

Monte Carlo study of polymer adsorption from dilute solutions

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We present results from Monte Carlo simulations of a lattice model for long molecules in a dilute solution emphasizing adsorption on an attractive substrate. The model amounts to a self-avoiding random walk on a cubic lattice in a half-space with an attractive interaction between monomers on nearest-neighbor lattice sites. Also, a monomer at the edge of the lattice experiences an attractive interaction with a substrate which bounds the system. By varying the relative magnitudes of the monomer-monomer interaction, the substrate-monomer interaction, and the temperature, we are able to study the collapse of a molecule in solution from the extended-coil state to the globule state and also the transition from dissolved to adsorbed molecules (in effect a wetting transition) as well as the interplay or competition between these two phenomena. We present results for a variety of thermodynamic and geometrical properties of the molecules and a phase diagram showing the regions where different phases are found as functions of the relative sizes of the interactions and temperature.

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I. INTRODUCTION

Much research has been done on the properties of long chain molecules in dilute solution [1]. In particular, polymer adsorption at a solid-liquid interface is reviewed extensively, with many references, in a recent article by Kawaguchi and Takahashi [2]. For molecules in relatively poor solvents, so that there is an attractive effective interaction between monomers of the molecule relative to the monomer-solvent effective attraction, one expects to find, as the temperature is decreased or the strength of this effective interaction is increased, a collapse from an "extended-coil" configuration to a dense globule. Moreover, if there is a substrate bounding the system and if monomers of the molecule are attracted more strongly to it than to the solvent, then one also expects to find a transition from a dissolved state in which the molecule is not in close contact with the wall to an adsorbed state in which the molecule is attached to the wall [3]. The competition between different interactions and the thermal energy can lead to a number of interesting effects. The behavior becomes even more complex for block copolymers because they may have blocks comprising monomers that can either repel or attract one another and that can be either attracted or repelled by a substrate.

Theoretical efforts [2] directed toward the understanding of dilute solutions of homopolymers and polymer adsorption from such solutions have made use of a variety of approaches. There are numerous papers based on mean-field approximations using the basic ideas of Flory [4] and Lifshitz, Grosberg, and Khokhlov [5]; scaling arguments [6] and renormalization-group methods [7] have proved to be very powerful investigative methods in the limit of long molecules; numerical simulations of polymers, pioneered by Wall, Hiller, and Wheeler [8] and by Rosen-

bluth and Rosenbluth [9] have also been used extensively to study polymers of intermediate length, typically 10 to 100 monomers, especially in conjunction with lattice models.

In this paper we present Monte Carlo studies of homopolymer adsorption using a three-dimensional lattice model. The model includes interactions between monomers in the chain as well as interactions between each monomer and a planar substrate that bounds the lattice in one direction. With these two interactions in place we are able to observe both the collapse transition of the molecule from the extended-coil state to the globule state and the transition between the dissolved and adsorbed state. Our work complements the theory of Johner and Joanny [3], which predicts many of the effects reported here. There are a number of papers describing work closely related to ours. One such paper is by Eisenriegler, Kremer, and Binder [10], who study adsorption using both simulations of a lattice model and scaling. In the simulations they do not include the monomer-monomer interactions and also have each polymer grafted to the substrate and so do not study the wetting transition. In another paper, Szleifer, O'Toole, and Panagiotopoulos [11] report Monte Carlo simulations of the bulk transition of homopolymers from the extended-coil to the collapsed state using a lattice model identical to the one we employ including nearest-neighbor monomer-monomer interactions. They emphasize the scaling properties of the system and the behavior of the second virial coefficient.

II. MODEL AND NUMERICAL METHODS

The homopolymer is modeled as a chain of identical monomers. Any given monomer occupies a site of a cu-

bic lattice in three dimensions, with adjacent monomers in the chain constrained to occupy nearest-neighbor sites. The lattice spacing is a . There is an interaction $-U$ between monomers on nearest-neighbor sites of the lattice [12]. The lattice sites occupy the domain $N_z a \geq z \geq a$. A monomer that is in either the first layer, $z = a$, or the (N_z) th layer, $z = N_z a$, has an interaction energy $-V$ with walls or substrates that occupy the domain outside of the lattice. Thus if we assign a site the indices i, j, k such that $x = ia$, $y = ja$, and $z = ka$, then there is a substrate potential $V_k = -V(\delta_{1k} + \delta_{Nk})$ and the lattice lies in the region $1 \leq k \leq N_z$. The system is invariant, and effectively infinite, in the x and y directions. A lattice site may be occupied by a single monomer. A linear polymer of N units is thus represented by a chain of N occupied sites and may be generated by a self-avoiding random walk (SAW) of $N - 1$ steps.

