41) $p_x(j(1),j(2),\ldots;i) =$

$$\frac{N_o(j(1),j(2)\ldots;i-1)}{N_o(j(1),j(2),\ldots;i)+\sum_k j(k).(n(+z,i-1)_k+n(-z,i+1)_k+n(y,i)_k)}$$

or

(42) $p_x(j(1),j(2),\ldots;i) =$

$$\frac{N_o(j(1),j(2),\ldots;i)}{L \quad - \sum_k j(k).n(x,i)_k}$$

We already know that $p_y(j(1),j(2),\ldots;i) = p_x(j(1),j(2),\ldots;i)$.

4.2 Connection with the Volume Fraction Approach

We derived earlier that a step in the +z direction from an empty site in layer i to a neighboring site in layer i+1 has a probability

(43)

$p_{+z}(j(1),j(2),..;i) = N_o(j(1),j(2)\ldots;i+1)/L-\sum_k j(k).(n(+z,i)_k+n(-z,i+1)_k$

of being successful given the presence of j(i) (i=1,...) molescules of conformation i. If we devide numerator and denominator by L, then(43) becomes the limit sum of a harmonic series

$$p_{+z}(j(1),j(2)...;i)=\frac{N_o(j(1),j(2),..;i+1)*}{L}$$

$$(44)\qquad *\sum_{n=o}^{\infty}\left(\frac{\Sigma j(k).(n(+z,i)_k+n(-z,i+1)_k)}{L}\right)^n$$

because

$$\sum_k J(k).(n(+z,i)_k+n(-z,i+1)_k)<L, \text{ at least}$$

for volume fractions smaller than one. For not too pathological ases one may even assume that

$$\sum_k j(k).(n(+zs,i)_k+n(-z,i+1)_k)<<L$$

holds, true of course for dilute systems, but probably also for more concentrated systems. Given this to be true, one can truncate the summation neglecting second and higher order terms:

$$(45)\quad P_{+z}(j(1),..;i)\approx(N_o(j(1),..;i+1)/L)*\{1+\sum_k j(k)\cdot(n(+z,i)_k+n(-z,i+1)_k)/L\}$$

Note that this equation consists of two parts:

(I) A classical Flory type of volume fraction term, giving the lowest order of approximation for the step probability;

(II) A correction term accounting for the cooperative ordering of bonds.

Similarly,

$$(46)\quad P_{-z}(j(1),...;i)\approx(N_o(j(1),..;i-1)/L^*)*\{1+\sum_k j(k)(n(-z,i)+n(+z;i-1))/L\}$$

(47)

$$P_x(j(1),j(2)...;i) \approx (N_o(j(1),...;i)/L) * \{1+\sum_k j(k).n(x,i)_k/L\}$$

Appendix A Higher Order Approximations

Consider a simple cubic lattice on which are placed rigid rods of length r (conform section (2.2.1). The probability that one can find (r-1) consecutive empty sites next to an empty site reads

$$\text{(AI)}\quad p\left(\prod_{k=2}^{r} r(k) \,|\, r(1)\right)=\prod_{k=2}^{r} p\left(r(k) \,\Big|\, \prod_{i=1}^{k-1} r(i)\right)$$

We approximated (AI) by

$$\text{(AII)}\quad p\left(\prod_{k=2}^{r} r(k) \,|\, r(1)\right) \simeq \prod_{i=2}^{r} p(r(i) \,|\, r(i-1)) \simeq (p(r(2) \,|\, r(1)))^{r-1}$$

this being a Markovian approximation. We might however want to include "three-segment correlations" in our analysis, i.e.

$$\text{(AIII)}\quad p\left(\prod_{k=2}^{r} r(k) \,|\, r(1)\right) \simeq p(r(2) \,|\, r(1)) * \prod_{k=3}^{r} p(r(k) \,|\, r(k-2)\cdot r(k-1)) \simeq$$
$$\simeq p(r(2) \,|\, r(1)) * (p(r(3) \,|\, r(1)\cdot r(2)))^{r-2}$$

It is not easy to determine $p(r(3) \,|\, r(1)\cdot r(2))$, but let use see how far we get using some simple notions from probability theory.

One can easily show that

$$\text{(AIV)}\quad p(r(3) \,|\, r(1)\cdot r(2)) = \frac{p(r(3)\cdot r(2) \,|\, r(1))}{p(r(2) \,|\, r(1))}$$

where $p(r(2)\mid r(1))$ is a known quantity. We further know that $p(r(3)\cdot r(2)\mid r(1))$ obeys the equation

$$\text{(AV)}\quad p(r(3)\cdot r(2)\mid r(1))+P(r(3)\cdot\overline{r(2)}\mid r(1)))+$$

$$+p\overline{(r(3)}\cdot r(2)\mid r(1))+p\overline{(r(3)}\,\overline{\cdot r(2)}\mid r(1))=1,$$

the horizontal bars indicating occupancy of a site. Let B( ) and B( ) be the number of (potentially empty) neighbors to rods pointing in respectively the same and a perpendicular direction to the direction of the three sites we are investigating. We define further more B(+) ≡ B( ) + B( ), being the sum of both. Using the same "Ansatz" as in Di Marzio's thin rod theory we find for the last term in (AV)

$$\text{(AVI)}\quad p(\bar{r}(3)\cdot\bar{r}(2)\mid r(1))=$$

$$\frac{B(\quad)}{N(o)\ +B(\quad+\ )}+\frac{B(\ )}{N(o)\ +\ B(\ +\quad)}\cdot\frac{B(\ +\quad)}{N(o)\ +\ B(\ +\quad)}$$

where N(o) is the number of empty sites. Equation (AVI) can be derived making use of the following observations:

a) if an empty site happens to neighbor a rod in the direction the rod is pointing, <u>both</u> consecutive sites in this direction are occupied by segments;

b) if an empty site happens to neighbor a rod in the direction perpendicular to the direction the rod is pointing in, then we know that if neighbor is occupied but we do not know whether the next to neighbor is occupied. We have to correct for that.

Using similar arguments we get for the second term of equation (AV):

$$\text{(AVII)}\quad p(r(3)\cdot r\overline{(2)} \mid r(1)) =$$

$$\frac{B(\ )}{N(o) + B(\ +\ )} \cdot \frac{N(o)}{N(o) + B(\ +\ )}$$

Note that (AVI and (AVII) obey the condition

$$\text{(A VIII)}\quad p(\overline{r(3)}\,\overline{\cdot r(2)} \mid r(1)) + p(r(3)\overline{\cdot r(2)}) \mid r(1) = p(\overline{r(2)}\ r(1))$$

furthermore that for example

$\text{(A IX)}\quad p(r(3)\cdot\overline{r(2)}\ r(1)) = p(\overline{r(2)} \mid r(1))\cdot p(r(2)\ \overline{r(1)})$ indicating that we have

gone further than the two-segment correlations of section (2.2.1).

The third term of (AV) is not as easy to determine as the second and fourth term. However, we do not expect $p(r(3).\overline{r(2)}\ r(1))$ and $p(\overline{r(3)}.r(2) \mid r(1))$ to differ much and some physical insight may help us to find a relationship between the two. Say we have a row of three consecutive sites on the cubic lattice, and say that the first site is empty, the second one occupied by a segment and the third again empty. The second site can only be occupied by a segment from rods perpendicular to our three sites. Let us have a look again at three consecutive sites but now the first two are empty and the third occupied. The third site can be occupied either by segments from rods perpendicular to the three sites or by a (single) segment from rods parallel to the three sites. This means that except for a correction term for the just mentioned parallel rods, both cases should be equally probable. This implies that

(AX) $p(r(3).\overline{r(2)}\ r(1))=p\overline{(r(3)}.r(2)\ r(1)).(1-B(\ )/B(\ +\ ))$.

This is good physics. To show that it is indeed good physics assume that the three sites be parallel to a "field" of nematic rigid rods. This means that $B(\ +\ ) = B(\ )$, or that $p(r(3).\overline{r(2)}\ r(1))=0$ which is of course to be expected. If the three sites be perpendicular to this nematic field of rigid rods, then $B(\ ) = 0$ and $p(r(3).\overline{r(2)}\ r(1))=p\overline{(r(3)}.r(2)\ r(1))$. This is obviously also true.

Using (AX) we find

(AXI) $p(r(3).\overline{r(2)}\ r(1)) = N(o).B(\ +\ )/(N(o)+B(\ +\ ))^2$

markedly enough a Markovian type of expression.

We now have enough information to determine $p(r(3).r(2)\ r(1))$, namely equations (AV), (AVI), AVII) and (AXI). This leads to

(AXII) $p(r(3).r(2)\ r(1)) = N(o)^2/(N(o)+B(\ +\ ))^2$ again an expression one would also obtain in the Markovian approximation.

This means that (a) our analysis is too naive, or (b) long range correlations along the chain are indeed taken care of at least to a second order approximation.

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Fig. (2.1) Flexible polymers on a square lattice.

Fig. (2.2) Rigid, rodlike molecules on a square lattice; 1 and 2 indicate the directions of the orthogonal base vectors.

Fig. (2.3) The free energy dF as a function of the orientational state of a 10-mer on a cubic lattice. The verical axis represents the free energy per k.T, per chain segment, the horizontal axis the fraction of rods S(1) pointing in the 1 direction. Different curves represent different volume fractions: (1) V_r = 0.01, (2) V_r = 0.1, (3) V_r = 0.2, (4) V_r = 0.4, (5) V_r = 0.6, (6) V_r = 0.8, (7) V_r = 0.99. The reference state is the "isotropic" state (S(1) = 0.5). Athermal system.

Fig. (2.4) The free energy per k.T, per polymer segment as a function of the volume fraction 10-mers on a cubic lattice. The reference state is the "isotropic" state. Three curves are indicated: (1) S(1) = 0.5 ("isotropic" state), (2) S(1) = 1.0 (nematic state) and (3) S(1) = 0.0 ("quasi cholesteric" state). Athermal system.

Fig. (2.5) Most probable curve for the free energy as a function of the volume fraction 10-mers on a cubic lattice (see also fig. (2.4)). A transition for the "isotropic" phase 1 (S(1) =

	0.5) to the nematic phase 2 (S(1) = 1.0) can be seen. In order to get a transition to the "quasi cholesteric" phase 3 we need an energy term to assist.
Fig. (2.6)	Free energy as a function of the chainlength r for rods on a cubic lattice at a volume fraction of V_r = 0.99. The dashed curve represents the "isotropic" state (S(1) = 0.5): the reference state is chosen to be the isotropic one. Results for S(1) = 1.0 (nemetic system) and S(1) = 0.0 (quasi cholesteric system) are indicated.
Fig. (2.7)	Identicial to Fig. (2.6), but now for V_r = 0.6.
Fig. (2.8)	Rigid rods on a lattice: the classical way to pack the rods (left) and the way to pack when we want to include more than 2 directions (right).
Fig. (2.9)	Calculation of the excluded volume two rods experience when at angle e.
Fig. (2.10)	When stepping in the i direction, only A, B and C can obstruct our path, not D. D is shielded by B. Similarly, when stepping in the j direction only A and D can obstruct our path, not B and E.
Fig. (3.1)	The average number of configurations ⟨g⟩ as a function of the number of runs (i.e. the number of iterations) for trimers on a square lattice of N=225 sites. There are 10 trimers on the

lattice ($N_r = 10$), half the rods point in the 1 direction and half in the other direction ($S(1) = 0.5$). The resulting volume fraction rods is $V_r = 0.1333$.

