By substituting (A-5) into (A-4) and (22), one gets the correlation functions in the homogeneous melt $\tilde{S}_{11} = \tilde{S}_{22}$ and $\tilde{S}_{12}$. Similarly, the coefficient $\Gamma_{22}(\vec{q})$, eq 25, in the expansion of the free energy may be calculated, and one gets

$$\xi^2 = 2R^2\{1 - \chi^2 N^2 \phi(1-\phi)/8k^2\}/3|\chi N(1-\phi) - 2| \qquad \text{(A-7)}$$

In the case of diblock chains, $k = 1$, this formula reduces to (29).

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Estimates of the Bound Fraction of an Adsorbed Polymer at the Solid–Liquid Interface. Exact Enumeration Study of a Self-Avoiding Walk Model

Terence Cosgrove

Department of Physical Chemistry, School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, England.

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ABSTRACT: Exact enumeration results of terminally attached self-avoiding walks on the tetrahedral lattice have been used to calculate $\langle p \rangle$, the fraction of polymer segments of an adsorbed polymer lying in an interface, as a function of the adsorption energy (ϵ). Neville table estimates have been used to extrapolate the $\langle p \rangle$ results to infinite chain lengths as a function of ϵ. Below a critical value of ϵ, $\langle p \rangle$ is found to vary inversely with the degree of polymerization. Comparisons of $\langle p \rangle$ estimates on various lattices are also made.

1. Introduction

The adsorption of polymers at solid surfaces from solution is unique in the sense that only a few segments need be in contact with the surface for the polymer to be essentially irreversibly adsorbed. Although considerable experimental data exist on adsorbed polymer systems,[1] basically only two experimental parameters have been used to describe the microscopic structure of the adsorbed layer. One of these, the adsorbed layer thickness, has been measured by several techniques, including ellipsometry,[2] photon correlation spectroscopy,[3] and viscous flow.[4] The difficulty with these techniques, however, is that there is at present no unambigous way to relate the experimental measurement to a theoretically calculable quantity such as the segment density distribution of the adsorbed polymer. Recently, the segment density distribution[5,25,26] has been measured explicitly by small-angle neutron scattering and this should prove a useful test of theories of polymer adsorption.

The other experimentally accessible quantity is $\langle p \rangle$, the mean fraction of monomers in direct contact with the surface. This can be measured by a variety of techniques, including infrared spectroscopy,[6] electron spin resonance,[7] nuclear magnetic resonance,[5,22] and microcalorimetry.[6] The dependence of $\langle p \rangle$ on the degree of polymerization and temperature has been predicted by a variety of theories of polymer adsorption.[8-14] Theories of the high surface coverage regime use a Flory–Huggins mean field approach.[12,14] At low surface coverage, however, the polymer molecules do not interact appreciably with one another and a model based on an isolated chain is more appropriate. Although random walk models of an isolated chain can be treated exactly,[1,8,9] the incorporation of the excluded volume effect makes a detailed analytical treatment very

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difficult.[10,11] An alternative approach is to use either Monte Carlo[13,15] or exact enumeration coupled with series analysis.[16-21]

In this paper exact enumeration results of the self-avoiding walk model of an adsorbed polymer (on the tetrahedral lattice) are presented and analyzed to obtain the chain length and adsorption energy dependence of the mean fraction of adsorbed monomers. In addition, data available in the literature for other lattices are also used to form estimates of $\langle p \rangle$. Comparison between lattices enable some qualitative predictions to be made on the effect of flexibility.

2. Notation and Exact Enumerations

Consider a three-dimensional lattice in which a particular place ($z = 0$, say) represents a surface. Consider a self-avoiding walk of n steps beginning at the origin (i.e., terminally attached to the surface plane) and restricted so that all vertices of the walk have a nonnegative z coordinate. Let the number of n-step walks having m vertices in the plane $z = 0$ be $(n,m)_s{}^V$. If the energy of interaction of a vertex with the surface is ϵ if the vertex is in the surface plane and zero otherwise, then the appropriate configurational partition functions can be defined. If $\lambda = \exp(-\epsilon/kT)$, then

$$Z_n{}^V(\lambda) = \sum_{m=1}^{n+1} (n,m)_s{}^V \lambda^m \tag{2.1}$$

The mean fraction of vertices in the plane $z = 0$, $\langle p \rangle_V$, is related to $Z_n{}^V(\lambda)$ by

$$\langle p \rangle_V = \frac{\sum_{m=1}^{n+1} m(n,m)_s{}^V \lambda^m}{(n+1)\sum_{m=1}^{n+1} (n,m)_s{}^V \lambda^m} = \frac{n}{n+1}\,\frac{\partial(n^{-1}\log Z_n{}^V(\lambda))}{\partial \lambda} \tag{2.2}$$

It has been shown[18] that there is a critical value λ_c such that for $\lambda < \lambda_c$

$$\lim_{n\to\infty} n^{-1} \log Z_n{}^V(\lambda) = 0 \tag{2.3}$$

so that, provided that the order of operations can be interchanged,

$$\lim_{n\to\infty} \langle p(\lambda) \rangle_V = 0; \qquad \lambda < \lambda_c \tag{2.4}$$

The n dependence of $\langle p \rangle$ over the whole range of λ values and the λ dependence in the $n \to \infty$ limit can thus be investigated by exact enumeration.