The procedure by which we do the simulations is to generate an ensemble of SAW's and then to evaluate means of various quantities over this ensemble. The ensemble is generated in such a way that it becomes an equilibrium Boltzmann ensemble in the limit of an infinite number of members. We start from a monomer around the center of the chain. It is located at $i = 0 = j$, with the z position k chosen according to the Boltzmann factor $\exp(-V_k/kT)$, where T is the temperature and k the Boltzmann constant. This procedure will, of course, not give the correct distribution of polymers with respect to the substrate interaction, but that is corrected in later steps as explained below. The random walk proceeds by adding monomers to the chain, first on one side of the original monomer and then on the other side. Hence the chain grows outward from its middle in both directions rather than from one end. The former procedure has the advantage over the latter one in that it requires a smaller lattice in the x and y directions and hence less computer memory.

From this point, the chain is generated using the prescription given by Meirovitch [13]. At each step, we consider the consequences of placing the next monomer at each of the six neighboring positions to the previous one. Any occupied site, and there is always at least one, is not allowed and so a step to those sites is assigned a zero probability. If the energy change that would result from adding a monomer at a particular site is δE , then that particular move is assigned a relative probability of $\exp(-\delta E/kT)$. In this way we generate a biased SAW, which is much more representative of the equilibrium distribution at temperature T than would be a random one. After determining the probabilities of the possible moves, one move is selected on the basis of comparison with a computer-generated random number. If there are no moves possible because all nearest-neighbor sites are occupied, then the chain is rejected and a new one started. Finally, as the chain is generated, a correcting weight for the chain is developed. At each step i that weight is

$$w_i = \sum_{k=1}^{n(i)} e^{-\delta E_{ik}/kT}, \quad (1)$$

where δE_{ik} is the energy change that would accompany the particular move k out of the $n(i)$ possible choices at

this step. The total weight for the chain is the product of w_i over all steps,

$$W_l = \prod_i w_i. \quad (2)$$

The subscript l has been included in the total weight to indicate that it is the weight for the l th chain generated. Notice that for a SAW with a noninteracting chain, the factor w_i is just the number of possible moves at step i and all possible moves have the same probability of being selected.

We have tested the Monte Carlo procedure on relatively short chains with $N = 10$ by comparing the results for typical thermodynamic quantities such as the energy, the dispersion of the energy, and the radius of gyration, with those found from an exact evaluation obtained by enumerating all possible chains. The agreement is perfect, aside from expected statistical uncertainties associated with the use of a finite ensemble in the simulations.

Finally, the mean value of any quantity Q over the ensemble of chains generated is

$$\langle Q \rangle = \sum_l W_l Q_l / \sum_l W_l, \quad (3)$$

if Q_l is the value of Q for the l th chain in the ensemble and provided the temperature at which $\langle Q \rangle$ is to be obtained is the same as that at which the ensemble is generated. One may also use an ensemble generated at temperature T to find Q at T' through the relation

$$\begin{aligned} \langle Q(T') \rangle &= \sum_l W_l Q_l e^{-E_l(1/T' - 1/T)} / \sum_l W_l e^{-E_l(1/T' - 1/T)}, \end{aligned} \quad (4)$$

where E_l is the energy of the l th member of the ensemble. This procedure will work well if T' is not too different from T and also if neither temperature is very small. This and related points are discussed in some detail in Ref. [11].

The final point that must be discussed concerning the ensemble of chains is the value of z or k at which the chain is started. As stated above, the first chain, or more correctly, the first set of 64 chains, is generated starting with a unit near the middle distributed in k according to $\exp(-V_k/kT)$. Once these chains are generated, we then find a new distribution for starting a second set of the same size by computing the distribution in k of the middle portions of all of the chains generated in the first set. "Middle portion" means all monomers except the five at each end. The next set of polymers is generated by starting the middle monomer of each chain at a z or k determined from this new distribution. Next, a third set of chains is generated from the second set using a distribution found as just described. And so on. The starting distribution rapidly—usually by the time 1000 chains have been generated—settles down and, aside from fluctuations, does not change as further sets of chains are generated. At this point we determine the starting distribution not just from the preceding set of 64 chains but

from all chains that have been generated following the achievement of equilibrium. Finally, we remark that the distribution is not sensitive to the number of monomers that are not included at the chain ends provided that number is larger than about two (at each end) and provided the chains are reasonably long, i.e., $N \geq 30$.

In our studies of adsorption phenomena we have employed primarily polymers with $N = 90$. For bulk three-dimensional polymers, we have systematically studied the properties of ones with N from 10 to 135. Bulk two-dimensional chains have been investigated primarily for $N = 90$. In three dimensions, there is no problem generating chains considerably longer than we have employed, in the sense that not many chains have to be rejected because at some point during the generating sequence there are no possible sites at which to add the next monomer, as a consequence of all accessible sites being occupied. In two dimensions, however, for chains of length 135, only about one attempted chain in ten reaches the desired length, except at relatively low temperatures, kT/U smaller than about 1.5. One may overcome this difficulty by adopting an algorithm for chain generation that looks further ahead than a single move at each step [14]. Szleifer, O'Toole, and Panagiotopoulos [11], for example, have employed such an approach to advantage. We have not done so in the work reported here.