Fig. (3.2) As Fig. (3.1), but now for $V_r = 0.6667$.

Fig. (3.3) As fig. (3.2), but now for a larger number of iterations.

Fig. (3.4) The fraction of unsuccessful trials as a function of the volume fraction trimers ($S(1) = 0.5$, $N = 225$). A trial is unsuccessful whenever not all rods intended could be placed.

Fig. (3.5) Entropy per lattice site as a function of the volume fraction. System: trimers on a square lattice of $N=225$ sites ($S(1) = 0.5$); (1) Monte Carlo results, (2) theoretical prediction using the site fraction method, (3) theoretical prediction using "Flory" type of volume fraction approach.

Fig. (3.6) Relative difference ("deviation") between Monte Carlo (MC) calculation and site fraction prediction of the entropy, as a function of the volume fraction. Error bars are indicated. Identical system as in fig. (3.5).

Fig. (3.7) Influence of the lattice size on the results: The vertical axis represents the relative error (between MC and theoretical prediction of the entropy), the horizontal axis the inverse lattice size 1/N. Results for three volume fractions V_r are shown (R=3, S(1) = 0.5).

Fig. (3.8) Comparison of different orientational states. The relative error as a function of volume fraction is given for two orientational states: S(1) = 0.1 and S(1) = 0.5, on two different lattice sizes (N=225 and N=900).

Fig. (3.9) Identical to Fig. (3.0), but now for hexamers and three orientational states: S(1) = 0.1667, S(1) = 0.25 and S(1) = 0.5.

Fig. (3.10) Lattice size influence on the relative difference between theory and MC for hexamers (S(1) = 0.5). Three volume fractions are indicated.

Fig. (3.11) The Herzfeld method to do the lattice statistics for thick rods. Explanation of the method can be found in the text.

Fig. (3.12) Configurational entropy of squares of size 3x3 sites as a function of the volume fraction. Open circles give the MC results, the curve gives the theoretical prediction due to Herzfeld. The lattice size is N=225.

Fig. (3.13) The relative error as a function of the volume fraction. Squares of 3x3 sites on three different lattices: N=225, N=900 and N=2025.

Fig. (3.14) The relative difference between MC and theoretical prediction as a function of the inverse lattice size. Squares of 3x3 sites; three volume fractions are indicated: V_r = 0.12, V_r = 0.38 and V_r = 0.60.

Fig. (3.15) The relative difference between MC calculation and theoretical predictions of the entropy of rods of dimensions 3x2 on a square lattice as a function of the volume fraction. Results for two orientational states and lattice sizes are given.

Fig. (3.16) As fig. (3.15) for rods of size 6x3, results for three lattice sites N are given.

Fig. (3.17) Lattice size dependence of the relative difference between theory and "experiment", for rods 6 sites long and 3 sites wide. Nematic state (S(1)=1.0). Results for three volume fractions V_r are given.

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I wish to express my gratitude to a number of people. First of all there is Ed Di Marzio. Apart from proposing the subjects studied in this report, he spent a huge amount of time discussing them with me. He has proven to be a great teacher, and has made my stay at NBS more than worthwhile. Then there is Frank McCrackin, who provided the basic algorithm for the Monte Carlo simulations and was of invaluable help when I programmed this algorithm. Last, but not least, I wish to thank Leslie Smith and Gerard Fleer. Without their help my visit to NBS would have been impossible.

fig. 2.1

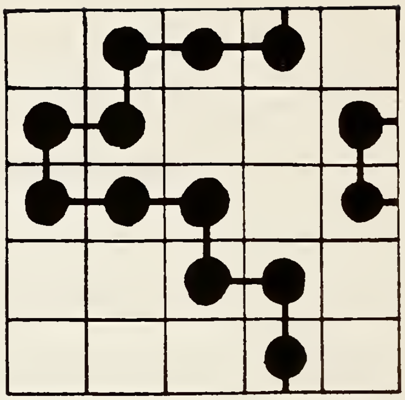
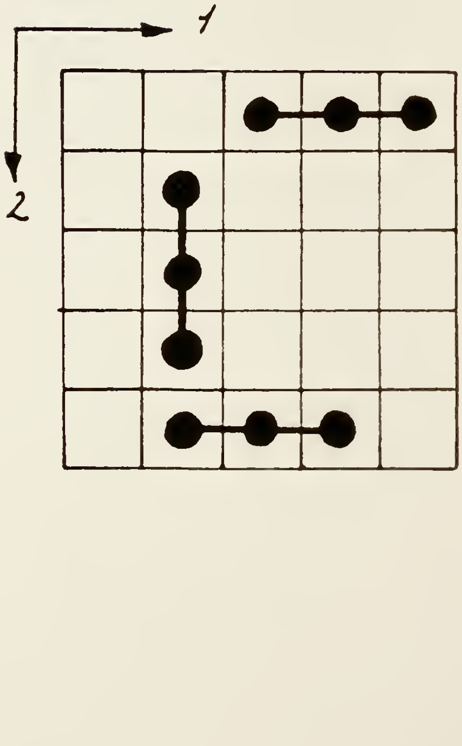
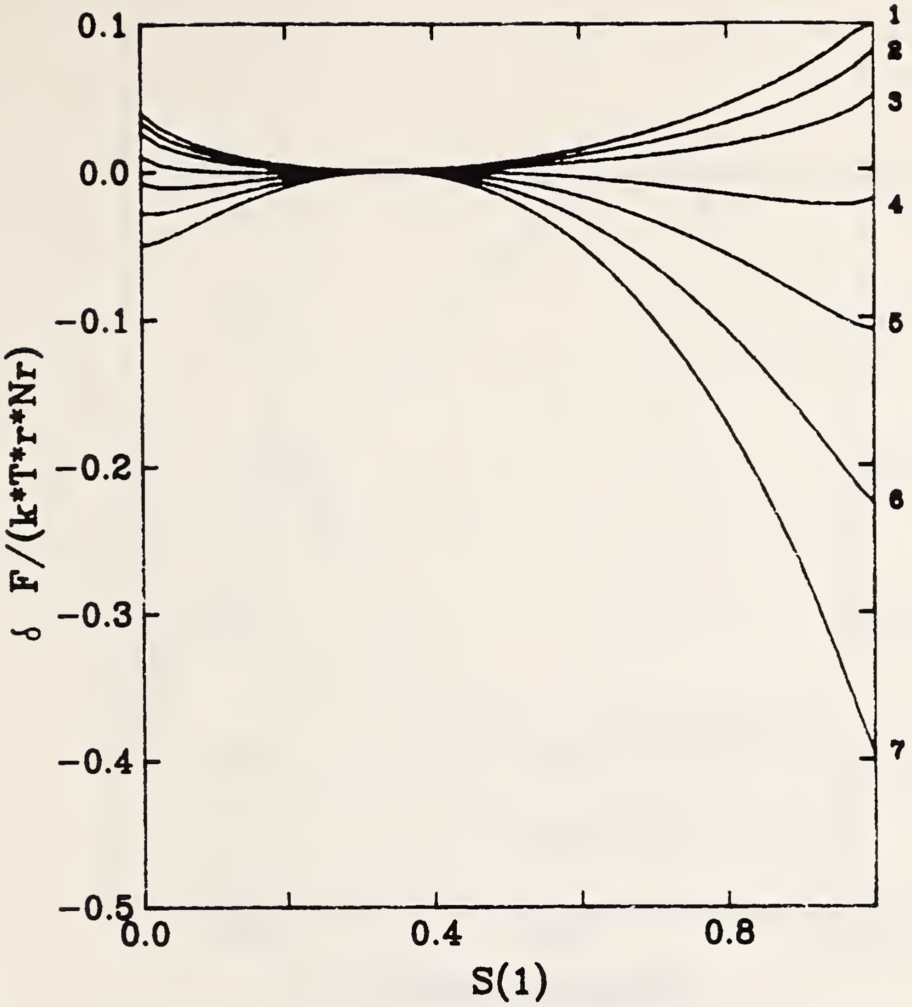


fig. 2.2

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0.1
0.0
−0.1
−0.2
−0.3
−0.4
−0.5
0.0
0.4
0.8
S(1)
1
2
3
4
5
6
7

