PEO, making reliable data difficult to obtain. Yet another possible cause of the very slight disagreement is the fact that the molecular weight of our PEO sample is much larger than those used by Booth and Devoy.[8]

Of the suggested explanations, the last seems to us to be the least likely to be correct. Although the molecular weight of WSR-301 is much larger than either 205F or 6100F, the Booth and Devoy benzene activity data are virtually identical for both 205F and 6100F PEO samples, indicating little affect of polymer molecular weight on the results. Such a conclusion is qualitatively corroborated by standard polymer solution theory.

We cannot now determine the cause of the difference between our data and those of Booth and Devoy,[8] but we are at present extending our glc study of benzene in PEO to finite concentration to attempt to resolve the question.

Acknowledgments. The authors thank the Institute for University Research and the Institute for New Applications of Physical Science of Texas Tech University for financial support. The authors also wish to thank the Computer Center of Texas Tech University for the use of their facilities. The authors especially thank Mr. Yen-huang Chang for assistance in resolution of some difficult experimental problems and Mr. Alan Graham for assistance in the early phases of the project.

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Polymer Adsorption on a Surface by an Exact Enumeration Study

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Received February 27, 1974

ABSTRACTS: The exact enumeration method was used to study the effect the excluded volume constraint has on configurational properties of polymer molecules adsorbed on a planar surface. The adsorbed molecules were computer simulated on a four-choice simple cubic lattice system with the assumption of an energy of adsorption between the polymer atoms and the surface, ranging from 0 to $1.5kT$. The excluded volume constraint is found to have a marked effect on the configurational properties investigated. In particular, the root mean square end-to-end distance data disclose some very interesting observations; namely, that γ shows values greater than 1.2. It appears that the adsorbing surface and energy of adsorption restrict the adsorbed polymer molecule and the system behaves as if it is in a less than three-dimensional environment.

I. Introduction

In the past 20 years much research[2-4] has been accomplished in the theoretical investigation of the mean configurational properties of flexible high-polymer molecules adsorbed on planar surfaces. Only recently has considerable effort been expended to introduce the excluded volume effect[5] into the adsorption treatment. Investigators involved with the simulation of lattice polymers in dilute solutions using the Monte Carlo method[6-9] as well as other investigators using the exact enumeration method[10,11] have shown that the mean-square end-to-end distance, $\langle R_N^2\rangle$, may be expressed by an equation of the form

$$\langle R_N^2\rangle = aN^\gamma \tag{1}$$

Domb[12] correlated results for a variety of two- and three-dimensional lattices and concluded that the exponent, γ, should be only a function of dimensionality and independent of any particular lattice structure. He reported the following asymptotic relationships

$$\langle R_N^2\rangle \cong \begin{cases} A_1(\theta)N^{6/5} + A_2(\theta), & \text{three dimensions} \\ B_1(\theta)N^{3/2} + B_2(\theta)N, & \text{two dimensions} \end{cases} \tag{2}$$

where θ is a parameter related to lattice structure. It turns out that the study of adsorbed polymers offers an opportunity for investigating γ as a function of dimensionality.

II. Model

The exact enumeration method as described by Martin,[13] with modifications to take into account the symmetry of our particular lattice model, was used. The self-avoiding chains ($N \leq 14$ bonds) were simulated on a four-choice simple cubic lattice system with the first atom confined to the origin. The direction of each step of the chain was perpendicular to the direction of the preceding step. The adsorbing surface was taken as the $Z = 0$ plane and no atoms were allowed to go below this plane. Each atom in the $Z = 0$ plane was considered an adsorbed atom and contributed an energy of adsorption ϵ to the Boltzmann factor for the energy of that configuration. If the jth enumerated configuration of the chain of length N has n_{Nj} atoms on the surface, each contributing an energy of ϵ to the total energy of the configuration ($n_{Nj}\epsilon$), then the Boltzmann factor for this configuration is $\exp(-n_{Nj}\epsilon/kT)$. An average parameter of the configurations of the chain of length N, $\langle Z_N\rangle$, is then given by

$$\langle Z_N\rangle = \frac{\sum_{j=1}^{J} Z_{Nj}\exp\left(-\frac{n_{Nj}\epsilon}{kT}\right)}{\sum_{j=1}^{J}\exp\left(-\frac{n_{Nj}\epsilon}{kT}\right)} \tag{3}$$

where Z_{Nj} is the value of the parameter for the jth configuration (for example, squared end-to-end distance) and j is the total number of configurations enumerated.

The following properties of the adsorbed polymer model were investigated: (1) the number of segments of the molecule that are on the surface; (2) the number of returns to the surface (loops); (3) the normal distance of the end of the molecule from the surface; (4) the square of this normal distance; (5) the distance to the surface from the segment farthest from the surface; (6) the end-to-end distance.

These properties were determined for each enumerated adsorbed polymer with the assumption of an energy of adsorption between the polymer atoms and the surface, ranging from 0 to $1.5kT$. After all the configurations had been enumerated, the mean configurational averages were calculated according to eq 3. The computer programs were written in Fortran and run on the CDC 3300 computer housed at the Adelphi University Computer Center.

In most of our figures we have plotted a configurational property *vs.* the energy of interaction ($-\epsilon/kT$). The curves labeled 4 to 14 are the exact enumeration results. We have also included a curve for the infinite chain molecule. This curve is of course not exact, since it was obtained by an extrapolation procedure. How the infinite chain curves were obtained is explained in the body of the Results section. In order to test our infinite chain results, we generated exact enumeration data without excluded volume up to $N = 12$ and extrapolated the data in the same manner as the excluded volume results obtaining the infinite chain. We were able to reproduce, quite successfully, Rubin's analytical nonexcluded volume results of an infinite chain for $-\epsilon/kT \geq 0.375$ (see Figure 4). For $-\epsilon/kT < 0.375$, the extrapolation procedure failed. That is, there was too much "noise" in the data to allow reliable predictions. Because of this, our excluded volume results for the infinite chain are given only for $-\epsilon/kT \geq 0.375$, which is the range reproduced for the nonexcluded case.

