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A new Monte Carlo method for direct estimation of cluster partition functions. Application to micellar aggregates

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A new Monte Carlo method for direct and unbiased estimation of cluster partition functions is established. The method is a generalization of the technique of inversely restricted sampling used in the study of linear polymer statistics. The essential generalization is a correct weighting of the various branching events possible in the cluster growth algorithm. The method applies directly both to ordinary continuous space clusters as well as to simpler lattice clusters. As an example, the method is applied to the calculation of cluster partition functions for the hard core chain molecule aggregates associated with a simple model micellar aggregate investigated previously.

I. INTRODUCTION

In this paper we present a new Monte Carlo technique which provides a direct and unbiased estimation of cluster partition functions. Physical clustering in macroscopic equilibrium systems is a topic of wide interest.¹⁻¹¹ Significant computational effort has already been applied to the study of physical clusters.⁴⁻¹¹ However, available techniques for the calculation of the cluster partition functions needed to determine cluster size distributions are quite circuitous. One available method is to use standard computer simulation techniques together with thermodynamic integration or charging parameter formulas.⁷⁻⁹ This requires a series of computations to connect the thermodynamic system of interest with a reference system of sufficient analytical simplicity. The second available method is to simulate large enough systems over long enough times that a reliable direct observation of the cluster size distribution can be made.^{10,11} This avoids prior determination of cluster partition functions. Such a procedure neither requires nor takes advantage of special ingenuity in sampling interesting clustering configurations. Of course, if this latter procedure is feasible, it will provide a broader range of information.

The new procedure arose from our study of micellar aggregates.¹² That is a case where the determination of the cluster size distribution is of paramount importance. It is also a case where neither of the available methods seemed practical. The new method that was developed fits in neither of these two categories, but is a generalization of the technique of inversely restricted sampling (IRS).¹³⁻¹⁷ The new method is of intrinsic interest in its own right, and a major part of this paper is devoted to its exposition. However, we also apply the method to the estimation of cluster partition functions of the hard core chain molecule aggregates associated with our previous study of micellar systems. These results will be of direct use in further development of theories of micelle formation. Thus, this paper also represents an extension of our work on micelle structure and stability.

Aside from the particular application in this paper, there are several other problems for which this new

method looks especially well suited. In order to convey the utility of the method it is appropriate to give a few examples. One such problem is the analysis of hydrogen bonding patterns in clusters formed from species like HF, and H₂O in the gas phase. It is clear that there must be appreciable and interesting topological differences between the hydrogen bond networks in these clusters even though the hydrogen bonding interaction strengths are substantially the same. It seems likely these qualitative topological differences play an important role in differentiating the thermal properties of liquid HF from liquid H₂O.¹⁸ Of course the structure and thermal properties of ice crystallites in super-saturated vapors is a topic of some importance in nucleation theory and cloud physics. However, previous computational studies of these clusters have been limited to a few configurations of especial simplicity.¹⁹ A second example problem is the study of amorphous clusters grown by serial deposition of atomic species.²⁰ These objects have been considered good empirical models of glass structure.²¹ The new technique provides, among other things, a direct method for definition and calculation of the entropy difference between the distribution governing growth of the cluster and a Gibbs distribution. These two examples should suffice to give an impression of the scope of these techniques.

In the next section we provide the necessary theoretical analysis to develop the new method and to prove that it is unbiased. For simplicity, we focus particularly on the lattice systems to which we plan to apply the method. The principles of the method apply to continuous space systems also. In closing Sec. II, we indicate how the continuous space sampling problem might be approached without making reference to any lattice. In Sec. III A we apply the statistical method to a problem which has been exactly solved: evaluation of the partition function sums (enumeration of strong embeddings) on the two-dimensional square lattice.²²⁻²⁴ The purpose here is just to compare statistical results with exact results for a nontrivial but sufficiently simple case where the exact results are available. We note in passing that much effort has been invested in the study of clustering within the context of percolation phenomena.^{25,26} Although many of the tools developed in these studies are also relevant to the problems discussed here, the basic objectives are frequently

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very different. Therefore, we do not discuss these percolation problems in any direct way. In Sec. III B, we use the statistical method to study the chain molecule clusters associated with the surfactant aggregate (micelle) problem.¹² Section IV provides a conclusion.