The exact values of $(n,m)_s{}^V$ have been published for the simple cubic,[18] face centered cubic,[21] and tetrahedral lattices.[16,17] However, the orientation of the surface plane chosen for the tetrahedral lattice was such that only alternate vertices could lie in the surface plane.[17] For the calculations reported here an alternative surface plane was chosen, so that for a walk in the extended zigzag (all trans) conformation, every vertex can lie in the surface plane. This orientation has also been studied by Monte Carlo methods[13] and allows a useful comparison between the results of the two approaches. The exact values of $(n,m)_s{}^V$ are given in Table I. Values of $\langle p(n,\lambda) \rangle_V$ can be calculated directly via eq 2.2, and the λ dependence for typical values of n is shown in Figure 1. In order to extrapolate to $n \to \infty$, one needs the functional dependence on n at a given λ. For $\lambda = 1$

$$\langle p(n,1) \rangle_V = \sum_{m=1}^{n+1} m(n,m)_s{}^V / (n+1) \sum_{m=1}^{n+1} (n,m)_s{}^V \geq n^{-1} \tag{2.5}$$

and $\langle p(n,1) \rangle_V \leq 1$, which suggests that $\langle p \rangle \sim n^{-\theta}$ with $0 \leq \theta \leq 1$. To estimate θ it is convenient to form the estimates

$$\theta_n = \tfrac{1}{2}n\{1 - \langle p(n,1) \rangle_V / \langle p(n-2,1) \rangle_V\} \tag{2.6}$$

$$\theta_n{}^{(1)} = \tfrac{1}{2}\{n\theta_n - (n-2)\theta_{n-2}\} \tag{2.7}$$

and

$$\theta_n{}^{(2)} = \tfrac{1}{4}\{n\theta_n{}^{(1)} - (n-4)\theta_{n-2}{}^{(2)}\} \tag{2.8}$$

(the successive columns of a Neville table), which all converge to θ. The results are shown Table II. It appears that θ is close to unity and it is likely that this result will be valid for all $\lambda < \lambda_c$. If this behavior also applies above λ_c, it suggests $\langle p(n,\lambda) \rangle_V$ can be extrapolated against $1/n$; this can conveniently be accomplished by forming linear and quadratic extrapolants analogous to (2.7) and (2.8). The n dependence of these extrapolants is shown in Figure 2 for typical values of λ and the λ dependence of the estimated limiting values for $\langle p \rangle_V$ is shown in Figure 1.

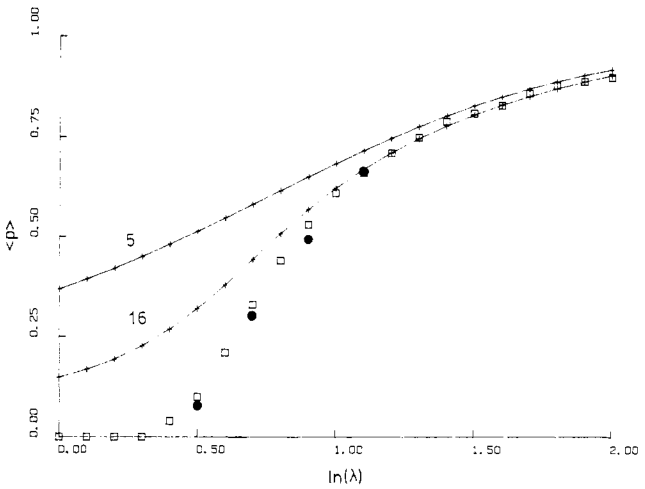

Figure 1. Variation of $\langle p \rangle_V$ as a function of ln λ for chain lengths 5 and 16 (+) and extrapolated to $n \to \infty$ (□) for the tetrahedral lattice. (●) Results of Lal and Stepto.[13]