III. Results

The number of atoms on the surface was counted for each of the enumerated adsorbed molecules and stored as a function of the number of bonds N and the adsorption energy ϵ. After all the adsorbed molecules were enumerated, the average number of atoms on the surface was determined according to eq 3. The average fraction of adsorbed atoms was obtained from these numbers by dividing by the number of atoms ($N + 1$) in the chain of length N bonds. Figure 1 contains the average fraction of atoms adsorbed on the surface as a function of the energy of adsorption, for the different length polymer chains enumerated, and also contains the extrapolated curve for infinite length molecules.

Figure 1 shows that for a given adsorption energy the fraction of atoms on the surface decreases as the length of the molecule increases. This effect is a result of the model chosen, since each molecule starts with the first atom on the surface. Every molecule has at least one, and in many cases several, of its initial atoms on the surface. An adsorbed polymer does not necessarily have to have one end tied to the surface. Therefore, it will have on the average fewer segments on the surface than these simulated molecules. This end constraint will become less important with increasing chain length and increasing adsorption energy ($-\epsilon/kT > 0.375$), as is evident from the asymptotic curve for infinite length molecules in Figure 1.

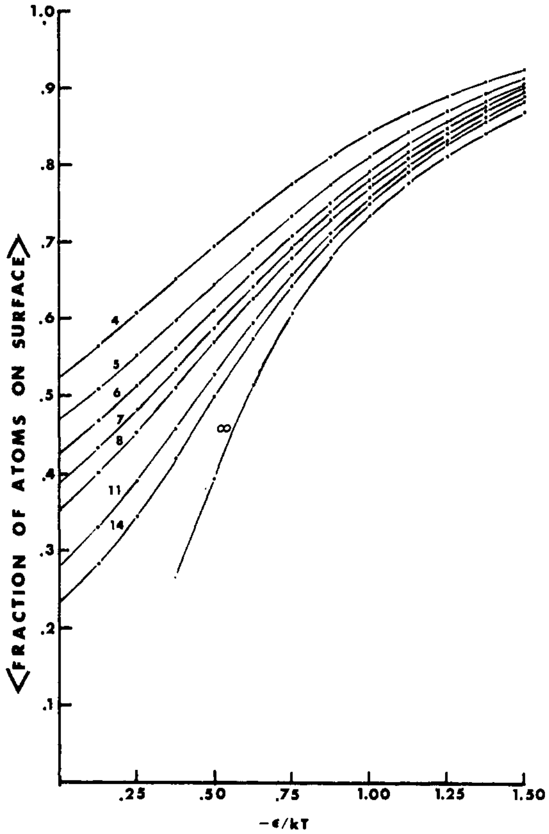

Figure 1. A plot of the average fraction of atoms adsorbed on the surface *vs.* the energy of adsorption per atom.

In Figures 2 and 3 the fraction of atoms on the surface for constant values of the adsorption energy is plotted *vs.* the reciprocal of the number of atoms in the chain. This enables one to determine values for the fraction of atoms on the surface as a function of adsorption energy ($-\epsilon/kT > 0.375$) for an adsorbed molecule of infinite length. These curves were extended to intersect the $1/(N + 1) = 0$ axis. These intercept values correspond to the values of the fraction of atoms on the surface for a molecule of infinite length. To yield more accurate extrapolated values, the points were least-square fitted to first and second degree polynomials of the form

$$\langle \text{fraction on surface} \rangle = A(\epsilon) + \frac{B(\epsilon)}{N + 1} + \frac{C(\epsilon)}{(N + 1)^2} \tag{4}$$

The second-degree polynomials were found to fit the points with smallest error. The $A(\epsilon)$ values correspond to the fraction of atoms on the surface for a molecule of infinite length. These values are plotted in Figure 1. Figure 4 contains these $A(\epsilon)$ values which include the excluded volume effect (EV (——)), along with the values obtained by Rubin[14] for an infinite length molecule without excluded volume (NEV (- - -)). The solid NEV curve represents our exact enumeration data for an infinite length molecule without excluded volume up to $N = 12$ included for comparison.

Figure 4 is a plot of the average fractions of atoms on the surface *vs.* the energy of interaction with and without excluded volume. Rubin's nonexcluded volume case is also presented for comparison. The data for our nonexcluded volume study were obtained up to $N = 12$ and extrapolated in the same manner as the excluded volume case obtaining the infinite chain. We attempted to investigate the critical energy region in our NEV and EV studies. However, we were unsuccessful. Using the data generated we attempted quadratic extrapolations for $-\epsilon/kT < 0.5$ and were unable to reproduce Rubin's nonexcluded volume study. Although it was not possible to investigate the critical adsorption region which Rubin's nonexcluded volume study reports,