II. INVERSELY RESTRICTED SAMPLING AND STATISTICAL ESTIMATES OF CLUSTER PARTITION FUNCTIONS

A. Cluster partition function

Here we consider the cluster partition function defined by

$$VK_N(T) = \int d1 \dots dN H(1, \dots, N) \times \exp[-U(1, \dots, N)/k_B T] / N! \quad (1)$$

Here N is the number of particles in the cluster, and the notation $1, \dots, N$ indicates the collection of N Cartesian position vectors which specify the configuration of the system. V is the volume of the container. For the lattice systems under consideration here the integral is interpreted as a sum over all lattice points for each of the N vectors. The intermolecular potential energy is given by $U(1, \dots, N)$. If U includes only excluded volume interactions, any near neighbor and longer ranged interactions being set to zero, we denote the energy by $U^{(0)}(1, \dots, N)$. The cluster partition function for this case is $K_N^{(0)}$. The function $H(1, \dots, N)$ imposes the connectivity constraint. In particular,

$$H(1, \dots, N) = \begin{cases} 1, & \text{if the cluster is connected,} \\ 0, & \text{otherwise.} \end{cases} \quad (2)$$

We focus particularly on the calculation of $K_N^{(0)}$ here. However, our method has somewhat greater generality. It is clear that $N!K_N^{(0)}$ is the total number of N point labeled connected graphs that can be strongly embedded on the specified lattice. These graphs are sometimes called lattice animals. Thus a direct evaluation of $K_N^{(0)}$ would appear to require an enumeration of these graphs.

Graph enumerations are a central component in a wide variety of problems of statistical physics.²² For self-avoiding, and otherwise restricted, random walks, inversely restricted sampling (IRS) provides an elegant method of obtaining unbiased statistical estimates of total numbers of walks.^{14,15} Of course, direct transcription of the IRS algorithm for the self-avoiding walk problem to the study of the statistics of lattice animals is transparently incorrect. Concurrent with the lack of a general unbiased or asymptotically unbiased technique for clusters some previous Monte Carlo studies of clusters have accepted an obvious bias.^{4,27} By considering the IRS method from a general point of view we will find an unbiased estimator of $K_N^{(0)}$. In view of previous studies of the IRS method for self-avoiding walks, it will then be clear that our technique will provide only an asymptotically unbiased estimate of the mechanical properties of the clusters. However, the Metropolis procedure provides a suitable alternative method for calculation of these mechanical properties.

For the self-avoiding walk problem, the IRS algorithm

is strikingly simple. The walks are generated (grown) in the following way. Consider a nontrapped walk of N steps. A trapped walk of N steps is a self-avoiding walk of N steps which cannot be extended to $N+1$ steps.¹⁵ Let $\Omega_j(N+1)$ be the number of unoccupied lattice sites adjacent to the position of the j th nontrapped walk after N steps. Then the $N+1$ step is chosen randomly to one of the $\Omega_j(N+1)$ adjacent vacancies. For a sample of m walks the quantity

$$E_1 = \frac{1}{m} \sum_{j=1}^m \left[\prod_{i=2}^N \Omega_j(i) \right] \quad (3)$$

is an unbiased estimator of the total number of walks of N steps.¹⁵ Of course, walks in the sample which are trapped before N steps contribute zero to the sum.

Next consider a lattice animal which grows according to a slightly different rule. Here, a lattice animal is defined as a connected strong embedding on a specified regular lattice. Labeled points are added to the animal sequentially. Point number 1 is placed on an arbitrarily designated lattice point. Next let $\Omega_j(p+1)$ be the number of vacant lattice sites adjacent to the j th animal of p points. Then the $p+1$ point is placed randomly among the $\Omega_j(p+1)$ adjacent vacancies. We will refer to this method of generating the animals as the growth algorithm. It is easy to see that, for this algorithm, E_1 does not estimate the total number of connected strong embeddings of N points. This can be explicitly verified by direct calculation, e.g., for three-point lattice animals on the two-dimensional square lattice. The problem is traced to the fact that for this algorithm some labeled strong embeddings are not generated at all.

In fact, we will show that an unbiased estimator of the number of N point labeled strong embeddings is

$$E_2 = \frac{N!}{m} \sum_{j=1}^m \left[\prod_{i=2}^N \Omega_j(i) \right] \prod_{i=1}^N \frac{1}{\omega_j(i)}. \quad (4)$$

The sample is generated from the growth algorithm above, and the $\omega_j(i)$ are calculated as follows. Consider the j th labeled strong embedding and erase labels $i, i+1, \dots, N$. Then $\omega_j(i)$ is the number of unlabeled points which are directly bonded to labeled points. By convention $\omega_j(1)=N$, for a N -point animal. Figure 1 gives some examples of the calculation of the $\omega_j(i)$.