Temperatures and substrate potentials are varied relative to the monomer-monomer interaction in the ranges $0 \leq kT/U \leq 20$ and $0.1 \leq V/U \leq 3.0$. Anywhere from 64 000 to several million chains are generated for each set of parameters. Generally speaking, good results require a larger number of replicas at $kT \approx U$ than at very high or low temperatures. For the bulk two- and three-dimensional chains, we compute the energy, the radius of gyration, and their dispersions. Specifically, the center of mass of a chain is

$$\mathbf{r}_c = \frac{1}{N} \sum_i \mathbf{r}_i, \quad (5)$$

where \mathbf{r}_i is the position of the i th monomer. The squared radius of gyration for the monomers in a single chain is

$$r_g^2 = \frac{1}{N} \sum_i |\mathbf{r}_i - \mathbf{r}_c|^2. \quad (6)$$

The mean-squared radius of gyration is found from r_g^2 according to Eq. (3), and the root-mean-squared radius of gyration, which we shall refer to simply as the radius of gyration and write as $\langle r_g \rangle$, is

$$\langle r_g \rangle = \sqrt{\langle r_g^2 \rangle}. \quad (7)$$

The energy of a chain is simply $-U$ times the number of nearest-neighbor pairs in the chain M : $E = -UM$. As stated earlier, we exclude those pairs that comprise adjacent monomers in the chain. Finally, the dispersion in the mean-squared radius of gyration is

$$\langle (\Delta r_g^2)^2 \rangle = \langle r_g^4 \rangle - \langle r_g^2 \rangle^2, \quad (8)$$

while the dispersion of the energy is

$$\langle (\Delta E)^2 \rangle C = \langle E^2 \rangle - \langle E \rangle^2. \quad (9)$$

The latter would be simply related to the heat capacity if E were really the energy [15]. Although it is not, the dispersion in the energy as a function of T is nevertheless useful in that a peak in the dispersion is a signal that the molecule is rearranging itself rapidly as a function of T . Hence we monitor the energy dispersion per monomer,

$$\langle (\delta E)^2 \rangle \equiv \frac{1}{N} \langle (\Delta E)^2 \rangle, \quad (10)$$

and present the results in the form of a specific heat,

$$C = \langle (\delta E)^2 \rangle / kT^2. \quad (11)$$

We also compute the density of each chain relative to its center of mass and average over the ensemble to find the mean density distribution of the chains $\langle n(r) \rangle$. That is done by introducing concentric shells with evenly spaced square radii around the center of mass of a molecule and determining how many monomers are within each shell. The density is normalized so that the sum of the densities in the various shells is equal to N . The increment in r^2 employed is $0.5a^2$.

For the studies of adsorption, we again compute the radius of gyration, the energy, and the dispersion of the energy. Because the interaction with the substrate can produce distortions of a typical molecule's shape from one of spherical (or cubic, because of the underlying lattice) symmetry, it is also useful to consider the anisotropy of the radius of gyration. Hence we compute separately the contributions to the radius of gyration associated with the spreading of the molecule in the z direction and in the transverse directions. We designate these as r_{gz} and $r_{z\perp}$, respectively. In the absence of the substrate one finds $\langle r_{gz}^2 \rangle = \langle r_{z\perp}^2 \rangle / 2$. The extent to which the shape is distorted is conveniently measured by the eccentricity ϵ , defined by

$$\epsilon \equiv 1 - \frac{2\langle r_{gz}^2 \rangle}{\langle r_{z\perp}^2 \rangle}; \quad (12)$$

in particular one expects that ϵ will go to unity for a very strongly attractive monomer-substrate interaction, which will compress the polymer into a single layer at constant $z = a$; in the absence of anisotropy produced by the substrate, $\epsilon = 0$. We compute also the density $\langle n_k \rangle$, which is the mean number of monomers per molecule in the k th layer. We take the mean of the densities on the two sides of the system to obtain the final results, which are then presented for $1 \leq k \leq N_z/2$.

III. RESULTS

We first present results for the bulk two- and three-dimensional systems. These are useful for comparison with the results for adsorption. Also, in three dimensions it is useful to make comparison with an unrestricted random walk, especially for the radius of gyration. Figure 1 shows the radii of gyration in three dimensions of

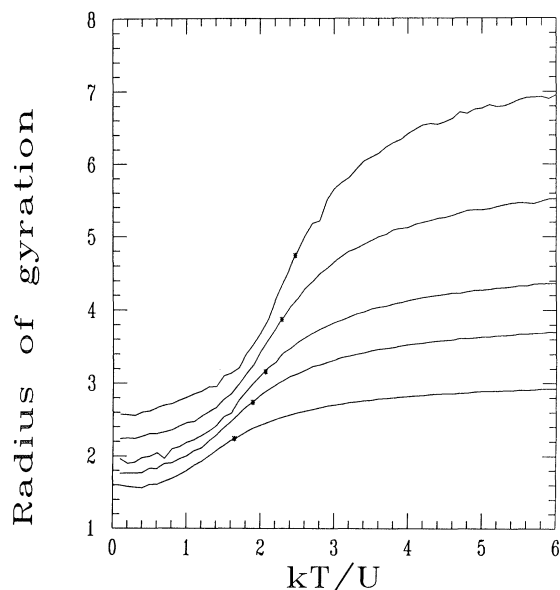


FIG. 1. Radius of gyration $\langle r_g \rangle/a$ is plotted against kT/U for interacting molecules in three dimensions with lengths $N = 30, 45, 60, 90,$ and 135 . Asterisks (*) indicate the points at which the radii of gyration of interacting and ideal molecules with the same number of monomers are equal. Individual curves may be identified from the fact that $\langle r_g \rangle$ increases with N .