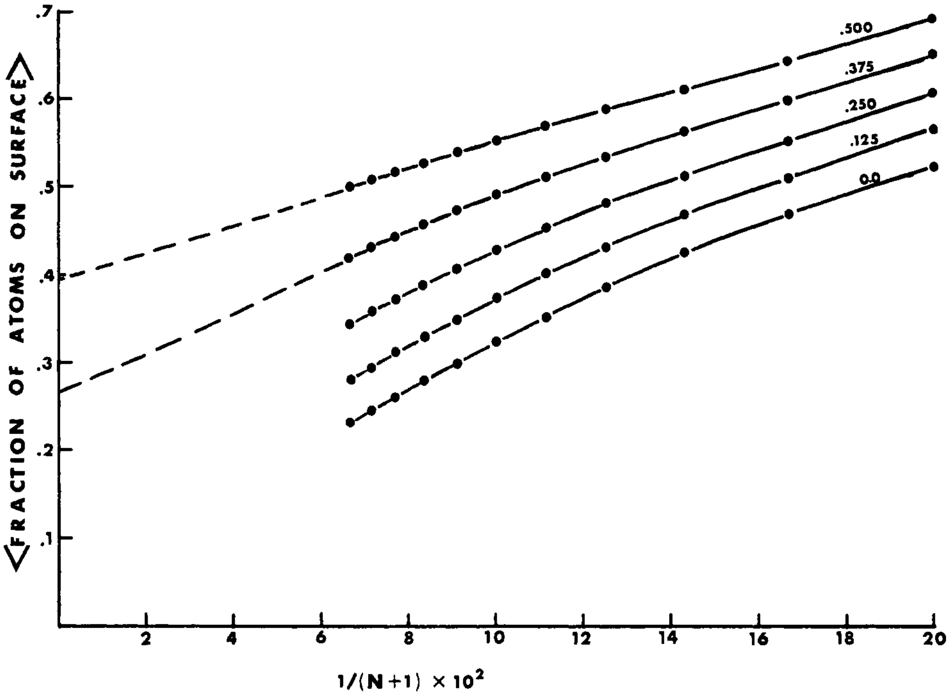

Figure 2. A plot of the average fraction of atoms adsorbed on the surface *vs.* $1/(N + 1)$. Curves are at constant adsorption energy ranging from 0.0 to $0.5kT$.

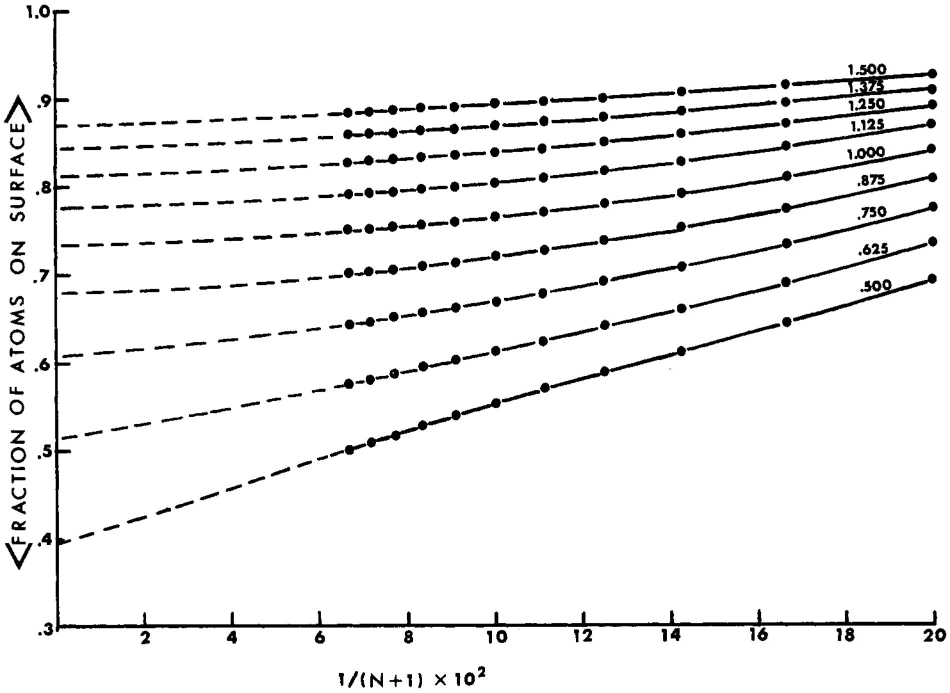

Figure 3. A plot of the average fraction of atoms adsorbed on the surface *vs.* $1/(N + 1)$. Curves are at constant adsorption energy ranging from $0.5kT$ to $1.5kT$.

some trends are suggested by our excluded volume curve (EV). Rubin found a critical value for the adsorption energy of $-\epsilon/kT = 0.212$, below which the fraction of atoms on the surface is zero. Our NEV curve is the same as Rubin's curve for $-\epsilon/kT > 0.375$. Above $-\epsilon/kT = 0.375$ our EV curve has the same form as Rubin's curve without excluded volume, although our values for the fraction on the surface are less than those reported by Rubin. Our EV curve is displaced to the right and roughly "parallel" to Rubin's curve.

McCrackin,[5] in his Monte Carlo investigation, reported similar reductions in the fraction of atoms on the surface when excluded volume was considered, although his values are lower than those found in this study. An explanation for this difference could be problems encountered with Monte Carlo samples when intramolecular potentials are applied as suggested by Wall, Windwer, and Gans.[15] We encountered such problems in applying the Monte Carlo method to an adsorption study.[16] Another explanation may be the errors in our own extrapolations to the infinite chain.

Comparison of the three curves in Figure 4 reveals that above $-\epsilon/kT = 0.375$ the excluded volume constraint has a marked reducing effect on the fraction of atoms on the surface. An insight as to how the excluded volume constraint

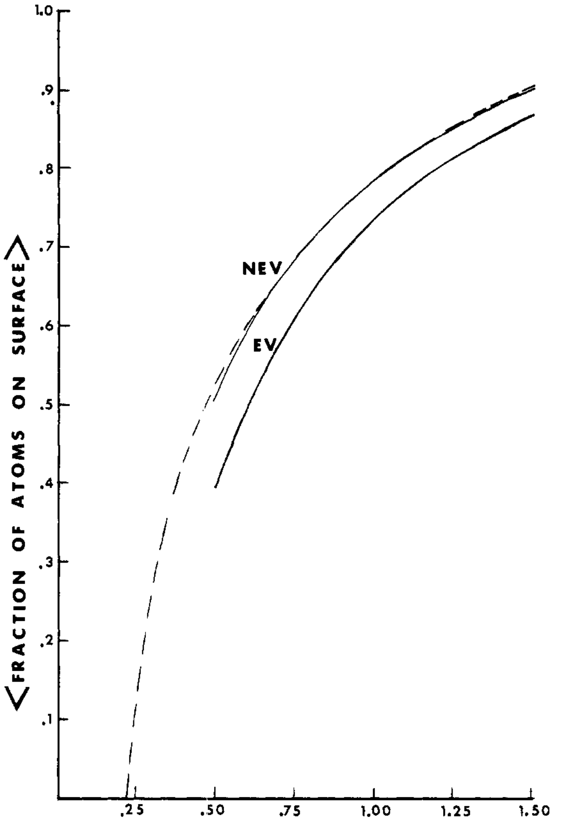

Figure 4. A plot of the extrapolated curve for an infinite length molecule with excluded volume (EV) and without excluded volume (NEV (——)) and Rubin's curve without excluded volume (NEV (- - -)) *vs.* the energy of adsorption per atom.