To construct E_2 we economize notation and consider evaluation of integrals of the type

$$W_N = \int d\Gamma I(\Gamma), \quad (5)$$

where the configuration $1, \dots, N$ is denoted by Γ . Obviously, $N!K_N^{(0)}$ is an integral of this type with $I(\Gamma)$ the appropriate indicator function for an allowed graph. To estimate W_N we construct an algorithm which generates configurations Γ , with probability $P(\Gamma)$. The algorithm must have the property that all configurations with $I(\Gamma) \neq 0$ occur [have $P(\Gamma) \neq 0$]. Additional desirable properties of the algorithm are that $P(\Gamma)$ be easily calculated, and that $I(\Gamma)/P(\Gamma)$ is a slowly varying function of Γ . The integral is then written as

$$W_N = \int d\Gamma \{I(\Gamma)/P(\Gamma)\} P(\Gamma), \quad (6)$$

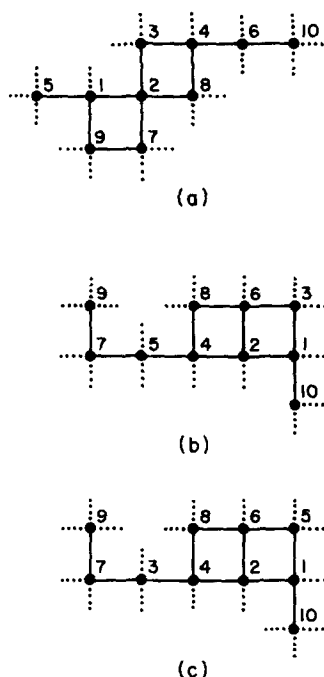


FIG. 1. Some ten-point lattice animals on the two-dimensional square lattice (a) $\prod_{i=1}^{10} \omega_a(i) = 10 \cdot 3 \cdot 5 \cdot 5 \cdot 5 \cdot 4 \cdot 4 \cdot 3 \cdot 2 \cdot 1$; (b) $\prod_{i=1}^{10} \omega_b(i) = 10 \cdot 3 \cdot 4 \cdot 3 \cdot 4 \cdot 4 \cdot 3 \cdot 3 \cdot 2 \cdot 1$. Note that (c) is just a re-labeling of (b), but (c) cannot be a result of the growth algorithm.

and an unbiased estimator of W_N is

$$E = \frac{1}{m} \sum_{j=1}^m I(\Gamma_j) / P(\Gamma_j). \quad (7)$$

The sample consists of $\Gamma_j, j=1, \dots, m$. The estimator E_1 is of this form, with

$$I(\Gamma_j) = \begin{cases} 1, & \text{if } \Gamma_j \text{ forms a sequentially labeled chain,} \\ 0, & \text{otherwise,} \end{cases} \quad (8)$$

and $1/P(\Gamma_j) = \prod_{i=2}^n \omega_j(i)$. This development does not work for the described growth algorithm because for some $I(\Gamma) \neq 0$, $P(\Gamma) = 0$: Some labeled connected strong embeddings are not generated by the algorithm. Figure 1 gives an example.

Although the growth algorithm does not generate all required labeled graphs it does produce all required unlabeled graphs. Furthermore, in most cases of interest $I(\Gamma)$ is independent of the labels given to the particles. Thus, the problem to be solved is to devise a weighting for the sampled labeled graphs which can be incorporated into the estimator to give a correct measure of the subset of labeled graphs which cannot be sampled. This is a nontrivial step. More than one such weighting can be devised, so that it is also a nonunique step. However, the estimator E_2 [Eq. (4)] is remarkably simple, and overwhelmingly more efficient than the alternatives we have been able to derive.

To construct the desired weighting, break up the integration region into sets of configurations corresponding uniquely to each unlabeled graph. Let the unlabeled graphs be identified by the index g . Then write

$$W_N = \sum_g \int d\Gamma I(\Gamma). \quad (9)$$

We first do the integral over the region associated with g , and then sum over all unlabeled graphs. We assume $I(\Gamma)$ depends only on the unlabeled graph, and write its value I_g . Since there are $N!$ labelings of the unlabeled graph of N points for the graph enumerations, Eq. (9) becomes

$$W_N = N! \sum_g I_g. \quad (10)$$

Now recall that the growth algorithm actually generates a subset, l' , of the labeled graphs corresponding to g . In order to be able sum over the members of l' , rather than all the labeled graphs corresponding to g we must guarantee that

$$N! I_g = \sum_{l'} q_{l'}. \quad (11)$$

A useful example is $q_{l'} = N! I_g p_{l'}$, where $p_{l'}$ is a probability rule on the set l' . In particular,

$$\sum_{l'} p_{l'} = 1. \quad (12)$$

Then

$$W_N = \sum_g \sum_{l'} N! I_g p_{l'}. \quad (13)$$

With the growth algorithm described, we then find the unbiased estimator

$$E = \frac{N!}{m} \sum_{j=1}^m I_g \left[\prod_{i=2}^N \Omega_j(i) \right] p_{l'}. \quad (14)$$

A correct, but grossly inefficient, choice for $p_{l'}$ would be $p_{l'} = \text{constant}$. The reason that this choice is inefficient is that the members of l' have to be enumerated, or their numbers suitably estimated, to determine the constant. The result E_2 is found by choosing

$$p_{l'} = \prod_{i=1}^N \omega_i^{-1}(i). \quad (15)$$

That Eq. (15) satisfies Eq. (12) can be seen by considering the following stochastic process of labeling an unlabeled N -point graph: First, one of the N points [$\omega_1(1) = N$] is chosen randomly and labeled 1. Next, one of the $\omega_1(2)$ points adjacent to 1 is chosen randomly and labeled 2. After j points have been labeled, one of the $\omega_j(j+1)$ unlabeled points adjacent to already labeled points is chosen randomly and labeled $j+1$, and so on. The set of labeled graphs which results from this labeling procedure contains exactly the same members as those which result from the growth algorithm.