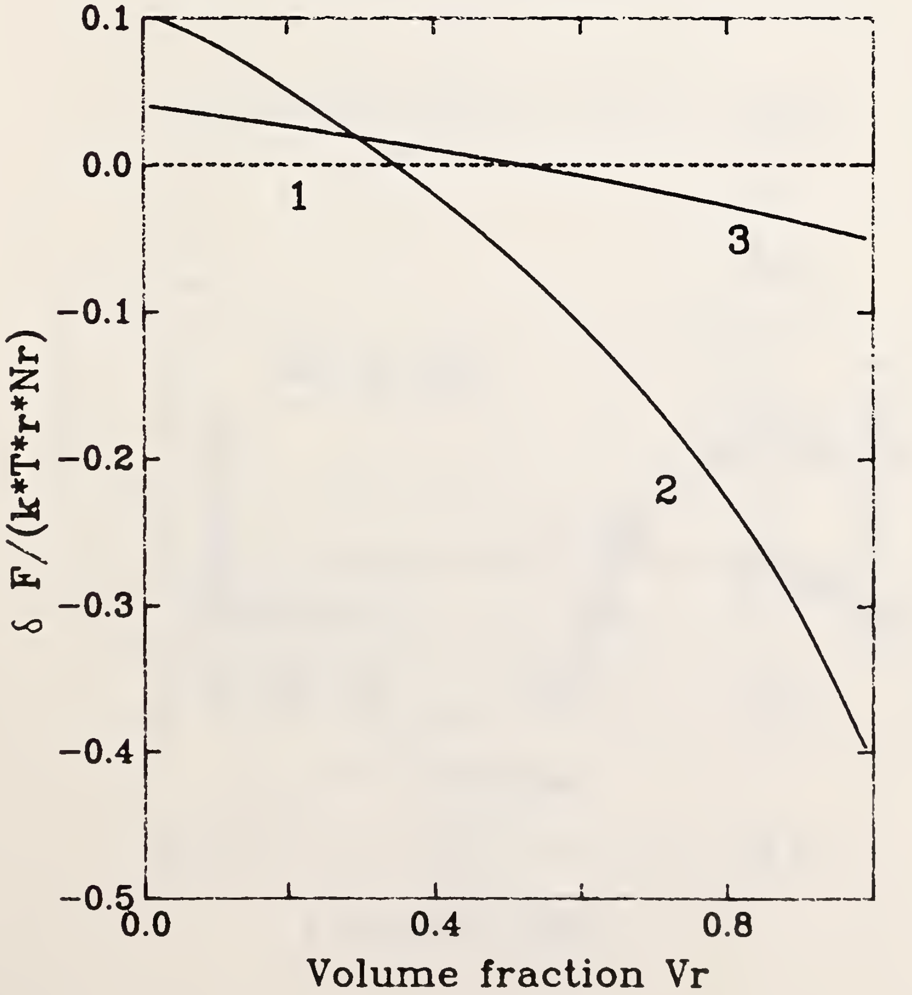
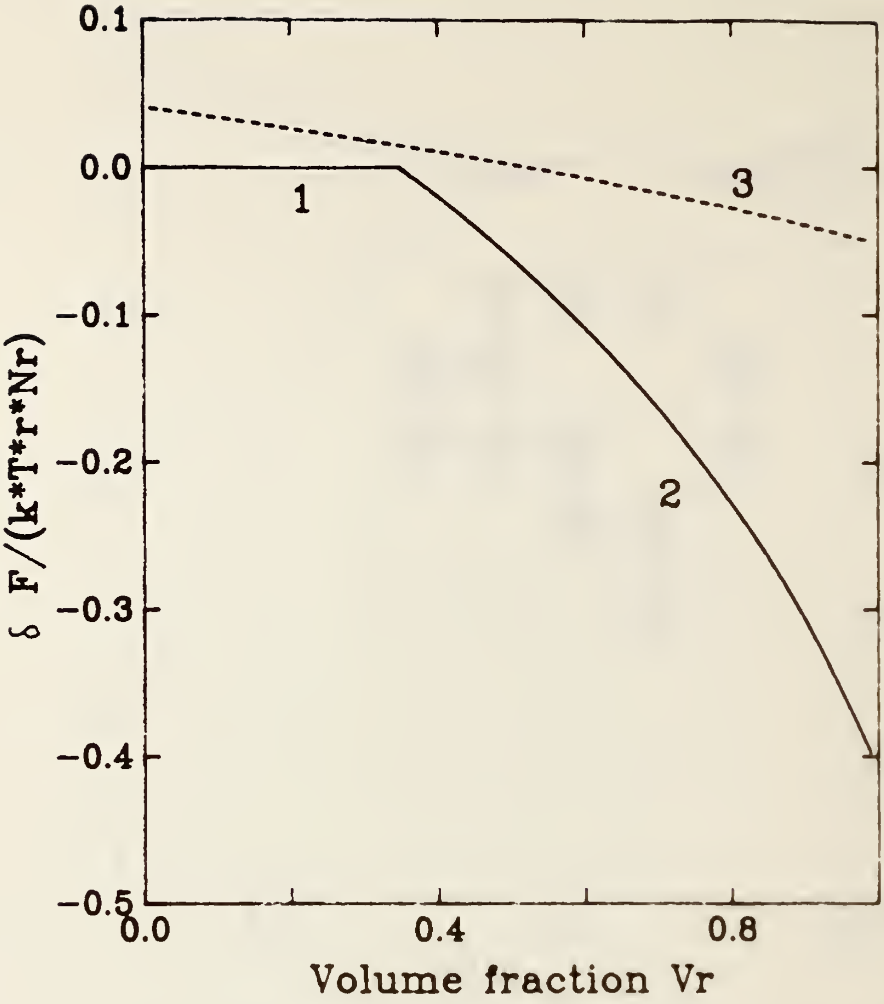

δ F/(k*T*r*Nr)
0.1
0.0
−0.1
−0.2
−0.3
−0.4
−0.5
0.0
0.4
0.8
Volume fraction Vr
1
2
3

fig.
2.5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0.0
−0.1
−0.2
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−0.4
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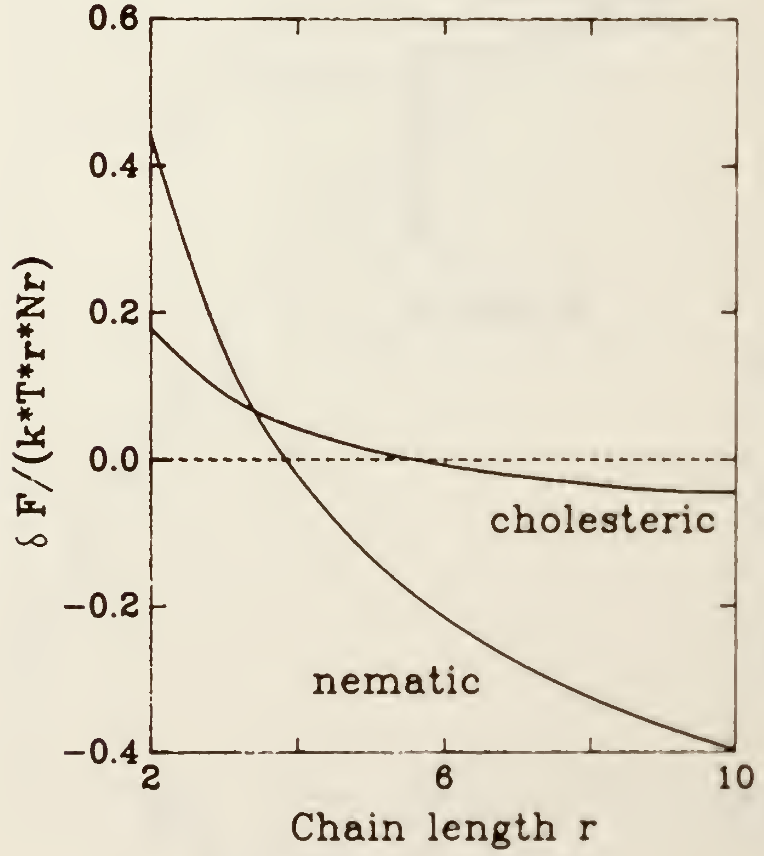
0.0
0.4
0.8
1
2
3
δ F/(k*T*r*Nr)
Volume fraction Vr

fig.
2.6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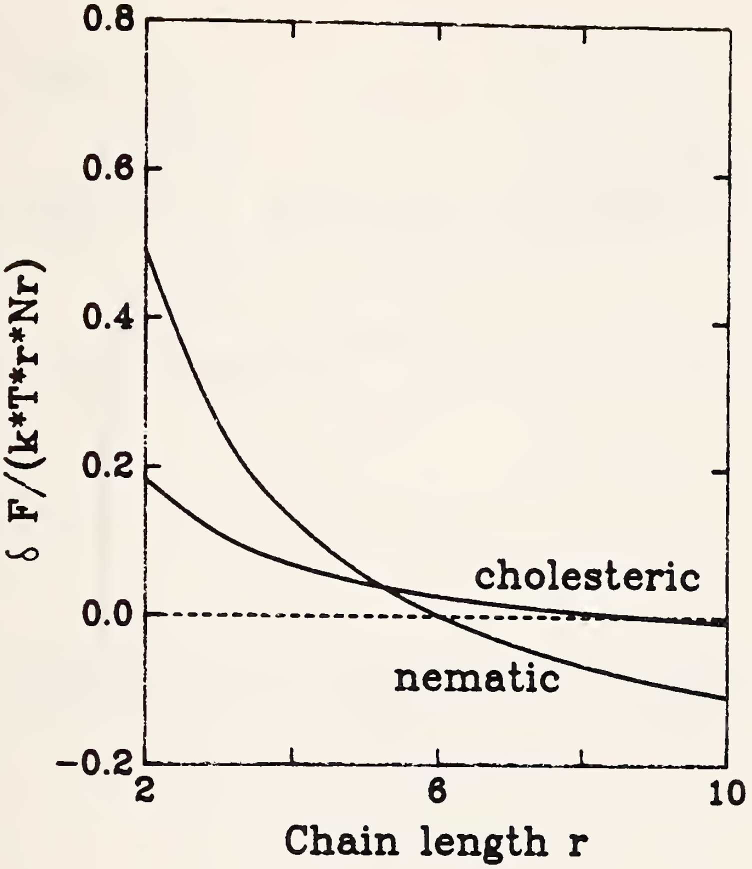
0.4
0.2
0.0
−0.2
−0.4
2
6
10
cholesteric
nematic
δ F/(k*T*r*Nr)
Chain length r

fig.
2.7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0.6
0.4
0.2
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δ F/(k*T*r*Nr)
cholesteric
nematic
2
6
10
Chain length r