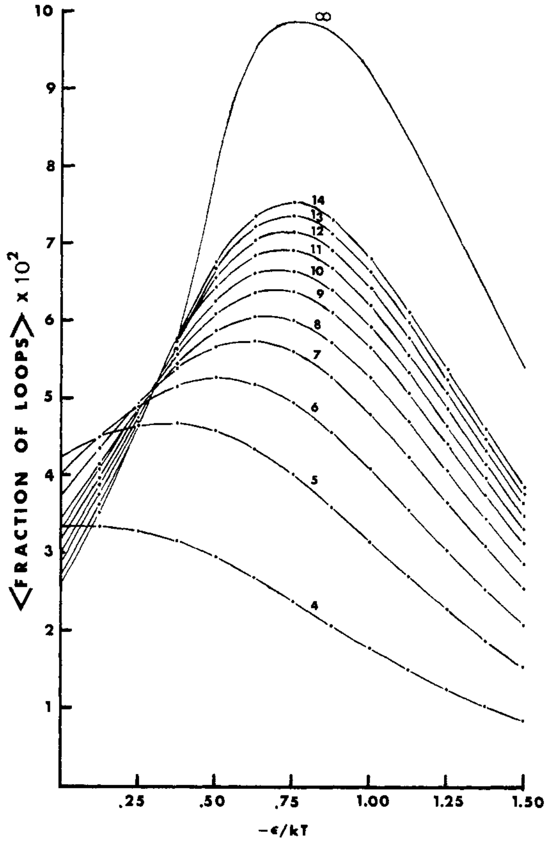

Figure 5. A plot of the average fraction of loops off the surface *vs.* the energy of adsorption per atom.

lowers the fraction of atoms on the surface was obtained by McCrackin[5] by examining how excluded volume affects the number of possible configurations for loops of the molecule off the surface and for trains of the molecule adsorbed on the surface.

Figure 5 shows the average number of loops off the surface divided by the number of atoms in the chain as a function of the energy of attraction for the different length polymer chains enumerated and also contains the extrapolated curve for infinite length molecules. In Figure 6 the average fraction of loops off the surface for constant values of the adsorption energy are plotted *vs.* the reciprocal of the number of atoms in the chain. These curves were extended to intersect the $1/(N + 1) = 0$ axis. This extrapolation was more difficult than in the case of Figures 2 and 3. All eleven data points and also just the seven end data points ($N = 8$ through 14) for given adsorption energy were least-square fitted to first- and second-degree polynomials of the form of eq 4. The intercept values corresponding to the fitted polynomials with the least error were used as the data points for the adsorbed molecule of infinite length plotted in Figure 5. All curves in Figure 5 show a maximum which for $N > 9$ occurs at $-\epsilon/kT + 0.75$. It was expected that the curves should show a maximum since initially as the adsorption energy increases the number of atoms on the surface and the number of returns to the surface increase. For larger adsorption energies the number of atoms on the surface increases mainly by increasing the length of trains on the surface, and for very large adsorption energies, since the molecule lies completely on the surface, the number of loops must decrease to zero. Below $-\epsilon/kT + 0.325$ the curves show first an increase and then a decrease of the fraction of loops with N. This is a result of the model constraint of starting each molecule with its first atom on the surface. The curve for infinite macromolecules shows a maximum at $-\epsilon/kT = 0.75$ and the value for the fraction of loops is always less than 0.1. This does not agree with McCrackin's Monte Carlo results. McCrackin reported values greater than 0.1 for the fraction of loops and reported that the maximum appears to occur between $-\epsilon/kT = 1$ and 1.5 for 50-segment molecules. This lack of agreement can again be attributed either to Monte Carlo sampling problems or extrapolation errors.

Figures 7 and 8 contain plots of normal distances to the surface. Figure 7 gives the average distance of the end of an adsorbed molecule from the adsorbing surface *vs.* energy of adsorption and also contains the extrapolated curve for a molecule of infinite length, along with the results reported by Rubin[14] (dashed line) for a molecule of infinite length without excluded volume. For small values of the adsorption energy the distance of the end from the surface varies greatly with the length of the molecule. Above $-\epsilon/kT = 0.75$ the curves approach one another and the distance of the end from the surface is relatively independent of the length of the molecule, with the end of the molecule less than one bond length from the surface. A comparison of our results for a molecule of infinite length with excluded volume with those of Rubin (Figure 7) for a molecule without excluded volume reveals that both predict infinite values for the average distance of the end from the surface for low values of the adsorption energy. As the adsorption energy increases the end is found closer to the surface; however, the excluded volume constraint is seen to increase the distance of the end from the surface above the values reported by Rubin. This is in agreement with the results reported in this study for the fraction of atoms on the surface (see Figure 4). McCrackin[5] also reported similar increases