Now that the basis of the method has been explained, it is fairly direct to use these ideas to estimate cluster partition functions for continuous space systems also. To make this explicit, here we briefly indicate one possibility. For definiteness, we consider clustering of a monatomic species such as argon. The definition of the continuous space cluster is entirely analogous to the lattice cluster definitions above. Consider N argon atoms in an arbitrary configuration. Lines are drawn between each pair of Ar atoms which are separated by a distance r_c or less. The N argon atoms form a cluster if the graph so produced is connected. In order

for these structures to form physically sensible clusters we expect that r_c should be not much more than roughly the separation of two argon atoms at the minimum of the interaction potential energy. Such a cluster might be grown as follows.

- (i) The position of the particle labeled 1 is fixed.
- (ii) A particle labeled 2 is located randomly in a spherical shell of volume v between two concentric spheres of radii r , and r_c with $r < r_c$. The radius of the inner sphere r is chosen so that the interaction potential energy of two argon atoms at that separation is many $k_B T$.
- (iii) To add particle 3, we first chose randomly between labels 1 and 2. Then we will attempt to insert particle 3 into a spherical shell of volume v surrounding the chosen labeled particle (either 1 or 2). This step is quite analogous to the various particle insertion techniques in more standard fluid Monte Carlo problems.¹⁷ Suppose 2 has been drawn. When 3 is inserted randomly into the spherical shell surrounding 2, sometimes 3 will end up nearly on top of 1. Such a configuration is physically nearly impossible, and very undesirable in a sampling scheme. More fundamentally, such a configuration would not be consistent with the intention to put particle 3 closer to particle 2 than to particle 1. To get around this we agree to make several trial insertions of 3. If the outcome of the trial has 3 closer to particle 1 than to particle 2, the configuration is considered unacceptable. If the outcome has 3 further from 1 than from 2, the outcome is judged acceptable. The trial insertions of 3 might be organized by deciding on a given fixed number of attempts A . Then we define:

$$t_3 = (\text{number of acceptable configurations produced})/A.$$

After the sequence of trial insertions, 3 is located at its position in the last acceptable configuration. If t_3 is found to be zero, the simplest strategy (though not necessarily most efficient),¹³ is to discard the structure, while duely increasing the size of the sample by one, and start growing the next cluster from the beginning.

- (iv) Particles 4 through N are now added to the structure in a manner entirely analogous to the placement of 3. If particle j is being placed, we draw from among labels 1, ..., $j-1$. We then attempt to insert particle j in a spherical shell of volume v centered on the position of the particle whose label was drawn. We then go through a series of trial insertions and score t_j .

After the cluster is grown, lines are drawn between any pair of atoms separated by less than r_0 . The $\omega_j(i)$ are then determined in precisely the same way as for the lattice case. Then an unbiased estimator of the cluster partition function is

$$E(N|K_N) = \frac{v^{N-1}}{m} N! \sum_{j=1}^m \left\{ \left[\prod_{i=3}^N (i-1)t_i \right] \left[\prod_{i=1}^N \frac{1}{\omega_j(i)} \right] e^{-\beta U_j} \right\}.$$

The U_j is the total potential energy of the j th cluster in the sample.

There are a variety of adaptations of this result which

are clearly of importance in a practical calculation. For example, uniform sampling in the spherical shell is unlikely to be the best choice. However, the type of nonuniform sampling chosen should depend on the interactions involved. Again, uniform random drawing of the labels of previously placed particles will not be optimum. Probably, particles with relatively few near neighbors should be preferentially chosen. In both cases, the algorithm above incorporates the crudest Monte Carlo alternative. Neither of these features are essential. The only subtle and essential point is the function of the $\omega_j(i)$. If their role is preserved, then a variety of well-known sampling techniques become directly applicable to the cluster problems.

III. APPLICATIONS

A. Numerical example: Clusters on the 2D square lattice

Although many features of Monte Carlo algorithms may be investigated analytically, some numerical experience is almost always necessary in order to accurately judge the usefulness of any proposed method. Therefore, in this section we use the growth algorithm above and the estimator E_2 to estimate the total number of connected strong embeddings of N points on the two-dimensional square lattice, for $N \leq 20$. We choose this example for two reasons. First, it is for this case that the exact enumeration has been carried out to highest N . Second, this is expected to be an especially severe test for the Monte Carlo method because of the low dimensionality and the importance of non-Gaussian fluctuations. It must be emphasized that the purpose here is just to test the method against exact results. Since the results for the two-dimensional square lattice are themselves not of primary interest in the present investigation we do not attempt to augment the known exact results by going to significantly higher N . Of course, when it is expedient to obtain the exact results, those will be the data of choice.