molecules of lengths $N = 30, 45, 60, 90,$ and 135 as functions of kT/U . Shown as asterisks on each curve are the radii of gyration of ideal molecules generated in purely random walks, i.e., molecules with neither excluded volume nor attractive interactions between neighbors. We shall denote the temperatures where the radii of gyration of the interacting and ideal chains are equal as T_c . These are functions of N ; from study of log-log plots of $T_0 - T_c$ against N , one finds that they fall on a straight line for $T_0 \approx 3.8U/k$, indicating that $T_c \rightarrow 3.8U/k$ as $N \rightarrow \infty$.

The density of the ideal and interacting chains may be easily computed and compared. Figure 2 shows the density profiles of interacting chains with $N = 90$ against r/a for $kT/U = 1.5, 2.28,$ and 3.5 ; r is the distance from the molecule's center of mass. For comparison, the profile of a noninteracting chain of the same length is also shown. For $N = 90, kT_c/U = 2.28$. Generally speaking, for an ideal molecule and an interacting molecule with the same radius of gyration, the excluded volume effect keeps the density at the center of the latter relatively smaller than at the center of the former; otherwise the densities match fairly closely.

Figure 1 demonstrates that T_c can be reasonably used as the nominal temperature at which the three-dimensional chain switches from the extended-coil state to the collapsed-globular state; that is, the figure shows that at this temperature the collapse, as measured by the radius of gyration of the molecule, is well under way. If we adopt as an alternative identification of the collapse temperature the point at which the derivative $d\langle r_g \rangle/dT$ is a maximum, that produces slightly smaller temperatures;

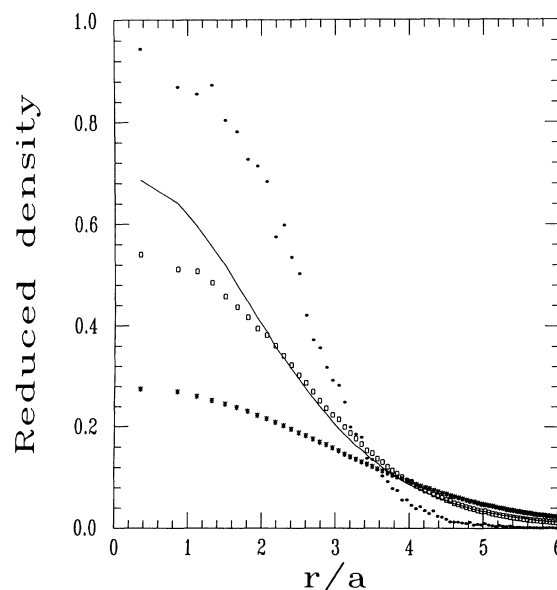


FIG. 2. Reduced densities $\langle n(r) \rangle a^3$ of molecules with length $N = 90$ are plotted as functions of r/a for $kT/U = 1.5$ (\bullet), 2.28 (\square), and 3.5 (*). The density of an ideal molecule with $N = 90$ is presented as a solid line.

for example, in a chain of $N = 90$, this criterion produces a collapse temperature around 2.0 to $2.1 U/k$. Alternatively, if we use the point at which $\langle (\delta E)^2 \rangle$ is maximized, the result is much the same, a temperature between 2.0 and $2.1 U/k$. In view of the fact that the collapse and all thermodynamic quantities associated with it are smooth rather than singular for polymers of finite length, the distinction between these different choices of the collapse temperature is not critical, and we shall simply use T_c in what follows. An additional reason for making this choice is that one may more easily obtain T_c accurately from simulations than the temperatures of the maxima in $d\langle r_g \rangle/dT$ or in $\langle (\delta E)^2 \rangle$. Note that any of these temperatures is significantly smaller than the one at which the second virial coefficient of the molecule vanishes, i.e., the θ point; the latter is about [11] $3.3U/k$ for a molecule with $N = 90$.