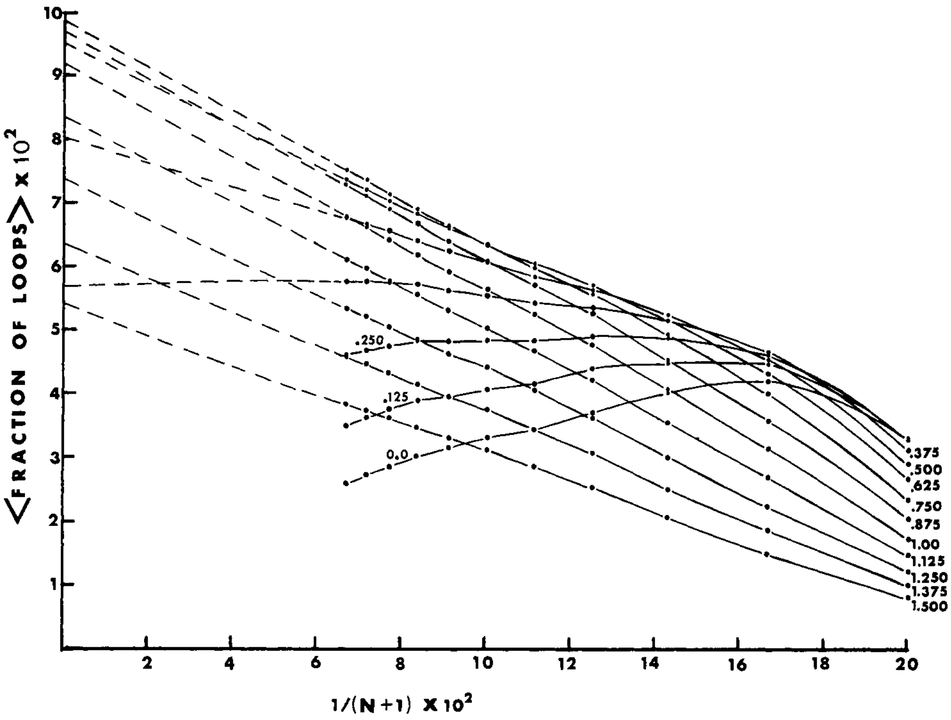

Figure 6. A plot of the average fraction of loops off the surface *vs.* $1/(N + 1)$.

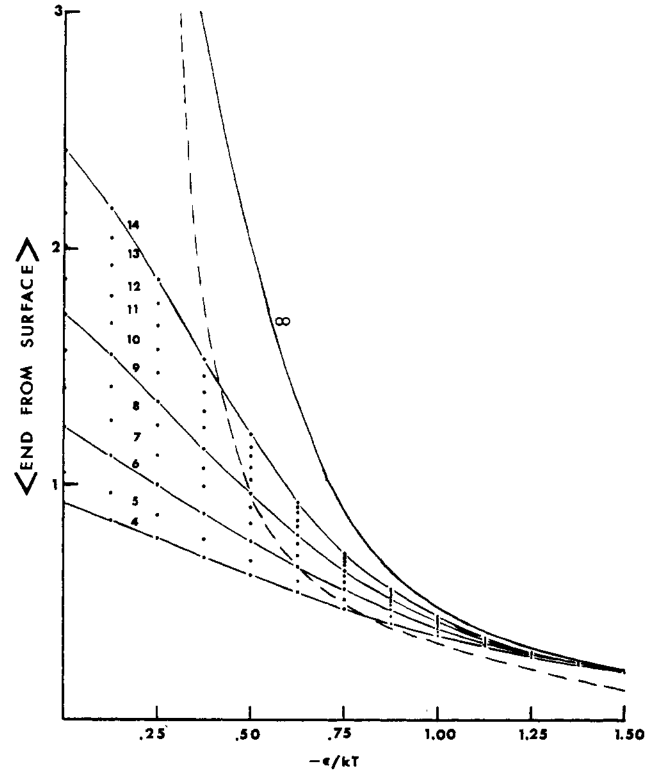

Figure 7. A plot of the average distance of the end of the adsorbed polymer molecule from the adsorbing surface *vs.* the energy of adsorption per atom. Rubin's calculated curve for molecules of infinite length is shown as a dashed (– – –) curve.

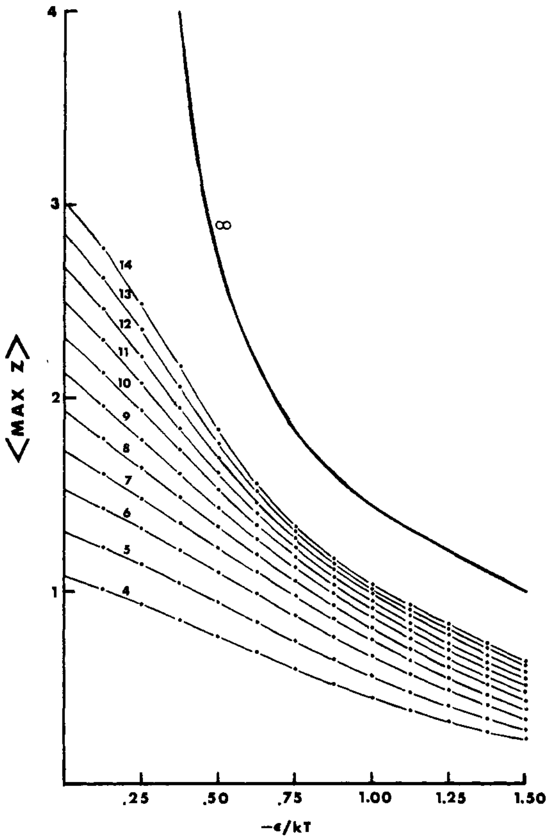

Figure 8. A plot of the average normal distance to the adsorbing surface from the atom farthest from the surface ⟨max Z⟩ *vs.* the energy of adsorption per atom.

for his Monte Carlo investigation. Our results indicate that above $-\epsilon/kT = 1.0$ the average distance of the end from the surface is less than 0.5 bond length.