Calculations were done with sample sizes of $m = 10^3$ and 10^4 . The results are shown in Fig. 2. The elements of the sample are strictly independent. Thus, the central limit theorem applies directly and the standard deviation of $K_N^{(0)}$ straightforwardly estimated. The error bars shown on Fig. 2 are plus/minus two standard deviations. For $N \leq 15$ the statistical uncertainties in $\ln K_N^{(0)}$ are relatively small, and the Monte Carlo estimates are in good agreement with the exact results. For $N \geq 16$, the sample sizes we have used are too small: The estimated standard deviations become large, there are significant differences between the results obtained with very different sample sizes, and there are significant deviations from the available exact results. We judge the first two attributes to be reasonable indicators of the insufficient sample size for $N \geq 16$. In passing we note that if the estimated $K_N^{(0)}$ for $N \leq 15$ are used to study the asymptotic variation of $K_N^{(0)}$ with respect to N via the standard Pade approximant analysis,²⁸ then they yield virtually the same asymptotic behavior as the exact results utilized in the same way. This may be obvious from Fig. 2. Statistical noise

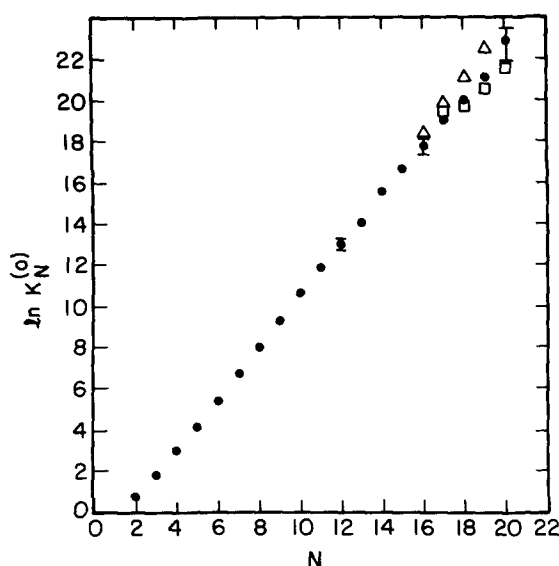


FIG. 2. $\ln K_N^{(0)}$ vs N for the 2D square lattice application. The dots are Monte Carlo results with sample size of 10^4 . The triangles shown for $16 \leq N \leq 19$ are exact results of Ref. 24. The squares are Monte Carlo results for $17 \leq N \leq 20$ with sample size of 10^3 . For $N < 15$ these various results are the same on the scale of the graph.

makes naive asymptotic methods based on graphical extrapolation less useful. Of course, it is well known that inference of the asymptotic behavior of $K_N^{(0)}$ even from the exact results is somewhat problematic, and especially so in 2D.^{29,30}

B. Chain molecule clusters

The lattice model studies here has been described previously.¹² The chain molecules, of l spherical extended atom groups, are embedded on a diamond lattice. Two chain molecules interact by excluded volume forces, plus attractive or repulsive near neighbor interactions between the pairs of groups, one group on each molecule. In addition, an intramolecular conformational energy is assigned to each rotational isomeric state that a molecule can adopt. Finally, we require that the entire system of N molecules form a connected aggregate.

There are several reasons, aside from analytical simplicity, for studying such a primitive model rather than one with more realistic molecular features. One reason is that micellar solutions have a remarkable diversity. In order to pin down the more global features of these systems, it is prudent to consider a model which captures features common to most micelles. On the other hand, if less global properties were of primary interest, it would have to be admitted that the interactions between surfactant molecules, including the effects of the solvent, are not well understood. In view of these uncertainties, an important ancillary consideration is how completely thermodynamic properties can be established for a range of physically reasonable interactions. Thus, computational expediency is of some importance. This is a less severe problem for the lattice models. For example, direct exact enumer-

ation has proved to be a feasible technique for small clusters of simple objects.²¹⁻²³

We have not used standard exact enumeration methods because the micelles are clusters of relatively complicated objects, namely the surfactant molecules. For our purposes in the present circumstance, exact enumeration is not a feasible alternative. Of course, if exact enumeration were feasible the exact results would be the data of choice. However, the techniques developed here are much less profligate of computer resources than are the exact enumerations. The results for chain molecule clusters presented below which might have been obtained by exact enumeration required about 5 min. computer time on a CDC 7600. Exact enumeration, at typical counting rates of 10^6 per minute, would have required in excess of 20 yrs of computer time.