fig.
2.8

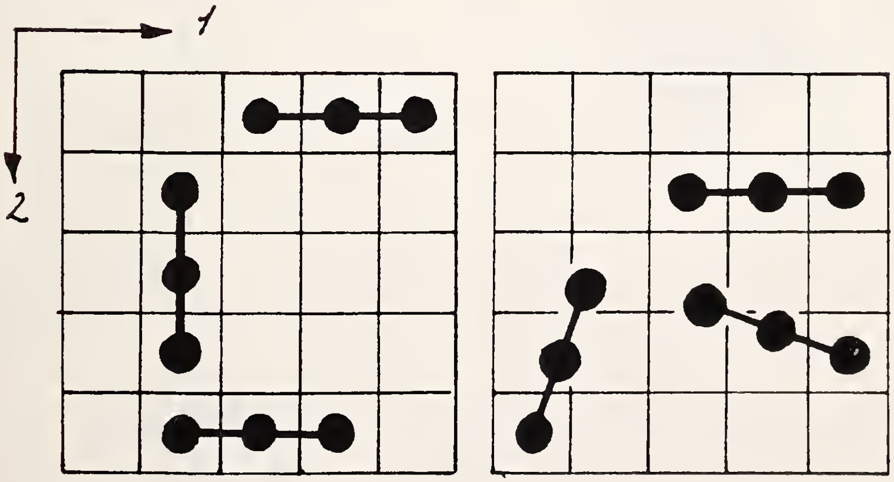

1
2

fig.
2.9

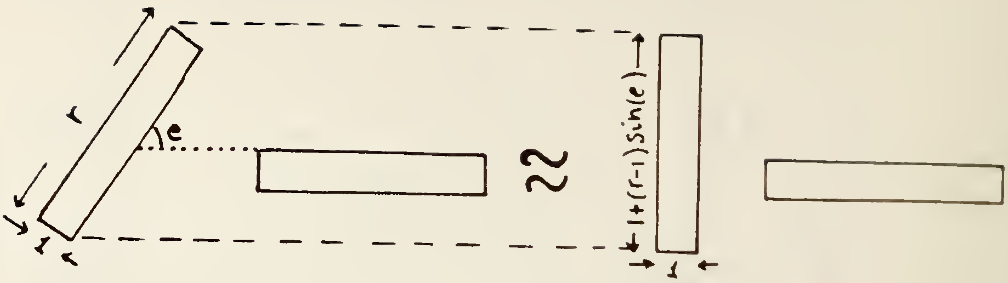


fig.
2.10

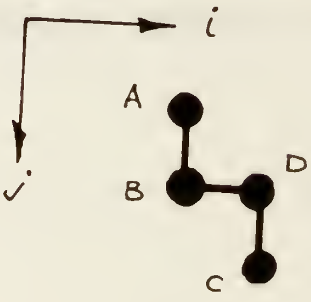
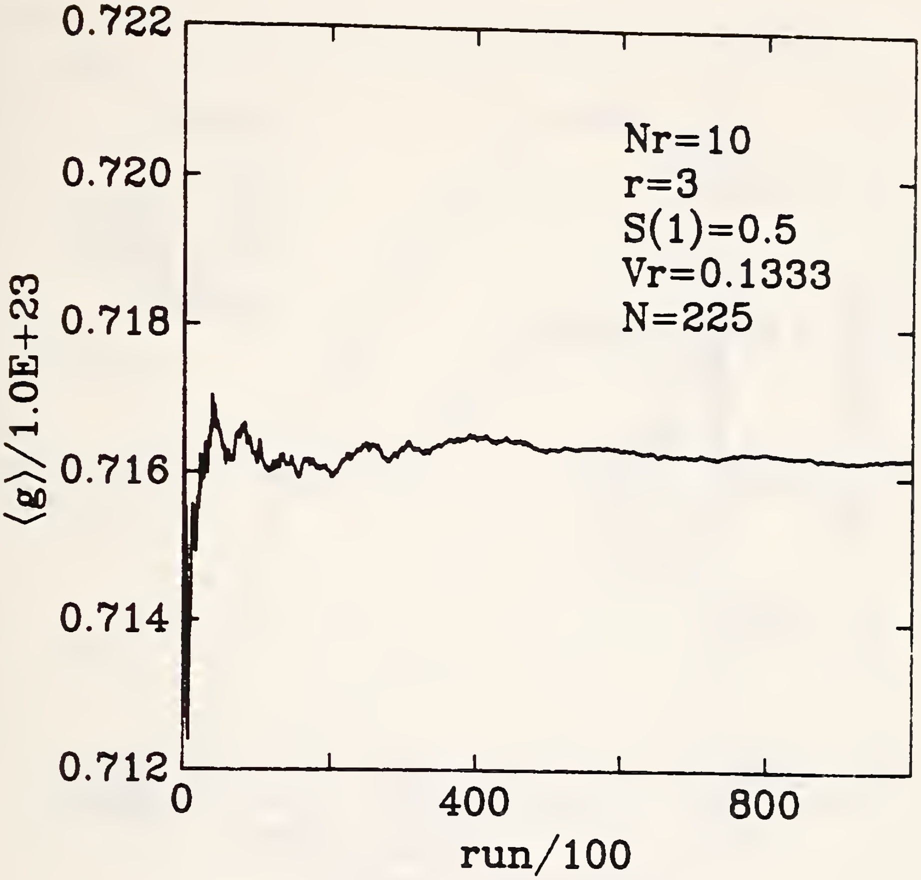


fig. 3.1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0.720
0.718
0.716
0.714
0.712
⟨g⟩/1.0E+23
0
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800
run/100
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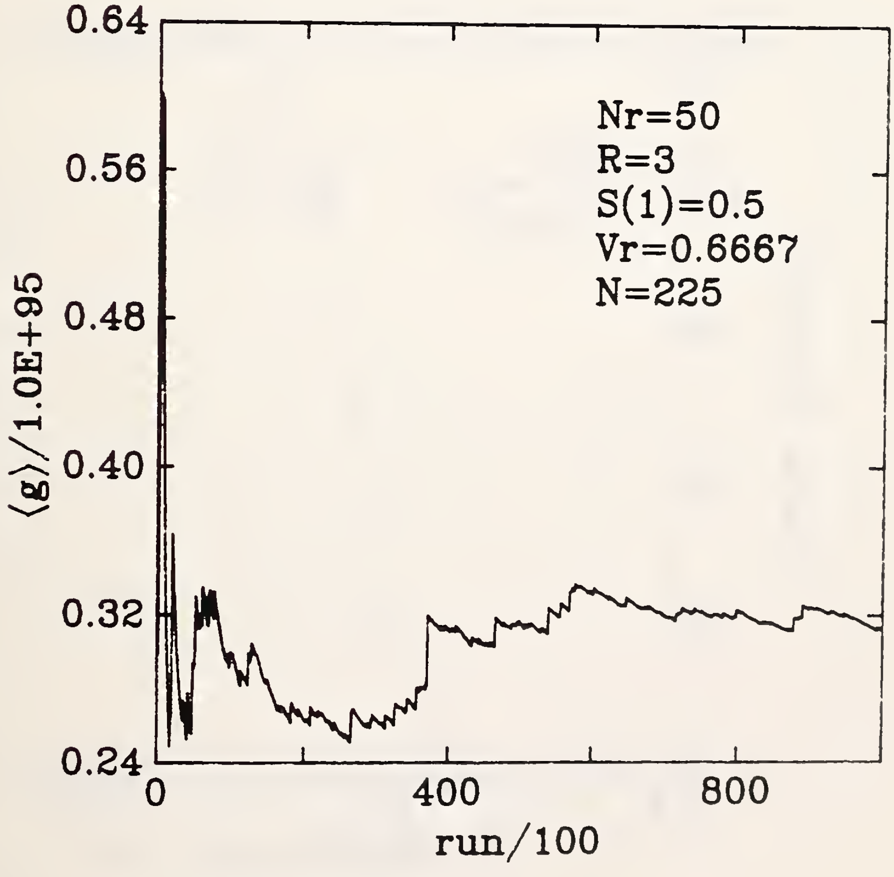
r=3
S(1)=0.5
Vr=0.1333
N=225

fig. 3.2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0.48
0.40
0.32
0.24
⟨g⟩/1.0E+95
0
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800
run/100
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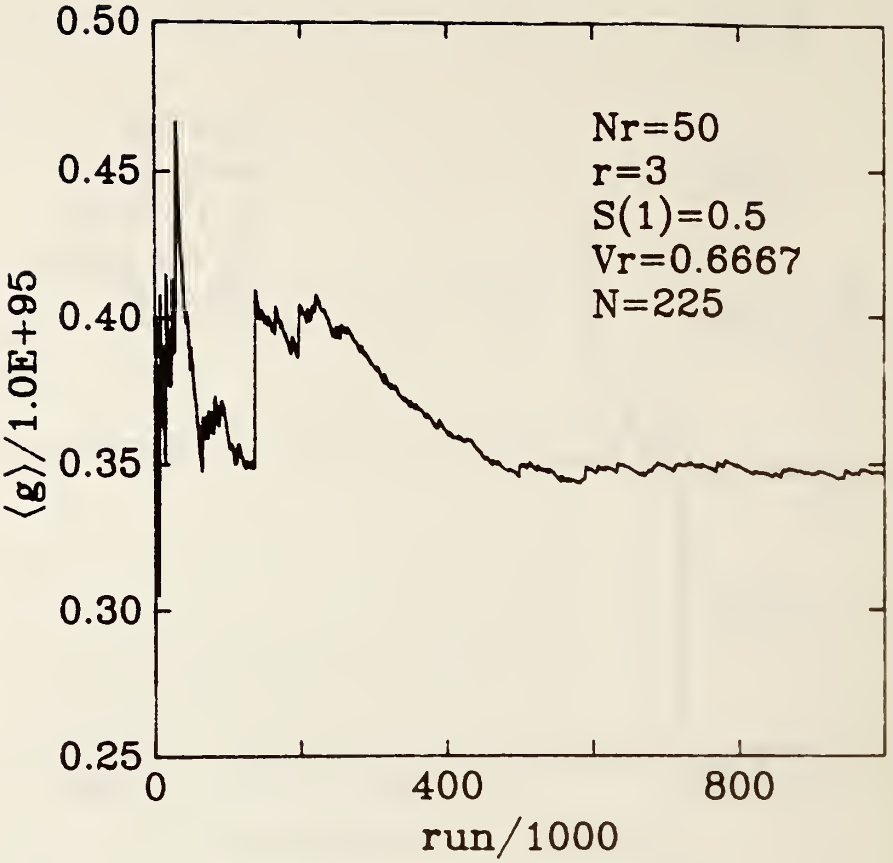
R=3
S(1)=0.5
Vr=0.6667
N=225

fig.
3.3



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0.45
0.40
0.35
0.30
0.25
⟨g⟩/1.0E+95
0
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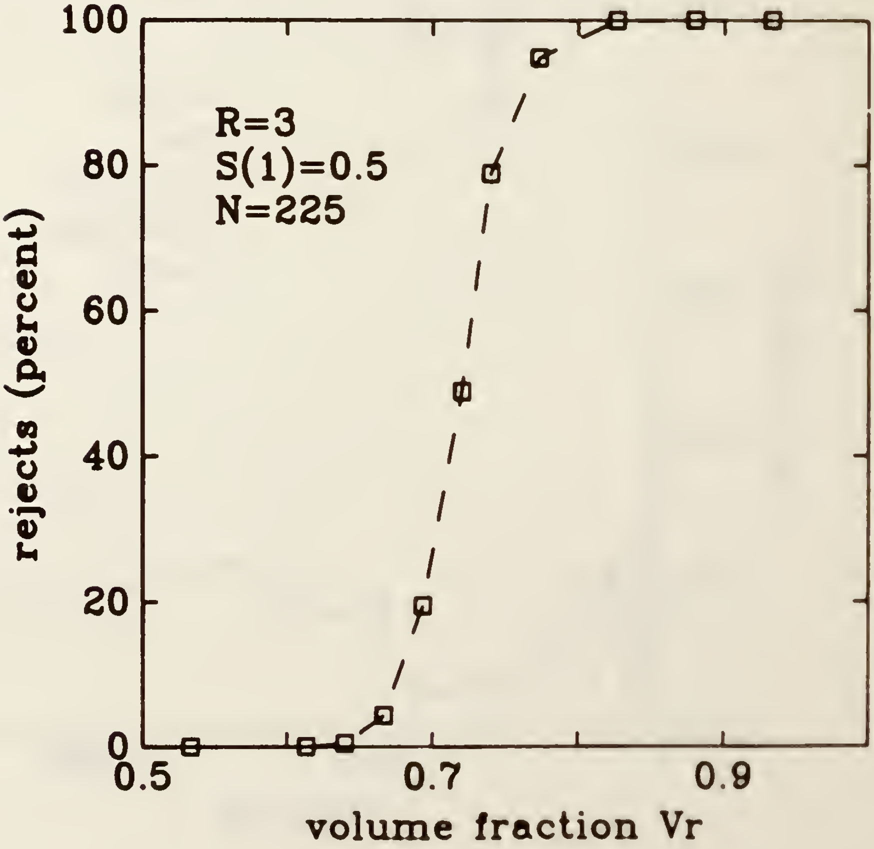
800
run/1000
Nr=50
r=3
S(1)=0.5
Vr=0.6667
N=225