Figure 9 gives the root-mean-square (r-m-s) distance of the end of a molecule from the adsorbing surface *vs.* energy of adsorption and also contains the extrapolated curve for a molecule of infinite length. The characteristics of the curves for the r-m-s and average distance of the end from the surface are similar, although the corresponding r-m-s values are greater in magnitude than the simple average values. Also, the curves do not approach one another as rapidly with increasing adsorption energy as do the simple average distance curves (Figure 7). For adsorption energies

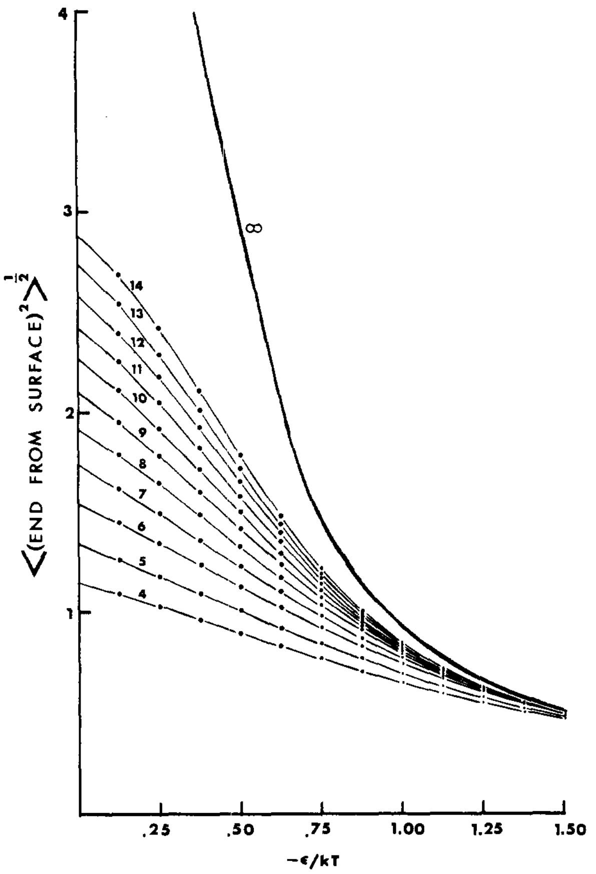

Figure 9. A plot of the root-mean-square distance of the end of an adsorbed polymer molecule from the adsorbing surface *vs.* the energy of adsorption per atom.

greater than kT, the r-m-s distance of the end of the molecule from the surface is less than one bond length.

Figure 8 gives the average distance of the atom farthest from the surface *vs.* energy of adsorption and also contains the extrapolated curve for a molecule of infinite length. Comparison of Figures 7, 8 and 9 reveals that the curves in Figure 8 for $\langle \max Z \rangle$ approach one another much less rapidly than do the curves for the average and r-m-s distance of the end from the surface. Also, for $N > 7$, the values of $\langle \max Z \rangle$ are greater in magnitude than the corresponding values for the simple average and r-m-s distances. Otherwise, the three curves for a molecule of infinite length show similar characteristics. For adsorption energies of $0.75kT$ and greater, the average maximum normal distance to the surface is less than two bond lengths, so that the entire molecule lies very close to the adsorbing surface.

The mean-square end-to-end distance of the adsorbed polymer molecules was studied as a function of adsorption energy ranging from 0 to $1.5kT$. Figure 10 contains the root-mean-square end-to-end distance *vs.* $-\epsilon/kT$ for the different length chains enumerated (N = 4 through 14). The data were also fitted to the asymptotic realtionship (eq 1) to determine γ as a function of adsorption energy. The exponent, γ, can be estimated by forming the ratios

$$\frac{\langle R_{N+1}^2 \rangle}{\langle R_N^2 \rangle} = \left(\frac{N+1}{N}\right)^\gamma = \left(1 + \frac{1}{N}\right)^\gamma \qquad (5)$$

Expanding the right-hand side, neglecting terms of order higher than N^{-1}, and rearranging terms, one obtains

$$\gamma_N \cong N\left[\frac{\langle R_{N+1}^2 \rangle}{\langle R^2 N \rangle} - 1\right] \qquad (6)$$

with

$$\gamma_\infty = \lim_{N \to \infty} \gamma_N$$

A plot of γ_N *vs.* $1/N$ extrapolated to $1/N = 0$ ($N = \infty$) yields the asymptotic value of γ_N. We found that the method of Fisher and Hiley[17] yielded graphs that were less difficult to extrapolate, and we used this method to calculate the quantity γ_N

$$\gamma_N^* = \frac{\gamma_N + \gamma_{N+1}}{2} \qquad (7)$$

These averaged γ_N values are plotted *vs.* $1/N$ to obtain γ_∞. Figures 11 and 12 represent such plots for various adsorption energies. Table I contains a list of the asymptotic exponents as a function of adsorption energy. Although averaged γ_N values are plotted, oscillations still exist for adsorption energies greater than kT and no attempt at extrapolation is made for these higher energy curves.

Figure 10 shows that as the length of the chain increases the r-m-s end-to-end distance also increases, as is expected. The r-m-s end-to-end distance curves show a minimum at $-\epsilon/kT = 0.375$ and thereafter increase with increasing adsorption energy. This is nicely shown in Figures 11 and 12 and Table I, where γ_∞ first decreases in value and for $-\epsilon/$