Here the $K_N(T)$ is similar in form to that Eq. (1) except that if each of the N molecules contain l interaction sites (beads) the integration variables include all the lN positions and additionally the right-hand side of Eq. (1) is divided by $(l!)^N$. Also the growth algorithm must be generalized slightly. We develop these modifications in this section.

For simplicity we initially consider just the estimation of $K_N^{(0)}$. The elements of the sample are grown according to the rule:

- (i) The first bead of molecule 1 is placed on an arbitrary lattice site.
- (ii) The second bead of molecule 1 is placed randomly on one of the lattice sites adjacent to the position of the first bead.
- (iii) The third bead is placed randomly on one of the vacant sites adjacent to either of the first two beads. Subsequent beads are placed randomly on one of the vacant lattice sites adjacent to the end beads of the molecule at the preceding stage of growth. This is continued until l beads have been placed or the structure becomes trapped. If trapping occurs, the configuration is discarded, the sample increased by one, and the procedure starts over. The structure which results is a chain molecule embedded on the diamond lattice. Note, however, that the numbering of the beads of the chain is not necessarily sequential.
- (iv) The first bead of molecule 2 is placed randomly on one of the vacant lattice sites adjacent to beads of molecule 1. Steps (ii) and (iii) are then repeated for molecule 2 until all l beads of molecule 2 are placed or the structure becomes trapped.

(v) Step (iv) is then repeated for each of the molecules 3, ..., N or until the structure becomes trapped.

When such a structure is successfully completed, lN beads will have been placed. For the purposes of estimating $K_N^{(0)}$, we define $\Omega(i)$, $i = 1, 2, \dots, lN$ as

$$\begin{aligned} \Omega(1) &= 1, \\ \Omega(i) &= [\text{number of possible choices (adjacent vacant sites) for the } i\text{th bead placement.}] \end{aligned} \quad (9)$$

For example, $\Omega(2)=4$, $\Omega(3)=6$, and $\Omega(4)=6$ for $l \geq 4$ on the diamond lattice. We also define two other properties of the labeling of the structures. One of these is $\omega(i)$, $i=1, \dots, N$. First

$$\omega(1) = Nl. \quad (10)$$

To calculate $\omega(i)$ for $2 \leq i \leq N$, the labels are erased from molecules i, \dots, N . Then

$$\omega(i) = [\text{number of unlabeled beads connected (directly bonded) to beads which are still labeled.}] \quad (11)$$

The last characteristic of the labeling that we require is very similar to $\omega(i)$ except it applies to each of the molecules separately. We define $\alpha(i, j)$, $i=1, \dots, N$; $j=1, \dots, l$ as follows:

$$\alpha(i, 1) = 1,$$

$$\alpha(i, l) = 1. \quad (12)$$

For $2 \leq j \leq l-1$, the labels $j, \dots, 1$ on molecule i are erased. Then,

$$\alpha(i, j) = (\text{number of unlabeled beads on molecule } i \text{ connected to labeled beads on molecule } i.) \quad (13)$$

Because the molecules have a simple chain structure, Eq. (13) can be expressed more simply. If the two end beads of molecule i are labeled k_1 , and k_2 , with $k_1 < k_2$, then for $j > 1$

$$\alpha(i, j) = \begin{cases} 2, & \text{if } j \leq k_1, \\ 1, & \text{otherwise.} \end{cases} \quad (14)$$

Now, suppose that a sample of m such structures have been grown. Then, an unbiased estimator of $K_N^{(0)}$ is

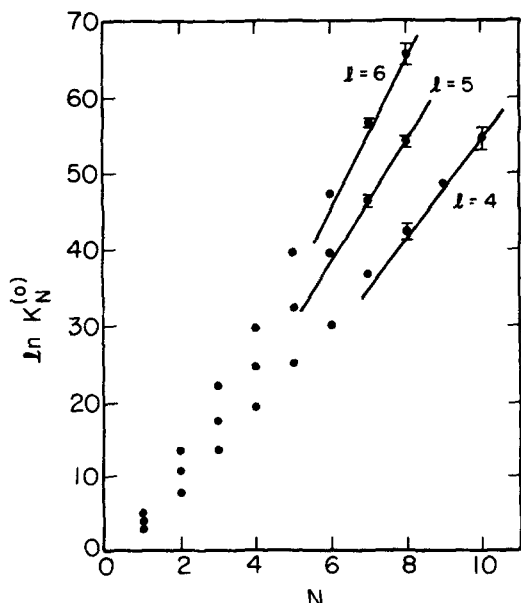


FIG. 3. $\ln K_N^{(0)}$ vs N for the chain molecule aggregates discussed in text. Sample size was 10^3 , error bars shown are twice the change in results found in increasing sample size from 10^2 to 10^3 . The solid lines indicate the asymptotic behavior discussed in the text.

TABLE I. $\ln K_N^{(0)}$ for hard core chain molecule clusters.