fig.
3.4



100
80
60
40
20
0
rejects (percent)
0.5
0.7
0.9
volume fraction Vr
R=3
S(1)=0.5
N=225

fig.
3.5

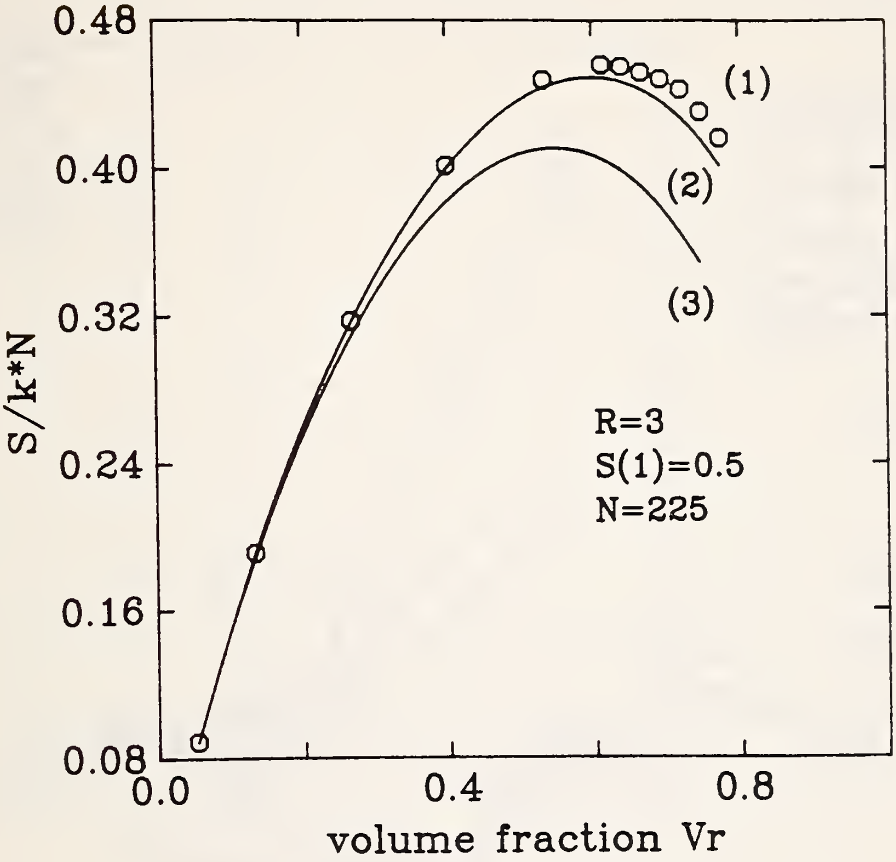

0.48
0.40
0.32
0.24
0.16
0.08
S/k*N
0.0
0.4
0.8
volume fraction Vr
(1)
(2)
(3)
R=3
S(1)=0.5
N=225

fig.
3.6

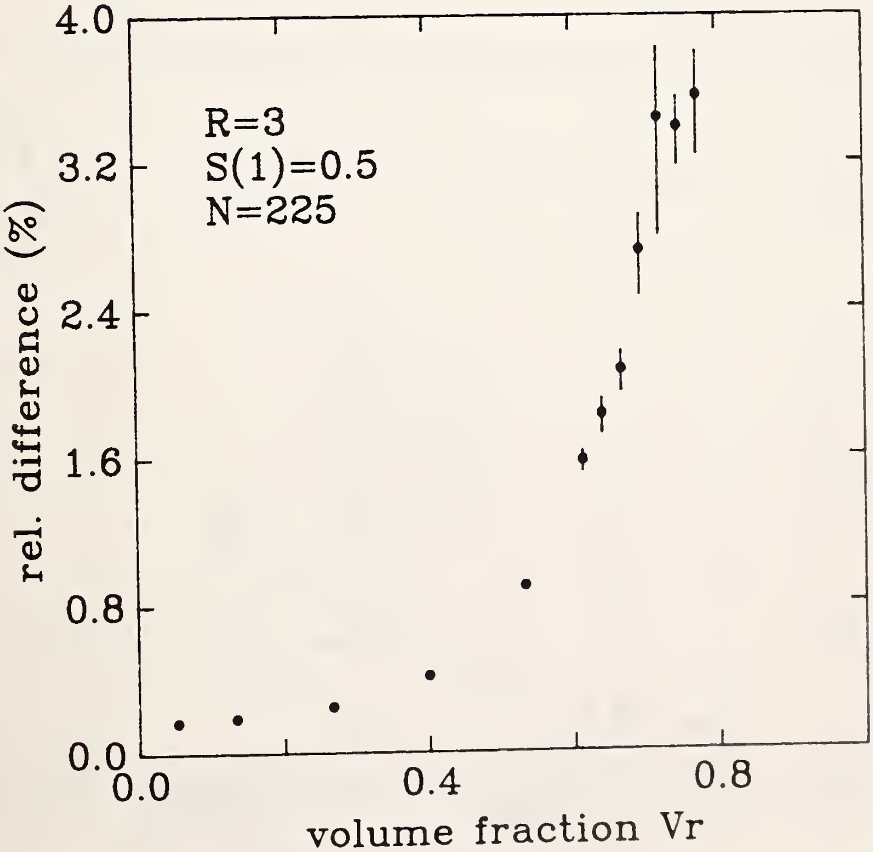

4.0
3.2
2.4
1.6
0.8
0.0
rel. difference (%)
0.0
0.4
0.8
volume fraction Vr
R=3
S(1)=0.5
N=225

fig.
3.7

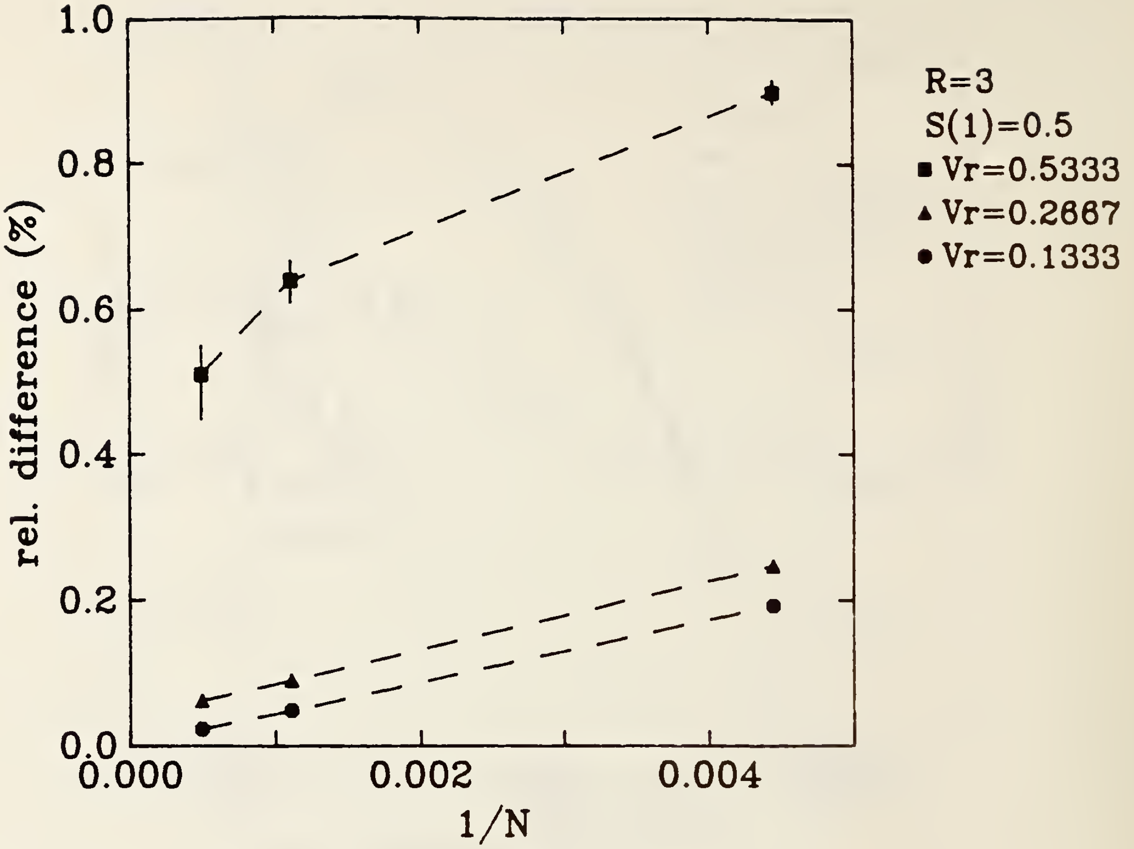
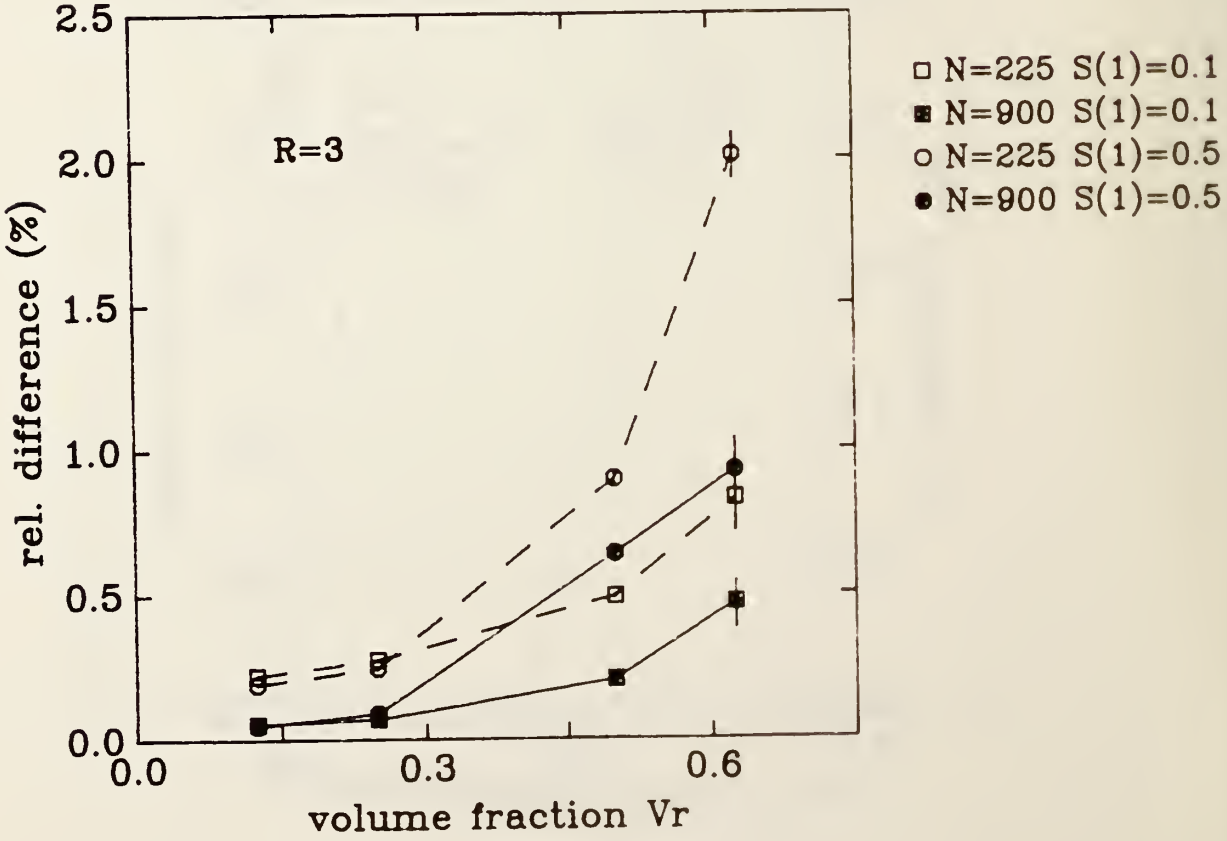