For strictly two-dimensional chains the situation is quite different. Even in the fully collapsed state, which is obtained for $T \rightarrow 0$, the radius of gyration is not significantly smaller than the radius of gyration of an ideal chain of equal length. The reason is that the condition of self-avoidance is much stronger in two dimensions than in three. This point is made abundantly clear by the behavior in the extreme case of one dimension where the self-avoiding chain's only possible configuration is one in which it is fully stretched, so that it always has a radius of gyration much larger than that of the ideal chain. Hence the temperature at which the radii of gyration of the interacting and ideal chains are equal is not in any way a reasonable one to use as the collapse temperature in two dimensions. In Fig. 3 we show the radius of gyration of a two-dimensional interacting chain with $N = 90$

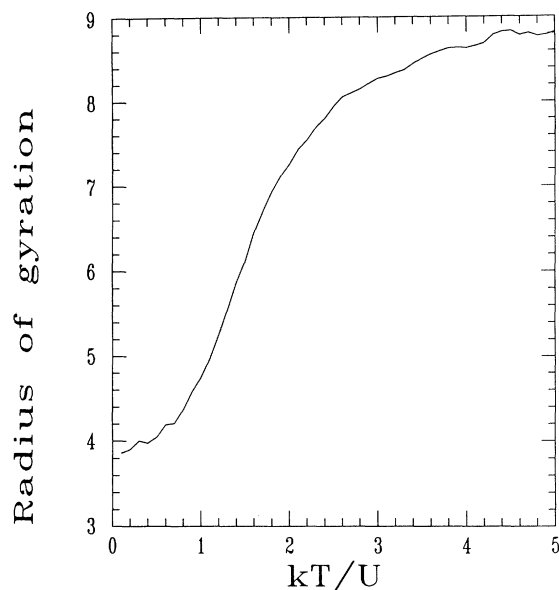


FIG. 3. Radius of gyration $\langle r_g \rangle/a$ is plotted against kT/U for a two-dimensional molecule with $N = 90$.

as a function of kT/U . Comparison with the behavior of $\langle r_g \rangle$ in that case and with our choice of the collapse temperature in $d = 3$ suggests that the collapse temperature of the two-dimensional chain with $N = 90$ is reasonably taken to be about $1.7U/k$; $d\langle r_g \rangle/dT$ is maximized slightly below this temperature.

We turn now to adsorption. We give results only for polymers with $N = 90$. The nearest-neighbor interaction is still $-U$ and the monomer-substrate interaction is $-V$ for monomers in a layer adjacent to a substrate. We have studied the relative interaction strengths $V/U \equiv v = 0.1, 0.5, 1.0, 1.5, 2.0, 2.5,$ and 3.0 . Figure 4 displays $\langle z \rangle/a$ as a function of the temperature for each of these. Because the width of the system in the z direction is just 48 layers with a substrate on either side, $\langle z \rangle/a$ is bounded and is never larger than about 18. In each case shown, as T is lowered there is a clear transition to the adsorbed state. One may nominally identify the temperature at which this occurs as being where $d\langle z \rangle/dT$ is maximized. In all cases, this maximum appears for $\langle z \rangle/a$ between eight and ten, so a simple workable criterion for the temperature T_a at which adsorption occurs is that $\langle z \rangle/a = 9$ at T_a . The criterion will, of course, depend on N_z . Another measure of the extent to which the molecule has been adsorbed is the density profile as a function of z/a . Figure 5 shows the profiles for $v = 1.0$ at temperatures $kT/U = 3.65, 3.75, 3.85, 4.00,$ and 4.50 ; $kT_c/U \approx 3.75$. Notice in particular that at the largest temperature the density is smaller close to the substrate than far from it. The reason is that constraints on the chain's configurations posed by the presence of the substrate reduce the configurational entropy and hence increase the free energy sufficiently that this effect overcomes the lowering of the energy (and the free energy) produced by the substrate potential acting on monomers in the first layer. The net effect is an effective repulsion between the chain

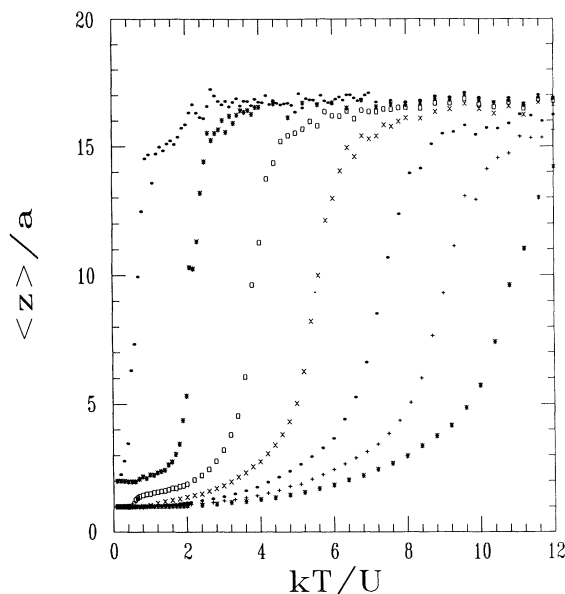


FIG. 4. For molecules with $N = 90$, $\langle z \rangle/a$ is plotted against kT/U at $v = 0.1, 0.5, 1.0, 1.5, 2.0, 2.5,$ and 3.0 . Individual curves may be identified from the fact that, for given $\langle z \rangle$, the temperature increases with v .

and the substrate.