$N \backslash l$	4	5	6
1	2.89	3.99	5.09
2	7.87 ± 0.07	10.9 ± 0.1	13.2 ± 0.1
3	13.3 ± 0.1	17.6 ± 0.1	22.1 ± 0.3
4	19.3 ± 0.2	24.9 ± 0.2	30.0 ± 0.3
5	24.9 ± 0.3	32.3 ± 0.3	39.5 ± 0.4
6	30.7 ± 0.5	39.6 ± 0.3	47.3 ± 0.4
7	36.8 ± 0.6	46.9 ± 0.5	56.6 ± 0.9
8	42.3 ± 1.3	54.2 ± 0.6	65.6 ± 1.2
9	49.2 ± 0.7		
10	54.6 ± 1.2		

$$E(K_N^{(0)}) = \frac{1}{m} \sum \left[\prod_{i=1}^{IN} \Omega(i) \right] \prod_{i=1}^N \left\{ \omega^{-1}(i) \left[\prod_{j=1}^l \alpha^{-1}(i, j) \right] \right\}. \quad (15)$$

The sum is, of course, over the value of the summand for each of the structures in the sample. This estimator differs from those discussed previously only by the presence of the $\alpha(i, j)$ factors which reflect the labelings internal to the individual surfactant molecules.

These techniques can be adapted to estimate K_N with nonzero near neighbor interactions. A particularly simple case occurs if all chain elements are of the same type, and thus

$$e^{-U(1, \dots, N)/k_B T} = \begin{cases} 0, & \text{if any elements overlap,} \\ z^b, & \text{if no elements overlap} \\ & \text{and there are } b \text{ near} \\ & \text{neighbor pairs.} \end{cases} \quad (16)$$

Here $z = e^{-\epsilon/k_B T}$ with ϵ a near neighbor interaction energy. Then we define

$$K_N(T) = \sum_b z^b K_{N,b}, \quad b \geq N-1, \quad (17)$$

where the coefficients $K_{N,b}$ are the total numbers of configurations with exactly b bonds, and thus are temperature independent. These coefficients can be estimated from the sample used with Eq. (10), in particular

$$E(K_{N,b}) = \frac{1}{m} \sum_{k=1}^m \delta_{b,k} \left[\prod_{i=1}^{IN} \Omega(i) \right] \prod_{i=1}^N \left\{ \omega^{-1}(i) \left[\prod_{j=1}^l \alpha^{-1}(i, j) \right] \right\}. \quad (18)$$

Here $\delta_{b,k}$ is one or zero, respectively, if the k th structure in the sample has b bonds or not.

These procedures have been used to estimate $K_N^{(0)}$ for $2 \leq N \leq 10$, and $l=4$, and for $2 \leq N \leq 8$ for $l=5, 6$. The results are shown in Fig. 3 and tabulated in Table I. The sample size was taken to be 10^3 . The magnitude of the indicated statistical uncertainties was taken to be twice the change in the estimated $\ln K_N^{(0)}$ upon increasing the sample size from 10^2 to 10^3 . It can be seen that the statistical uncertainties are quite modest. In this regard the three dimensional case appears more favorable to Monte Carlo estimation than the two-dimensional test case treated above. The asymptotic behavior of these quantities was investigated in the standard way. The $K_N^{(0)}$ are expected to vary as $e^{k_1 N + k_0 N^\theta}$ for large N . Here

k_0 , k_1 are constants which vary from system to system and the universal exponent θ is known to be $\theta = 3/2$.³¹ Therefore we examine the Padé approximants for the square of the generating function which yields the $K_N^{(0)}$.²⁸ The poles of the Padé then provide an estimate of e^{k_1} .²⁸ For the three chain lengths studies we found

$$l=4: K_N^{(0)} \sim \exp[-10.1 + (6.8 \pm 0.2)N - 1.5 \ln N],$$

$$l=5: K_N^{(0)} \sim \exp[-8.4 + (8.2 \pm 0.1)N - 1.5 \ln N],$$

$$l=6: K_N^{(0)} \sim \exp[-14.7 + (10.4 \pm 0.1)N - 1.5 \ln N].$$

In each case, the amplitude k_0 was chosen to achieve agreement of the asymptotic form with $K_N^{(0)}$ for the largest N studied. The indicated uncertainties in k_1 do not arise from statistical uncertainties in the determination of the $K_N^{(0)}$, but from the limitation on the size of clusters studied, i.e., the range of N . The estimates of k_1 from the Padé approximation still show a slight drift as N is increased in this range. The indicated error estimate thus reflects the uncertainty in extrapolation to $1/N \rightarrow 0$. Within the stated uncertainty any deviation of k_1 from linearity in l could not be discerned.