R=3
S(1)=0.5
■ Vr=0.5333
▲ Vr=0.2667
● Vr=0.1333
rel. difference (%)
1/N
0.0
0.2
0.4
0.6
0.8
1.0
0.000
0.002
0.004

fig.
3.8


R=3
□ N=225 S(1)=0.1
■ N=900 S(1)=0.1
○ N=225 S(1)=0.5
● N=900 S(1)=0.5
rel. difference (%)
volume fraction Vr
0.0
0.5
1.0
1.5
2.0
2.5
0.0
0.3
0.6

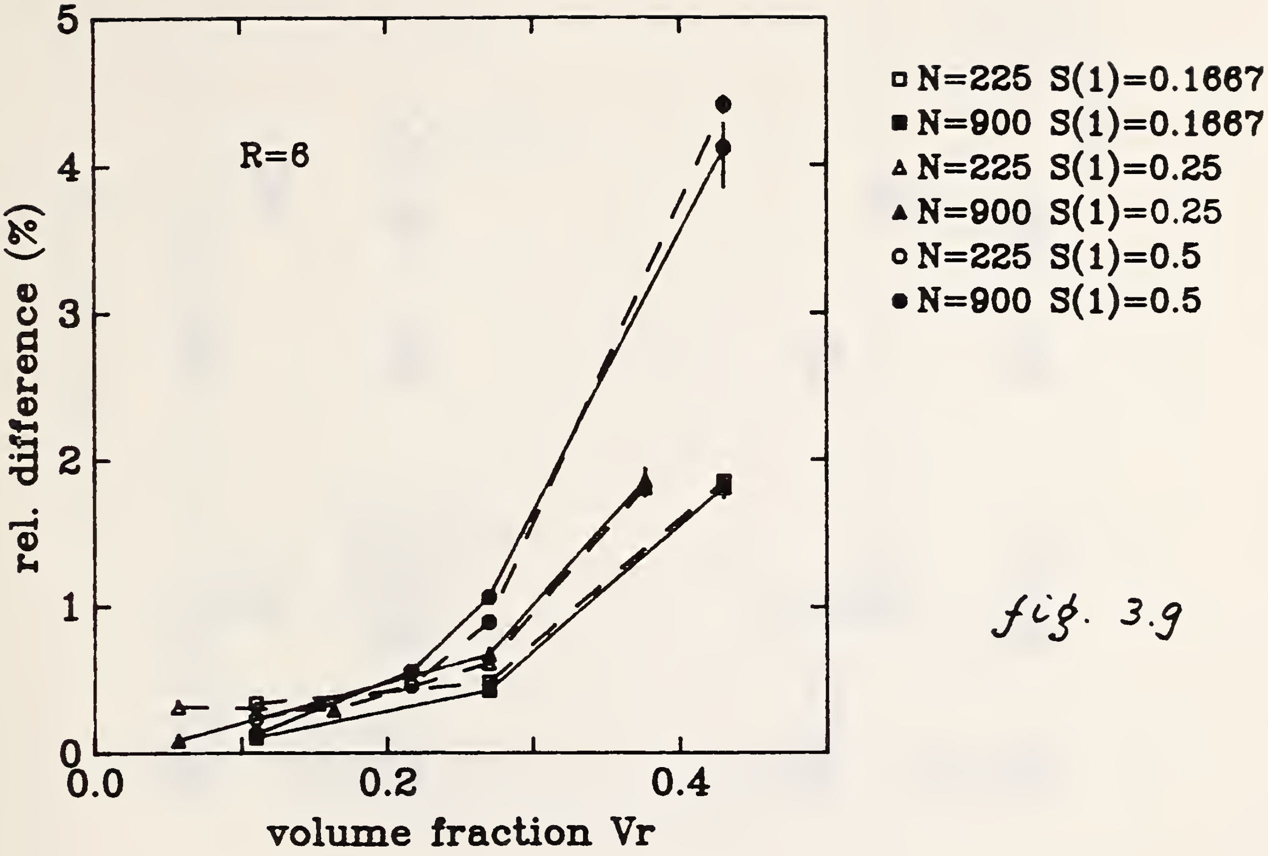


fig. 3.9

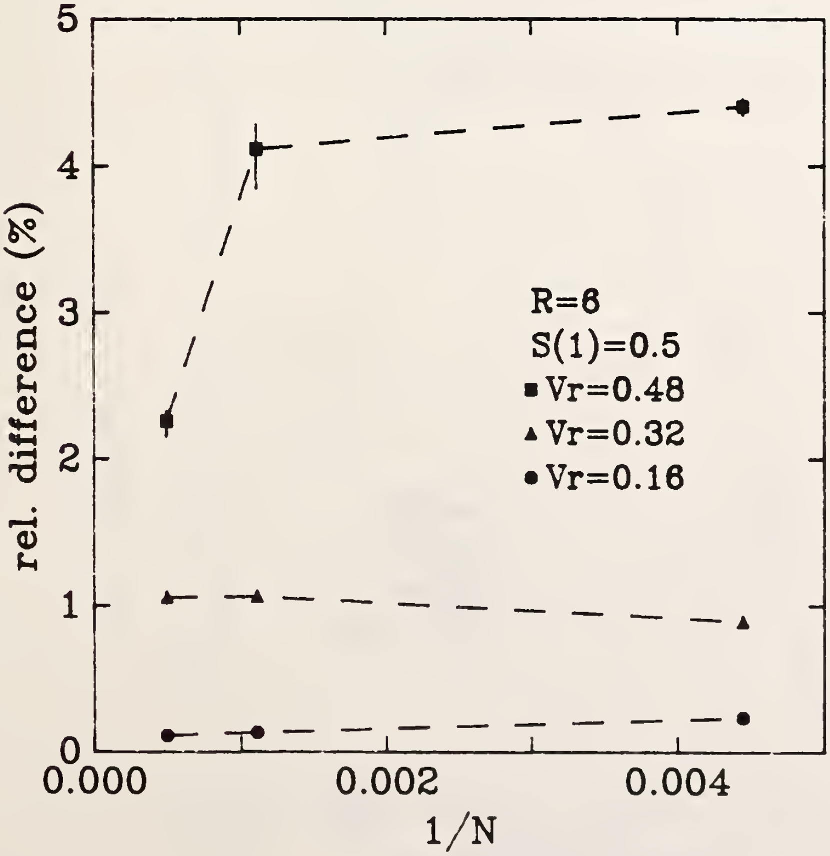


fig. 3.10

fig.
3.11