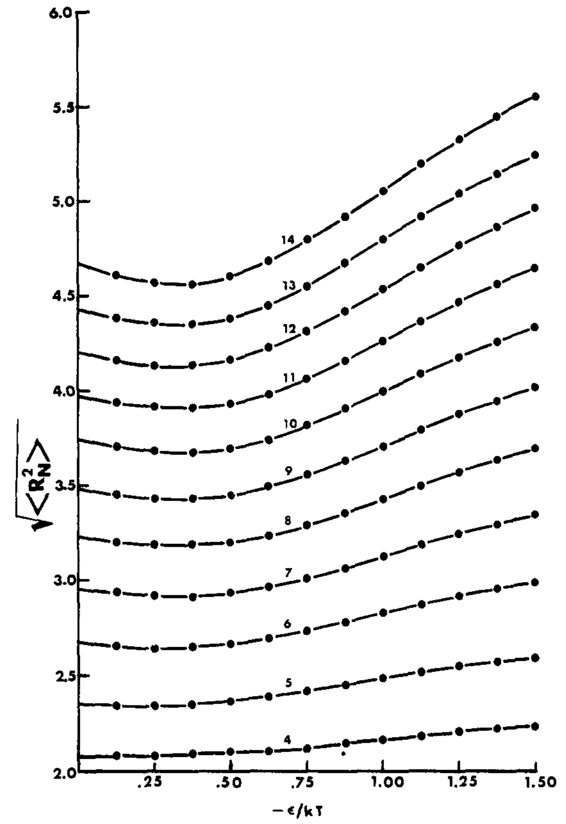

Figure 10. A plot of the root-mean-square end-to-end distance of an adsorbed polymer molecule *vs.* the energy of adsorption per atom.

Table I
Asymptotic Values of the Exponent γ from Equation 1 as a Function of Adsorption Energy

$-\epsilon/kT$	γ	$-\epsilon/kT$	γ
0.00	1.31	0.625	1.39
0.125	1.30	0.750	1.43
0.250	1.293	0.875	1.47
0.375	1.29	1.000	
0.500	1.33		

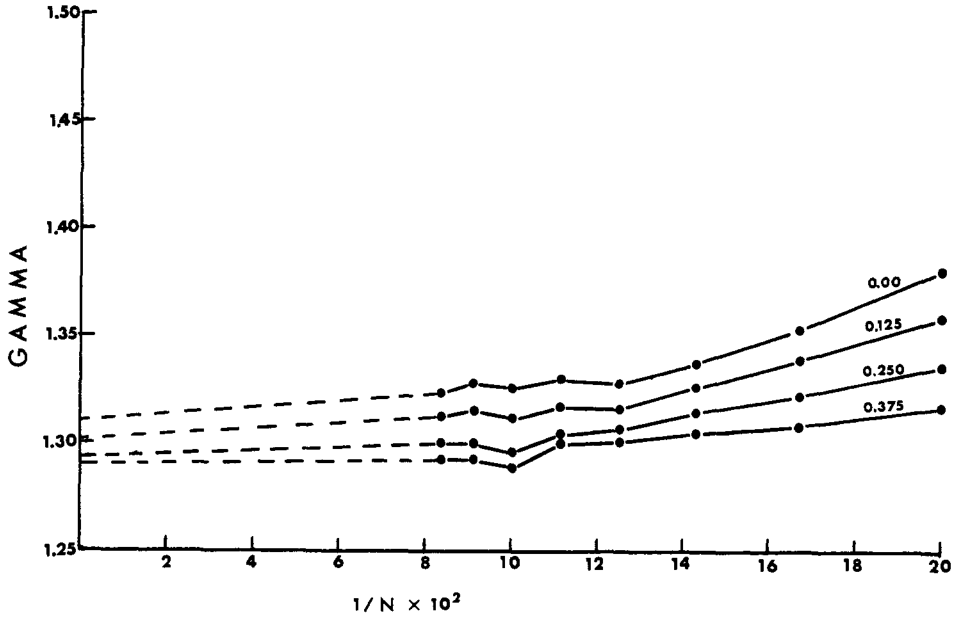

Figure 11. A plot of averaged γ values *vs.* $1/N$. Curves are at constant adsorption energy ranging from 0.0 to $0.375kT$.

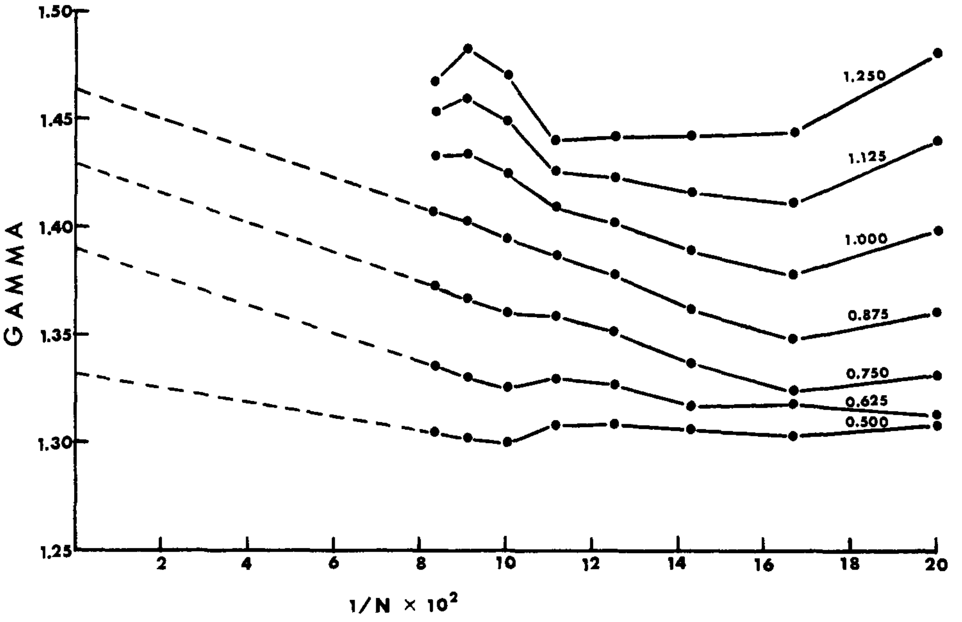

Figure 12. A plot of averaged γ values *vs.* $1/N$. Curves are at constant adsorption energy ranging from $0.50kT$ to $1.25\ kT$.

