Communications to the Editor

A Response to Mansfield's Paper "Concentrated, Semiflexible Lattice Chain Systems and Criticism of the Scanning Method"

Hagai Meirovitch

Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida 32306-4052

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In a recent paper,[1] Mansfield has studied phase transitions in extremely dense multiple polymer systems. Using his method,[2] he simulated 62 self- and mutual-avoiding chains contained in a 250 × 250 "box" on a square lattice and 64 chains in a 40×40×40 box on a simple cubic lattice. The chains of length $900 \leq N \leq 1100$ steps fully occupy the box. The entropy was calculated by thermodynamic integration over the specific heat. The author used this method only after failing to obtain reasonable results with the "hypothetical scanning method" (HSM) of Meirovitch, which motivated him to check the general validity of the scanning method and HSM. He reached the conclusion that for systems with long-range interactions or correlations, a complete future scanning is necessary, which means that these methods can be applied *reliably* only to very small systems. In this communication I respond to these claims and show that (1) the scanning methods is an *exact* procedure even if partial scanning is applied, (2) HSM (and its variant, the local states method) is approximate but has been found to lead to very accurate results for a variety of relatively large models, and (3) both methods are not suitable for treating Mansfield's highly dense many chain systems mentioned above.

Let me discuss first the scanning method,[3] and for simplicity, as applied to a single self-avoiding walk (SAW) of N steps on a square lattice. The procedure consists of two stages; the first was described almost correctly in ref 1, the second was ignored. A SAW is grown step-by-step; at step k, $k-1$ directions ν ($\nu = 1$, 4) have already been constructed, and the value of ν_k should be determined. For that one enumerates *all* the possible continuations of the chain in b future steps that start from ν; this number is proportional to the transition probability $p(\nu, k)$ with which ν is determined by a random number. Since for a long chain only part of the future can be scanned, the chain might get trapped in a dead end; in this case it is discarded, and a new one is started. The attrition ratio, $p_{\text{attr}} = n_{\text{succ}}/n_{\text{start}}$, is a measure for the efficiency of the method to generate n_{succ} N-step SAWs from n_{start} starting ones; p_{attr} increases with increasing b and decreases exponentially with increasing N. The construction probability $P_i(b)$ of SAW i is

$$P_i(b) = (p_{\text{attr}})^{-1} P_i^0(b) = (p_{\text{attr}})^{-1} \prod_{k=1}^{N} p(\nu_k, b) \qquad (1)$$

In practice $P_i(b)$ is *always* biased but can be improved systematically by increasing the scanning parameter b; $P_i(b)$ becomes exact, i.e. it is equal to the Boltzmann probability P_i^{B}, for a complete future scanning (then $p_{\text{attr}} = 1$). Notice that P_i^{B} is the same for all the SAWs, while $P_i(b)$ is larger for the compact SAWs than for the open ones. A *lower bound* of the exact entropy S is the functional $S(b)$,

$$S(b) = -k_{\text{B}} \sum_i P_i(b) \ln P_i(b) \qquad (2)$$

where k_{B} is the Boltzmann constant. $S(b)$ is estimated from the sample by $\bar{S}(b)$,

$$\bar{S}(b) = -k_{\text{B}} n_{\text{succ}}^{-1} \sum_{t=1}^{n_{\text{succ}}} \ln P_{i(t)}(b) \qquad (3)$$

where $i(t)$ is SAW i obtained at time t of the process. This is the first stage of the scanning method, which was described correctly by Mansfield,[1] except for his ignoring p_{attr}.

If only this part of the method existed, Mansfield would have been right in his criticism that practically the method is always approximate. However, as has been shown by Rosenbluth,[4] the bias can be removed *rigorously* in stage II by importance sampling, a fact that has been completely ignored by Mansfield. Thus, an estimation $\bar{S}$ for the correct S is

$$\bar{S} = k_{\text{B}} \ln[n_{\text{start}}^{-1} \sum_{t=1}^{n_{\text{succ}}} 1/P_{i(t)}^0(b)] \qquad (4)$$

Notice that in eq 4 the contribution of the compact SAWs is small due to their small $1/P_i^0$ factors, while the low probable open SAWs are associated with large such factors and therefore dominate the summation. Obviously, if the sample is highly biased and does not include the open chains (that are the most probable in a Boltzmann sample), this compensation mechanism would fail and the entropy will remain biased. However, in principle S can always be approached by increasing b, the sample size, or both, in contrast to eq 3 that leads to the approximate $S(b)$ for any sample size. Since the bias and the attrition increase with chain length, the method is practical for SAWs (in the bulk) of up to $N \sim 700$ and 1500 on a square and a simple cubic lattice, respectively. It has been applied successfully to a wide range of models such as polypeptides, self-attracting SAWs, trails, and random walks in the bulk and in the presence of an adsorbing surface; for the last model random walks of up to $N = 48\,000$ were studied[5] (references about these applications are cited in ref 6; for a more complete discussion about the efficiency of the method, see ref 3b). In all these studies the range of scanning ($b \leq 10$) is considerably smaller than the range of interactions which includes the whole chain.