The "specific heat" for systems with $v = 0.5, 1.0,$ and 2.5 is displayed as a function of kT/U in Fig. 6. As v becomes larger, the molecules adsorb at larger temperatures, producing a broad peak or a plateau in the heat capacity. In addition, there is a rather sharper peak at relatively small temperatures, at least for $v = 1.0$ and $v = 2.5$. Detailed study of the energy and configurations

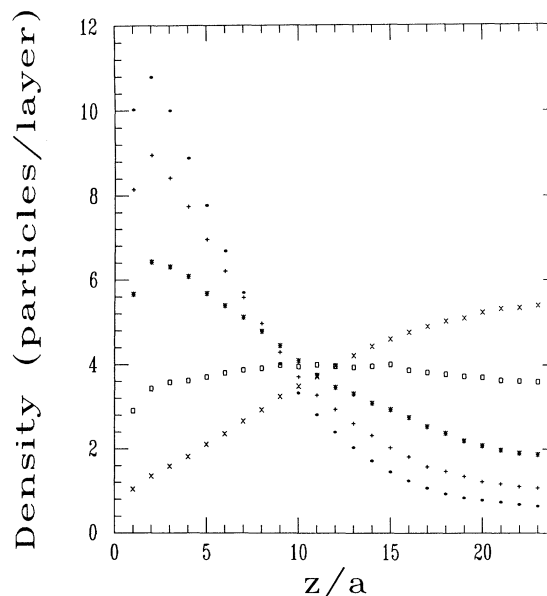


FIG. 5. Density profiles $\langle n(z) \rangle/a$ are shown as functions of z/a for $N = 90$ and $v = 1.0$ at $kT/U = 3.65$ (\bullet), 3.75 ($+$), 3.85 ($*$), 4.0 (\square), and 4.5 (\times).

of the system reveals that this peak, in the case of $v = 1$, reflects a rather sudden change with temperature of the number of monomers adsorbed in the layer adjacent to the substrate, producing a corresponding change in the amount of adsorption energy or polymer-substrate interaction energy. There is a corresponding, partially compensating, change in the number of monomer-monomer nearest-neighbor pairs because of the excluded volume effect, which reduces the number of nearest neighbors more drastically in two dimensions than in three. However, the change in adsorbate-substrate energy dominates. For smaller v , specifically $v = 0.5$, the substrate-adsorbate interaction is not strong enough to force all of the particles into the first layer, so the low-temperature peak in the specific heat is not present.

This change in the configuration of the adsorbed molecule from a "droplet" to, for v large enough, a mono-

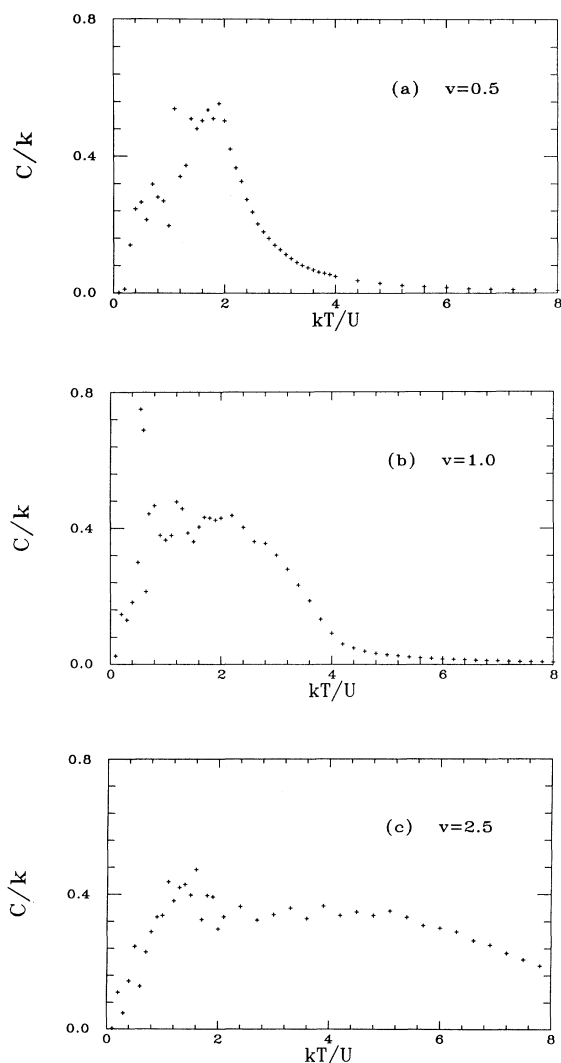


FIG. 6. Specific heat C/k is plotted against kT/U for systems with (a) $v = 0.1$, (b) 1.0, and (c) 2.5. The chain's length is $N = 90$.