IV. CONCLUSION

In this paper, we have established a new Monte Carlo method which provides a direct and unbiased method for estimation of cluster partition functions. The method is a generalization of the technique of inversely restricted sampling. The crucial aspect of this generalization is seen to be a correct statistical accounting of the topological variety possible with branching clusters compared with linear polymers. With this aspect of the problem solved, the technique can be applied to both lattice and continuous space clusters. A secondary object of the paper is to use the new method to study chain molecule clusters associated with simple models of micellar aggregates. The model studied was sufficiently simple that the general form of the results are well known. Nevertheless, the particular results obtained provide a quantitative solution to one aspect of surfactant aggregation phenomena for a well-defined model system. As such they will play a useful role in understanding micellar stability.

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- ¹F. F. Abraham, *Homogeneous Nucleation Theory* (Academic, New York, 1974).
- ²J. J. Burton, in *Modern Theoretical Chemistry* (Plenum, New York, 1977), Vol. 5.
- ³T. L. Hill, *J. Chem. Phys.* **23**, 617 (1955); F. H. Stillinger, *ibid.* **38**, 1486 (1963); H. Reiss and J. L. Katz, *ibid.* **46**, 2496 (1966); D. Chandler and L. R. Pratt, *ibid.* **65**, 2925 (1976); L. R. Pratt and D. Chandler, *ibid.* **66**, 147 (1977); H. P. Gillis, D. C. Marvin, and H. Reiss, *ibid.* **66**, 214, 223 (1977).
- ⁴D. J. McGinty, *Chem. Phys. Lett.* **13**, 525 (1972).
- ⁵D. J. McGinty, *J. Chem. Phys.* **58**, 4733 (1973).
- ⁶J. J. Burton, *J. Chem. Soc. Faraday Trans. 2* **69**, 540 (1973).
- ⁷J. K. Lee, J. A. Barker, and F. F. Abraham, *J. Chem. Phys.* **58**, 3166 (1973). See also N. G. Garcia and J. M. Rorroja, *Phys. Rev. Lett.* **47**, 186 (1981); B. N. Hale and R. C. Ward, *J. Stat. Phys.* (to be published).
- ⁸M. R. Mruzik, F. F. Abraham, D. E. Schreiber, and G. M. Pound, *J. Chem. Phys.* **64**, 481 (1976).
- ⁹W. C. Swope, H. C. Andersen, P. H. Berens, and K. R. Wilson, *J. Chem. Phys.* **76**, 637 (1982).
- ¹⁰M. Rao, B. J. Berne, and M. H. Kalos, *J. Chem. Phys.* **68**, 1325 (1978).
- ¹¹P. J. Rossky, J. B. Dudowicz, B. L. Temke, and H. L. Friedman, *J. Chem. Phys.* **73**, 3372 (1980).
- ¹²S. W. Haan and L. R. Pratt, *Chem. Phys. Lett.* **79**, 436 (1981); **81**, 386 (1981).
- ¹³J. M. Hammett and D. C. Handscomb, *Monte Carlo Methods* (Chapman and Hall, London, 1964), pp. 129, 130.
- ¹⁴J. M. Hammett and K. W. Morton, *J. R. Stat. Soc. B* **16**, 23 (1954).
- ¹⁵F. L. McCrackin, *J. Res. Natl. Bur. Stand. Ser. B* **76**, 193 (1972).
- ¹⁶R. L. Coldwell, *Phys. Rev. A* **7**, 270 (1973).
- ¹⁷J. P. Valleau and G. M. Torrie, in *Modern Statistical Mechanics* (Plenum, New York, 1977), Vol. 5, pp. 171-172.
- ¹⁸F. H. Stillinger, *Science* **209**, 451 (1980).
- ¹⁹B. H. Hale and P. L. M. Plummer, *J. Chem. Phys.* **61**, 4012 (1974).
- ²⁰C. H. Bennett, *J. Appl. Phys.* **43**, 2727 (1972).
- ²¹D. Turnbull and M. H. Cohen, *Nature (London)* **203**, 964 (1964).
- ²²See *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1974), Vol. 3.
- ²³W. F. Lunnon, in *Computers in Number Theory*, edited by A. O. L. Atkin and B. J. Birch (Academic, New York, 1971).
- ²⁴M. F. Sykes and M. Glen, *J. Phys. A* **9**, 87 (1976).
- ²⁵J. W. Essam, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1972).
- ²⁶H. Müller-Krumbhaar, in *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer, New York, 1979).
- ²⁷D. Stauffer, *Phys. Rev. Lett.* **41**, 1333 (1978).
- ²⁸D. S. Gaunt and A. J. Guttmann, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1974).
- ²⁹C. Domb, *J. Phys. A* **9**, L141 (1976).
- ³⁰D. S. Gaunt, M. F. Sykes, and H. Ruskin, *J. Phys. A* **9**, 1899 (1976).
- ³¹G. Parisi and N. Sourlas, *Phys. Rev. Lett.* **46**, 871 (1981).