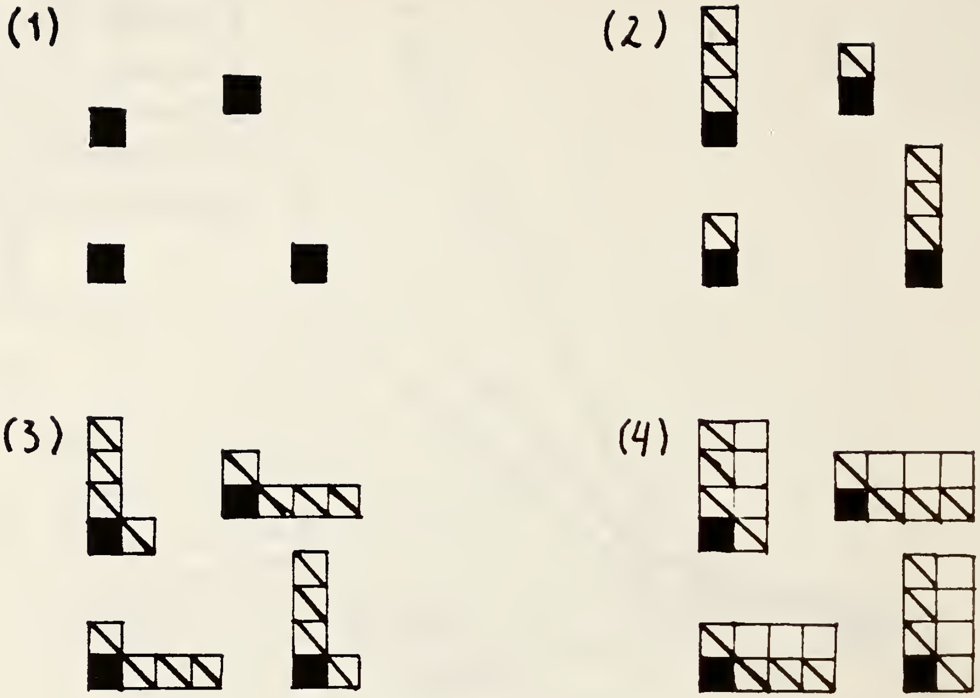
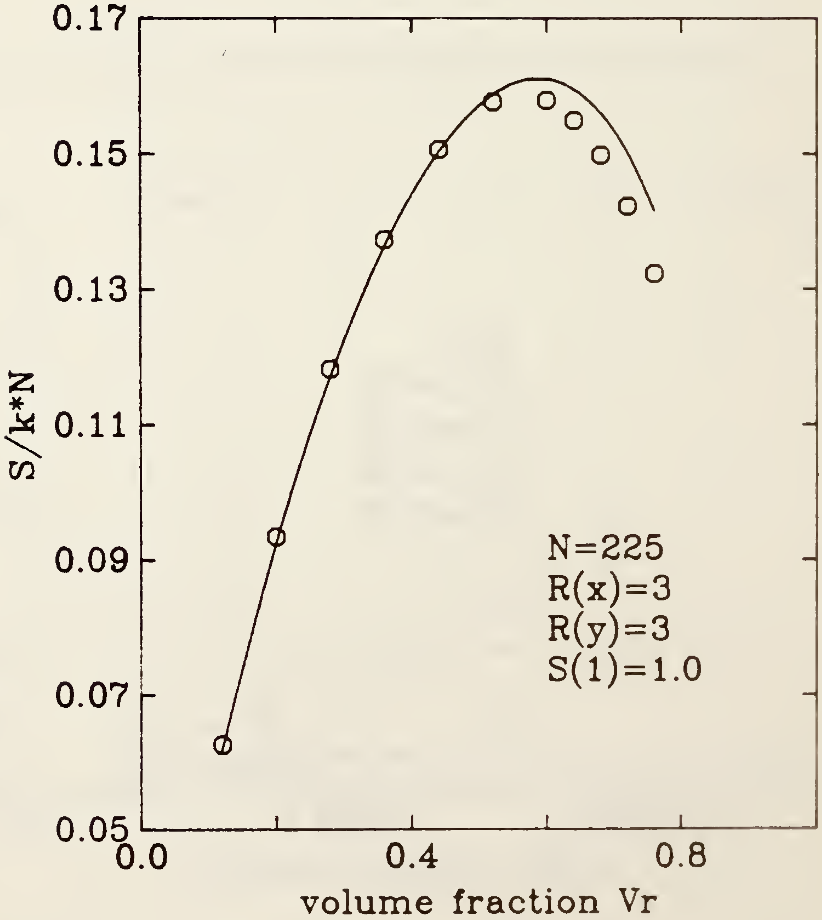
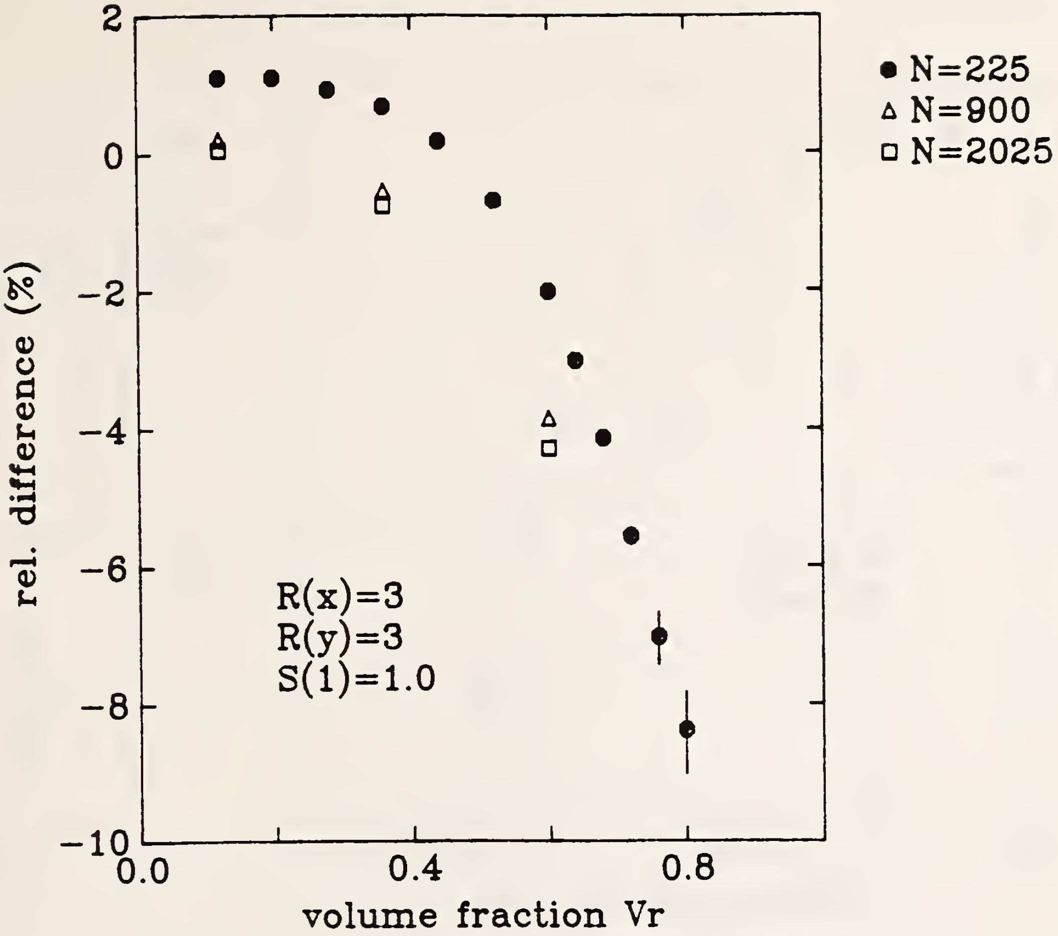
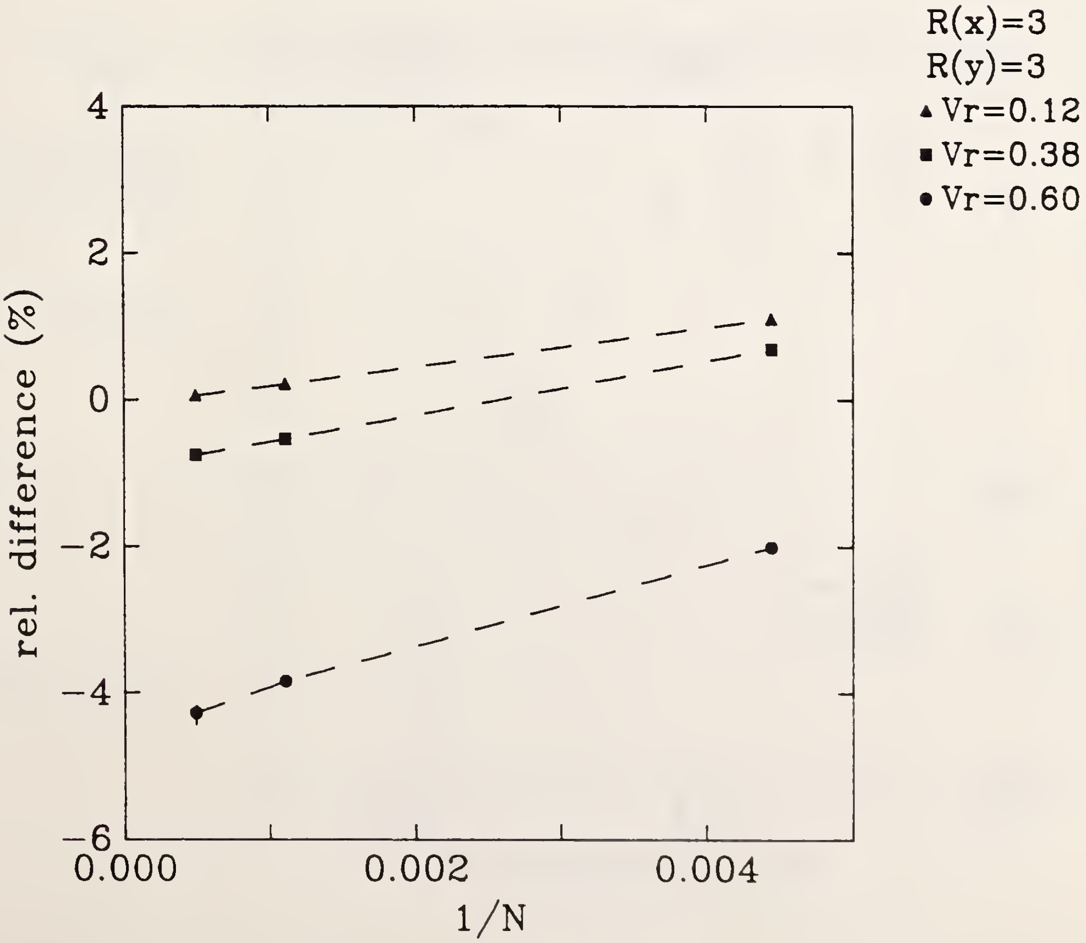


fig.
3.12





rel. difference (%)
2
0
−2
−4
−6
−8
−10
0.0
0.4
0.8
volume fraction Vr
● N=225
△ N=900
□ N=2025
R(x)=3
R(y)=3
S(1)=1.0



R(x)=3
R(y)=3
▲ Vr=0.12
■ Vr=0.38
● Vr=0.60
rel. difference (%)
4
2
0
−2
−4
−6
0.000
0.002
0.004
1/N