layer is, as discussed extensively by Johner and Joanny [3], effectively a transition from partial wetting to complete wetting analogous to the one that can be observed for an adsorbed droplet of a simple liquid. One may examine it in more detail by studying the eccentricity ϵ of the molecules as a function of kT/U for the various v 's. That is shown in Fig. 7. The temperatures T_0 are shown as arrows on the curves. One sees that ϵ becomes significantly different from zero when the molecule is first adsorbed, being distorted by the substrate's attractive force. This effect is, at this point, far from complete, however, with values of the eccentricity in the vicinity of 0.15. With further reduction in the temperature, ϵ continues to increase and approaches unity at the lowest temperatures if v is large enough ($v \geq 1$, for the cases shown), corresponding to complete wetting of the substrate by the molecule. Notice especially for $v = 1$ the sudden change of ϵ in the vicinity of $kT/U = 0.6$, which is to say, at the temperature of the sharp peak in the specific heat shown in Fig. 6(b). For the larger v 's, the approach to $\epsilon = 1$ is not so abrupt, and the associated specific-heat peak is correspondingly broadened.

For large values of v the molecules are already adsorbed on the substrate at temperatures considerably larger than the bulk collapse temperature T_c in either two or three dimensions. Hence the collapse that is produced by the monomer-monomer interaction, when it does finally occur, is pretty nearly a collapse in two dimensions. One may attempt to identify this collapse by studying the radius of gyration $\langle r_{g\parallel} \rangle$ as a function of temperature. That is shown in Fig. 8 for a variety of v 's. One can extract considerable information from this figure. First, for all v , there is the same behavior at sufficiently large T be-

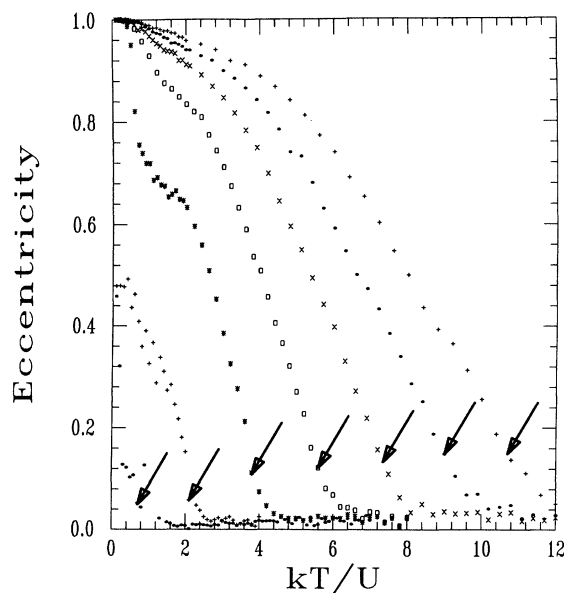


FIG. 7. Eccentricity ϵ of the molecules is shown as a function of kT/U for chains with $v = 0.1$ (\bullet), 0.5 ($+$), 1.0 ($*$), 1.5 (\square), 2.0 (\times), 2.5 (\odot), and 3.0 ($+$); $N = 90$. Arrows identify the points at which $\langle z \rangle/a = 9$.

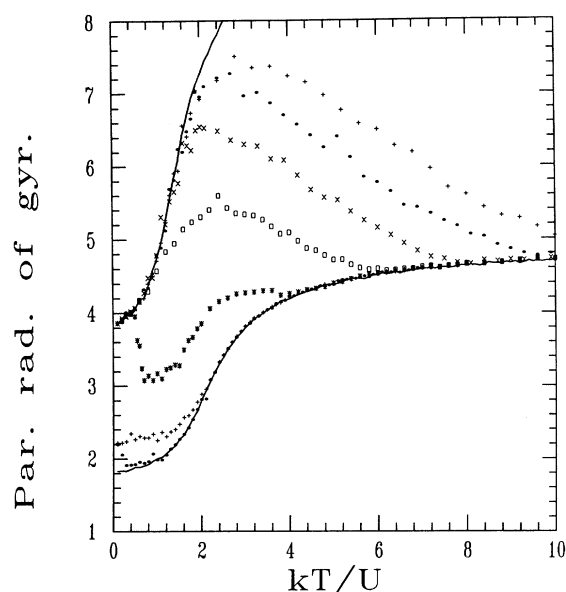


FIG. 8. Radius of gyration parallel to the substrate, $\langle r_{g\parallel} \rangle/a$, is plotted against kT/U for $v = 0.1$ (\bullet), 0.5 ($+$), 1.0 ($*$), 1.5 (\square), 2.0 (\times), 2.5 (\circ), and 3.0 ($+$); $N = 90$. The radius of gyration of a molecule in two dimensions with $N = 90$ appears as a solid line at the top of the figure, and $\sqrt{2/3}$ of the radius of gyration of a molecule in three dimensions with no substrate and $N = 90$ appears as a solid line at the bottom.