$kT > 0.375$ increases in value. These graphs also reveal some highly interesting results. As seen from eq 2, $\gamma \simeq 1.2$ for three-dimensional systems and 1.5 for two-dimensional systems. For $\epsilon = 0$ $\gamma \sim 1.3$, which is larger than the 1.2 value for three dimensions. The adsorbing surface has restricted the Z direction and the lattice system is somewhat less than three-dimensional. As $-\epsilon/kT$ increases to 0.375, the r-m-s end-to-end distance and γ decrease in value. Thus, initially, there is sufficient space to accommodate more atoms on and closer to the surface without causing the molecule to expand laterally. For $-\epsilon/kT$ greater than 0.375, the r-m-s end-to-end distance and γ increase with adsorption energy. The volume and surface available to the molecule approach saturation and a lateral expansion occurs which increases the end-to-end distance. Referring to eq 3, configurations with many atoms on the surface are weighted more heavily in the Boltzmann factor for higher adsorption energies. Since these configurations with many atoms on the surface are more extended, this results in an increase in the end-to-end distance with adsorption energy. For an adsorption energy great enough so that all atoms are on the surface, the end-to-end distance will reach a maximum constant value and will not increase in value for greater adsorption energies. At this energy the polymer will collapse to the two-dimensional planar surface with $\gamma = 1.5$, the value for two dimensions. If the curves in Figure 10 were extended they would level off at this energy and thereafter remain parallel to the $-\epsilon/kT$ axis. Another interesting point is brought out in Figure 12. As mentioned previously, due to oscillations, no attempt is made at extrapolation for $-\epsilon/kT > 1.00$. A two-dimensional lattice is more open than a three-dimensional lattice and the rate of convergence of γ *vs.* $1/N$ is not as fast. Since, for higher adsorption energies, these plots have increased two-dimensional character, these oscillations are exactly what is to be expected.

McCrackin,[5] in his Monte Carlo investigation, reported that the r-m-s end-to-end distance is approximately constant with respect to adsorption energy. This is not in agreement with our results. Rubin[4] has computed the mean-square end-to-end distance for molecules of infinite length without excluded volume. He reported that the mean-square end-to-end distance is constant for $-\epsilon/kT < 0.212$, decreases at this value, and increases for $-\epsilon/kT > 0.212$; *i.e.*, it is discontinuous. Our results are in partial agreement with these findings. We find that the end-to-end distance decreases continuously to a minimum at $-\epsilon/kT = 0.375$ and then increases for $-\epsilon/kT > 0.375$. Also, the excluded volume constraint increases the mean-square end-to-end distance to values greater than those reported by Rubin. We did not find any discontinuous change.

IV. Conclusion

The exact enumeration method, heretofore never applied to the adsorption problem, has been used, with interesting results. The excluded volume constraint has been shown to have a marked reducing effect on the fraction of atoms on the surface, as compared to the no excluded volume values reported by Rubin,[14] although to not as great an extent as reported by McCrackin.[5] The fraction of loops curves show a maximum at $-\epsilon/kT = 0.75$. This is considerably lower than the value suggested by McCrackin. For adsorption energies of $0.75kT$ and greater, the average distance of the atom farthest from the surface is less than two bond lengths, so that the entire molecule lies very close to the adsorbing surface.

The root-mean-square end-to-end distance data have disclosed some very revealing observations. The r-m-s end-to-end distance first decreases to a minimum at $-\epsilon/kT = 0.375$ and thereafter increases with adsorption energy. Investigation of the exponent, γ, in eq 1 shows that γ takes on values greater than 1.2, which is the value for γ in three-dimensional systems. In essence what has been accomplished is the adsorbing surface has restricted the Z direction and the lattice system behaves somewhat less than three dimensional. This first restriction of not allowing the molecule to penetrate the adsorbing surface imposes a constant constraint on the dimensionality of the system, resulting in a value of $\gamma > 1.2$ for $\epsilon = 0.0$. The second restriction on the dimensionality which is variable results from applying a variable energy of adsorption between the atoms of the polymer and the surface. This variation of adsorption energy may be looked at as a direct variation of dimensionality. For $\epsilon = 0.0$ the dimension is less than three but much greater than two; for $\epsilon > 0.75$ it is much less than three and very close to two. See Table I where γ *vs.* energies are listed. These two restrictions cause the minimum in γ values and the minimum in the r-m-s end-to-end distance curves. For $\epsilon = 0.0$, the adsorbing surface restriction has excluded all configurations, which would be included for a dimensionally unrestricted model, whose end atoms are close to the origin but which contain atoms below the adsorbing surface. Since these compact configurations do not appear in the summation of eq 3, this results in a greater r-m-s end-to-end distance than obtained for a dimensionally unrestricted lattice. As $-\epsilon/kT$ takes on values greater than zero, configurations with a few atoms on the surface, which are less extended, dominate the summation of eq 3. These configurations are more numerous than configurations with many atoms on the surface and have greater Boltzmann factors than the more extended configurations with very few atoms on the surface. Thus, less extended configurations dominate the summation resulting in a decrease in the r-m-s end-to-end distance. For $-\epsilon/kT > 0.375$ the Boltzmann factor for the fewer more extended configurations with many atoms on the surface becomes large enough to outweigh the combined effects of a greater number of configurations and a smaller Boltzmann factor for the less extended configurations. Thus, these more extended configurations with many atoms on the surface dominate the summation resulting in an increase in the r-m-s end-to-end distance with adsorption energy. For very large adsorption energies, the relatively few configurations with all atoms on the surface are expected to dominate the summation of eq 3, with the result that the polymer is expected to collapse to the adsorbing surface, with γ approaching 1.5, the value for two-dimensional systems.

Acknowledgment. We are indebted to the computing center staff and in particular the director, Dr. Mary L. Buchanan, for their great efforts in helping complete this work. We are also pleased to acknowledge Professors Walter H. Stockmayer and Alex Silberberg, who clarified a number of points for us, for their continued interest in this work.

References and Notes

(1) (a) Based in part on a thesis submitted by P. Mark to the Chemistry Department of Adelphi University in partial fulfillment of the Ph.D. degree.
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