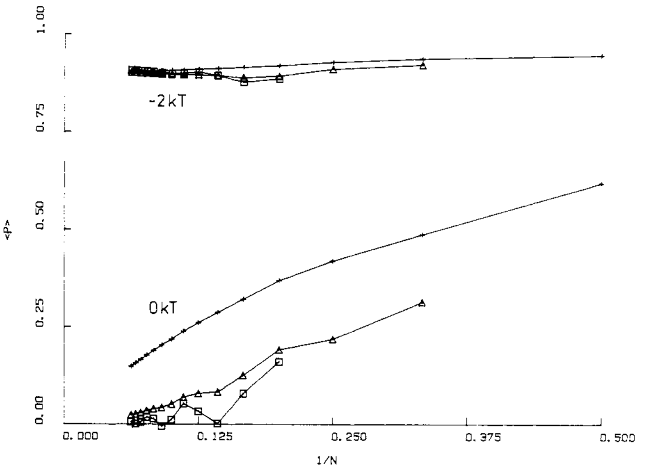

Figure 2. Variation of $\langle p \rangle_V$ (+) and the linear (△) and quadratic (□) estimates to $\langle p \rangle_V$ at values of the adsorption energy of 0 and $-2.0kT$, with $1/n$.

3. Discussion

As with other calculations of $\langle p \rangle$,[10], these results predict a critical energy of adsorption, ϵ_c, below which $\langle p \rangle = 0$ (Figures 1 and 2). Above ϵ_c, $\langle p \rangle$ increases with increasing ϵ as found experimentally.[7,24] Estimates of ϵ_c can be made from these plots and the value obtained is $(0.3 \pm 0.1)kT$.

Table I
Values of $(n,m)_s^V$ for the Tetrahedral Lattice

n	m																
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	1	2															
2	3	2	2														
3	7	8	2	2													
4	19	16	14	2	2												
5	53	42	26	22	2	2											
6	147	118	66	36	30	2	2										
7	401	324	200	110	46	38	2	2									
8	1123	862	544	328	174	56	46	2	2								
9	3137	2400	1460	906	498	268	66	54	2	2							
10	8793	6678	4052	2466	1370	718	380	76	62	2	2						
11	24599	18632	11460	6932	3938	2064	978	524	86	70	2	2					
12	69287	51738	31964	19572	11168	6090	3004	1282	684	96	78	2	2				
13	194967	145294	89416	55078	31840	17664	9096	4308	1622	880	106	86	2	2			
14	550361	407418	251080	154556	89956	50296	26616	13052	5998	2010	1088	116	94	2	2		
15	1552645	1147244	708684	436062	256784	144968	76956	39220	18244	8216	2430	1336	126	102	2	2	
16	4393021	3225590	1996244	1231350	726696	416378	224754	114718	56016	24650	10960	2902	1592	136	110	2	2

Table II
Neville Table Estimates for θ
Using $\langle p(n,1)_V\rangle$ Values ($\lambda = 1$)

n	θ_n	$\theta_n^{(1)}$	$\theta_n^{(2)}$
1	0.000	0.000	0.000
2	0.000	0.000	0.000
3	0.624	0.000	0.000
4	0.647	0.000	0.000
5	0.608	0.584	0.000
6	0.701	0.810	0.000
7	0.775	1.195	1.652
8	0.754	0.915	1.020
9	0.758	0.699	0.080
10	0.800	0.983	1.085
11	0.824	1.117	1.847
12	0.821	0.924	0.805
13	0.829	0.861	0.287
14	0.844	0.985	1.139
15	0.856	1.027	1.481
16	0.859	0.963	0.897

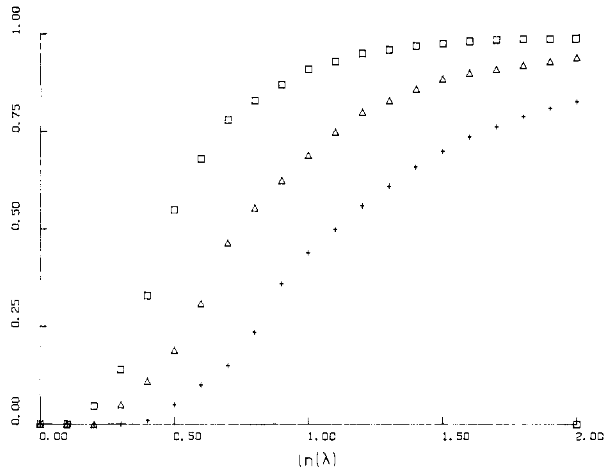

Figure 3. Extrapolated values of $\langle p\rangle_V$ as a function of ln λ: (+) fcc lattice with a square surface lattice; (△) fcc lattice with a triangular surface lattice. (□) cubic lattice with a square surface lattice.

For comparison, Monte Carlo estimates of $\langle p\rangle_V$ by Lal and Stepto[13] for a chain length of 100 bonds are also shown. These are systematically less than the values found here but do show the same overall trend of an increasing number of surface contacts with increasing values of ln λ.