cause there the molecule is not adsorbed and all cases are equivalent. Also, in this regime, $\langle r_{g\parallel} \rangle$ is equal to $\sqrt{2/3}\langle r_g \rangle$, which is shown as a solid line; $\langle r_g \rangle$ is the radius of gyration of a molecule in bulk solution. As T is lowered, the results at different v deviate from one another and from the solid line. The first to do so is the one with largest v because it is adsorbed at the highest temperature. The others follow suit until the case of $v = 1$, for which three-dimensional collapse and adsorption occur at roughly the same T . The adsorption will tend to increase $\langle r_{g\parallel} \rangle$ whereas the collapse will tend to decrease it. One can see a slight rise in the radius of gyration for $v = 1$ as T decreases, indicating the onset of adsorption, but then the radius of gyration falls significantly as collapse takes place; that is essentially collapse in three dimensions. Finally, $\langle r_{g\parallel} \rangle$ rises again as the molecule is flattened into a two-dimensional object. At this point, the temperature is smaller than the temperature of collapse in two dimensions. For still smaller v , such as $v = 0.5$ or $v = 0.1$, collapse in three dimensions dominates, producing a small $\langle r_{g\parallel} \rangle$ that remains relatively small as $T \rightarrow 0$ because the molecule never is flattened into a single layer; that is, wetting never becomes complete. As for the cases with larger v , they all follow a simple pattern, first having a markedly larger $\langle r_{g\parallel} \rangle$ as adsorption occurs and then all following a universal curve at low temperatures as the two-dimensional collapse takes place. The universal curve is the same as the radius of gyration of a molecule on a two-dimensional lattice. That is shown as a solid line in the figure.

On the basis of these results we may draw a phase diagram showing the behavior of the system in the kT/U - V/U plane. That is given in Fig. 9. The basic regions in the diagram are one for the adsorbed state and one for the nonadsorbed state. Within each of these are further subdivisions. In the nonadsorbed region one finds both the three-dimensional extended-coil (E3) and collapsed-globule (C3) states. In the region of adsorption, close to the line separating it from the nonadsorbed region, there is a domain where the molecule is essentially three dimensional in that its eccentricity is not yet unity (less than 0.9); that is the partial-wetting regime where the behavior is analogous to an adsorbed droplet. Within this domain there are further regions where the molecule is either extended (AE3) or collapsed (AC3). Finally there is the complete-wetting domain where the molecule is essentially confined to a single layer, and within this domain there are two regions where it is either collapsed (AC2) or extended (AE2) in two dimensions. Any of these states should be observable in real systems depending on the relative values of the temperature and the effective interactions. The boundaries of the regions should not be taken too seriously in view of the fact that the diagram is based on simulations of molecules of finite length ($N = 90$) so that we cannot tell precisely where the various phase transitions occur. All phase changes are gradual in our model. In particular, one cannot expect that four phases meet at a point in the limit of very long molecules.

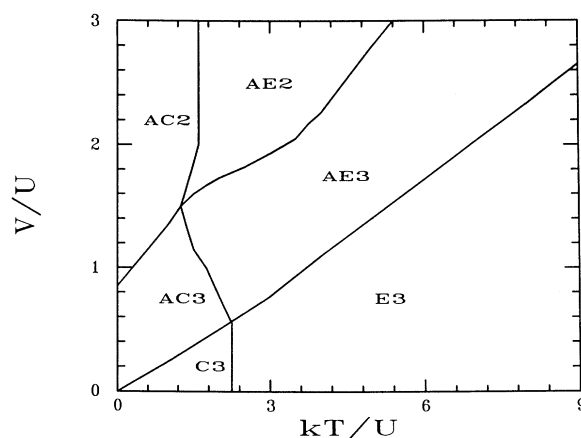


FIG. 9. Phase diagram in the V/U - kT/U plane. Each region is labeled according to the phase. Specifically, E3 is the extended-coil configuration in three dimensions while C3 is the collapsed-globule state in three dimensions; these are separated from adsorbed configurations by the solid line. AE3 and AC3 are regions of partial wetting, the former being extended adsorbed, essentially three-dimensional, droplets, and the latter, collapsed ones. There is complete wetting in regions AE2, extended configurations confined to a single layer, and AC2, collapsed two-dimensional configurations. The locations of lines separating regions should be regarded as approximate because the diagram is determined from study of molecules of finite ($N = 90$) length in a system of finite extent normal to the substrate.

IV. SUMMARY

We have presented results from Monte Carlo simulations of a lattice model for homopolymers. Emphasis is placed on the adsorption properties of a single molecule, but some results are also given for a single molecule in bulk solution in both two and three dimensions. The coil-globule collapse is clearly identifiable in both two and three dimensions, as are the transitions from non-wetting to partial-wetting to complete-wetting behavior. The interplay between the various transitions is displayed in some detail. The simulations complement nicely the theoretical work of Johner and Joanny, which contains descriptions of these phenomena, especially the partial-wetting and complete-wetting behaviors. At present we

are working on simulations of similar models for block copolymers. For these molecules there is a possibility of having unequal monomer-monomer effective interactions for monomers of different species. Similarly, the monomer-substrate interaction can depend on the type of monomer. Consequently block copolymers display additional and more complex adsorption and wetting behavior than homopolymers.

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