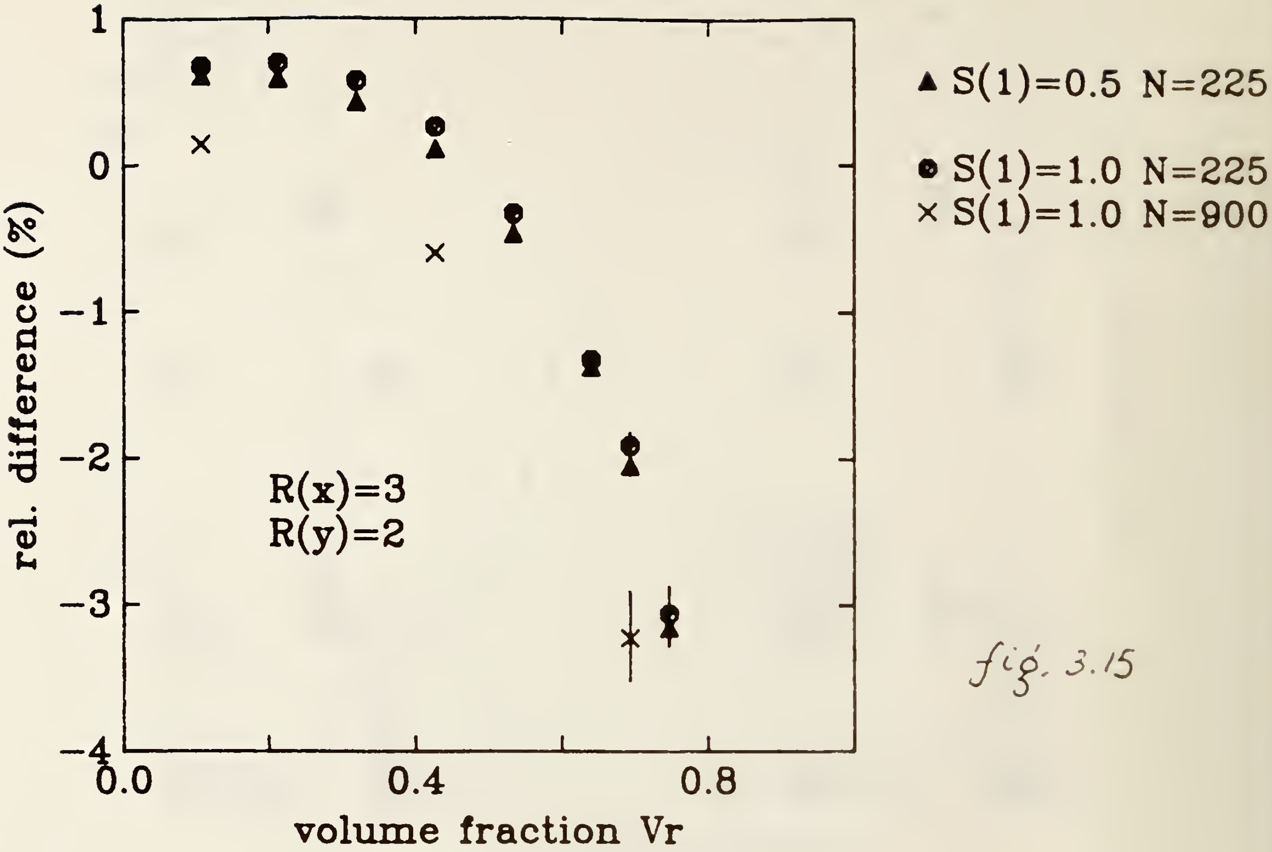


fig. 3.15

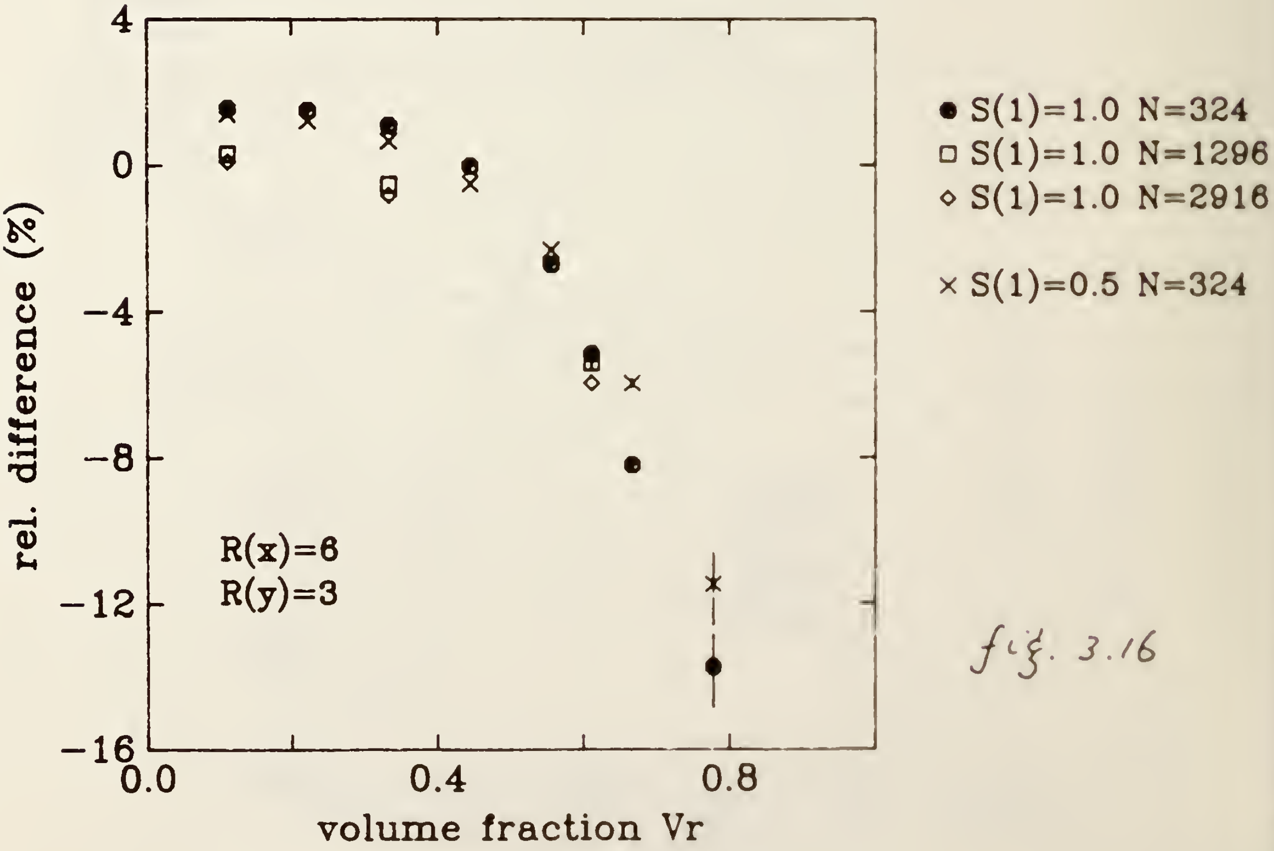
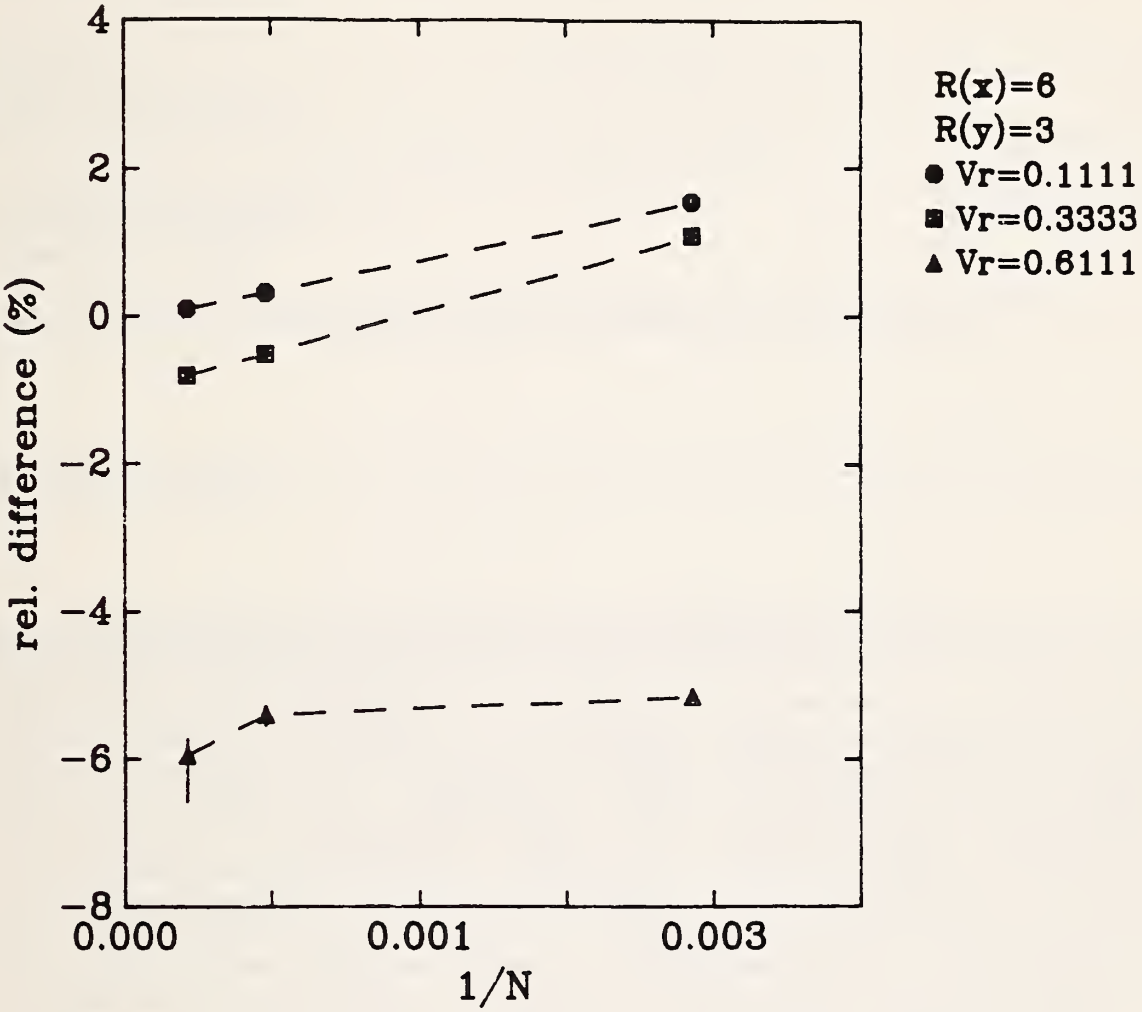


fig. 3.16

fig. 3.17


R(x)=6
R(y)=3
● Vr=0.1111
■ Vr=0.3333
▲ Vr=0.6111
rel. difference (%)
4
2
0
−2
−4
−6
−8
0.000
0.001
0.003
1/N

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This report can be thought of as consisting of three parts. In the first part a review is given of Di Marzio's site fraction concept to calculate the configurational entropy of polymers in a homogeneous system. The second part is concerned with Monte Carlo calculations, performed to check the validity of this concept. Results are presented of the packing of rigid, rodlike polymer chains on a square lattice, in the spirit of earlier work by McCrackin. Using a slightly adapted algorithm we also present results of calculations done on a refined lattice. It is shown that (a) the concept gives quite satisfactory results in the volume fraction range of 0.05 (the lowest volume fraction tested) to approximately 0.6, but (b) that one should be suspicious of the theory's validity at volume fractions approaching 1.0; it is furthermore shown that (c) the theory works better for small rods than for larger ones. This last point is partly ascribed to a Markovian approximation used in the theory. The third and last part of this report deals with the application of the site fraction treatment to the calculation of the configurational entropy of a polymeric system having a density gradient in one direction.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

packing entropy, orientation dependence, spacially dependent oritentation effect, liquid crystals., surface indured orientation.

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