It is also possible to calculate ϵ_c with a bond model, where n then becomes the number of bonds in the surface. Clearly, both these models are idealizations of the physical situation and reality may lie somewhere in between. An estimate of ϵ_c using the data of Ishinabe[27] gives a value of 0.5 ± 0.05, which is somewhat larger than for the site problem but is close to the error bounds for the extrapolation procedures used.

Tables of values for $(n,m)_s^V$ exist for several other lattices, including the cubic lattice[20] with a square lattice as the surface and the fcc lattice with both square and triangular surface lattices. Figure 3 shows the extrapolated values of $\langle p\rangle$ as a function of ln λ for various lattices.

The $\langle p\rangle$ estimates for the fcc lattice are smaller than those for the cubic lattice and this is because of the larger number of walks that can be realized on this lattice. Qualitatively, this can be compared with the results of Hoeve,[23] where the effect of an increasing flexibility parameter for a single chain was found to reduce $\langle p\rangle$. A similar effect is found by comparing the $\langle p\rangle$ estimates for the fcc triangular-based lattice and the fcc square-based lattice. In the former case, the $\langle p\rangle$ estimates are larger, corresponding to more surface flexibility.

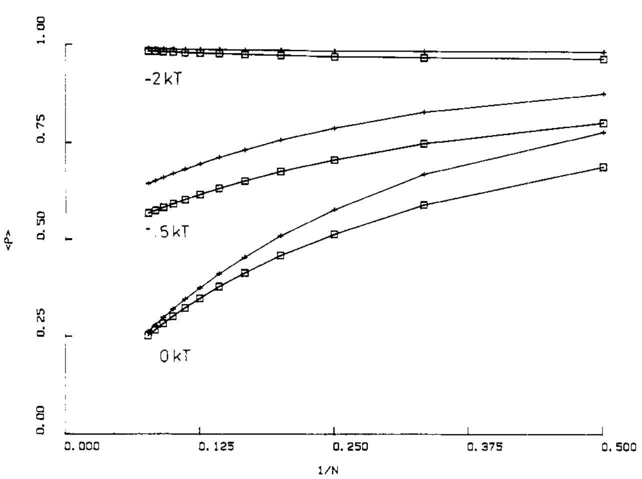

Figure 4. $\langle p \rangle_V$ estimates for the cubic lattice for a terminally anchored chain (+) and a chain with at least one vertex in the adsorption plane (□) as a function of the degree of polymerization at values of the adsorption energy of 0, −0.5 kT and −2.0kT.

In order to evaluate the effect of choosing a terminally anchored chain model, it is possible, using the results of Torrie et al.[20] for the cubic lattice, to calculate $\langle p \rangle$ for an attached walk (i.e., $m > 0$), where the attached segment can be chosen anywhere along the chain. Figure 4 shows the variation in $\langle p \rangle$ as a function of $1/n$ for selected values of ϵ. Clearly, for short walks there is a large difference between the models. As n increases, the extrapolated values become closer, showing that the terminally attached constraint is not a serious limitation.

The model proposed in this paper is for a single polymer molecule with fixed bond angles. The effect of the solvent is only taken account of in the net energy of adsorption; no entropy term has been included for solvent desorption. However, at fixed temperature the qualitative predictions are consistent with experimental evidence. Quantitatively, it is found that the $\langle p \rangle$ values calculated are over estimates, compared to the absolute values obtained by calorimetry,[6] though very few results exist for $\langle p \rangle$ at low coverages in systems where the enthalpy of adsorption is known exactly.

4. Conclusion

Exact enumeration studies of attached self-avoiding walks have been used to calculate $\langle p \rangle$, the fraction of polymer segments in contact with a surface, as a function of the adsorption energy. Reasonable agreement is found with Monte Carlo studies. Below the critical energy of adsorption, $\langle p \rangle$ varies as n^{-1} as the degree of polymerization approaches infinity.

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Calculation of Average Properties of the Pendant Chains in a Network

Miguel A. Bibbó and Enrique M. Vallés*

Planta Piloto de Ingeniería Química, UNS-CONICET, 8000 Bahía Blanca, Argentina.
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ABSTRACT: A recursive approach is used to evaluate number- and weight-average properties of the pendant chains in a network obtained by stepwise polymerization from polyfunctional monomers and comonomers. The results are valid for monodisperse and polydisperse reactive oligomers. The molecular parameters calculated here include the number- and weight-average molecular weight of the pendant chains, the average degree of branching, the average size of the longest chain through a pendant chain, and the extent of reaction at the pendant chains as a function of the overall extent of reaction.

Introduction

A detailed knowledge of the unique structure of rubbery materials is required to be able to relate their rheological properties to different molecular parameters and eventually to synthesis conditions. It is well-known, for example, that elastic properties of amorphous rubbers depend on the number of elastic chains per unit volume as predicted by the kinetic theory of rubber elasticity. This has been