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The scanning method has also been applied to a model of l SAWs enclosed in a "box" on a square lattice.[7] The chains are added gradually to an initially empty box, where each is grown by a scanning procedure, as described above. Here one calculates the *system* probability, which is the product of the construction probabilities of the individual chains. However, at step k of the construction of chain j, the "future" consists not only of the $N - k + 1$ undetermined steps of j, but also of all the possible configurations of the as yet ungrown $l - j$ chains in the vacant sites of the box. For a dilute system the chains do not "feel" each other and therefore increasing b will always improve the approximation of stage I, as for a single chain. On the other hand, for dense systems, increasing b might even worsen the approximation. For example, if the first chain added to the box is built with a large value of b, the chain is likely to be much more open than a typical chain in a dense system; therefore $b = 1$, which leads to the most compact chain, might be the best choice. For the last chain added to the box b should be maximal. Thus, a scanning build-up procedure based on gradual increase of b is probably the most efficient procedure, i.e. it leads to the largest system entropy $S^l(b_1,b_2,...)$, and hence requires a relatively small sample size for the importance sampling procedure in stage II (see Appendix B in ref 7a). On the square lattice, mostly because of strong attrition, the method was found to be practical for densities of up to 0.6 and $N \leq 50$. Therefore it would be impossible to construct systems of density 1 and $N \sim 1000$, as those studied by Mansfield.

Mansfield also discusses implementation of the scanning method to spin systems and provides results for a very simplified model of two rows of Ising spins. This system can be treated exactly by using eq 1, since one has to scan only a column of two spins at each step. Indeed, the entropy derived from this "proper scanning" fits very well the exact solution (Figure 7 of ref 1). In order to demonstrate the well-accepted fact[4] that using eq 1 for incomplete scanning leads to approximate results, Mansfield applies a "naive" scanning procedure, which treats only one spin at a time. As expected, he finds a good fit only at high temperatures (where the correlations are short range). Obviously, in order to obtain the correct results over the whole range of temperatures, Mansfield should have calculated the free energy by eq 4 (where 1 is replaced by a Boltzmann factor) for large enough samples, rather than by eq 1. It should be noted that the scanning method was originally developed for the much more complex 2D Ising model.[8] Thus, spins are added to an empty lattice step-by-step, line-by-line, as suggested by Alexandrowicz[9] using approximate transition probabilities that can be improved systematically. In this study, however, only stage I was applied, since it led to sufficiently accurate results even at the critical temperature T_c, and applying importance sampling (stage II), which requires significantly larger samples, was considered unnecessary. For an $L \times L$ lattice ($L = 120-150$) at temperatures $K = J/k_BT = 0.43$ and $K_c = 0.440\,68$ and 0.455 (J is the spin interaction) the scanning results for the free energy overestimate the correct values by only 0.003, 0.006, and 0.0001%, respectively. I am not aware of more accurate computer simulation results for the free energy of this model. It should be pointed out that in ref 8 the future scanning was carried out over a rectangle of 14×28 sites, while at K_c the range of correlations includes the whole lattice of 120×120. In summary, the scanning method is an exact procedure which can be applied efficiently, even with a limited scanning range, to relatively large systems that are characterized by long-range interactions or correlations. However, for dense many chains it is much less efficient than Mansfield's[2] or Pakula's[10] dynamical Monte Carlo procedures; this price in efficiency is compensated for by the ability of the scanning method (in contrast to other methods) to provide the *absolute* entropy.

HSM[7b,11,12] enables one to extract the entropy *approximately* from a sample simulated by *any* technique. It is based on the fact that two samples in equilibrium generated by different methods are equivalent, in the sense that they lead to the same estimates (within the statistical error) of average properties such as the entropy.[13] Therefore one can assume that a given sample of SAWs (produced correctly with P_i^B) has rather been generated with the scanning method. This enables one to reconstruct for each step the (hypothetical) scanning transition probabilities, where their product leads to the approximate chain probability $P_i^0(b)$ (eq 1) and to an approximation S^A for the entropy,

$$S^A = -k_B \sum P_i^B \ln P_i^0(b) \qquad (5)$$

S^A is an upper bound for S; it can be improved (i.e. decreased) systematically by increasing b. One can define another approximation S^B (for details see ref 11) which can be shown rigorously to satisfy $S^B \leq S^A$. However, for all the systems studied thus far we found that also $S^B \leq S$, where the deviations from S of S^A and S^B are approximately the same; therefore their average S^M becomes a better approximation than each one of them individually, and S^M converges rapidly to S as b is increased. For example, for SAWs of $N = 79$ on a square lattice $S^M = 0.1035(3)$, 0.110 81(3), and 0.110 89(2) for $b = 1$, 4, and 7, respectively (again, $b = 7$ is much smaller than N);[11] the last estimate is equal to the correct value obtained by the direct Monte Carlo method[14] (notice, that only because of the inefficiency of the latter method was N limited to 79). In order to show the approximate nature of HSM (which is, however, a well-accepted fact), Mansfield applies it with partial scanning to the $N \times 2$ Ising model. However, the *naive hypothetical* scanning results (for S^A, Figure 7 of ref 1) are quite accurate over a relatively large range of temperatures, which demonstrates the efficiency of HSM. Obviously, these results can still be improved, even within the framework of this limited scanning, by calculating S^M rather than S^A. It should be pointed out that typically *several* approximations (rather than one) for S^A, S^B, and S^M are calculated, and their convergence enables one to determine the correct entropy with high accuracy.

S^A was also calculated by Meirovitch for the simple cubic Ising model[15] of $L = 25$ and 30 (S^B was not known at that time), leading to 0.5856(1), 0.552(2), and 0.5052(3) for $K = 0.213$ and $K_c = 0.221\,69$ and 0.226, respectively, where the corresponding best series expansion estimates are 0.5856, 0.558, and 0.497. Highly accurate results for S^M were obtained for the square Ising lattice using the "local states method"[13,16] with which the transition probabilities are determined by the b spins preceding spin k, rather than by the future ones. For $L = 100$ and $K = 0.4$ the free energy obtained is F^M

$= -0.879\ 37(1)$ vs the exact value $F = -0.879\ 36$; at K_c ($L = 40$) $F^M = -0.9300(3)$ vs $F = -0.9301$. For many SAWs on the square lattice[7b] the results of S^M were found to deviate from those obtained by the scanning method (eq 4) (which are considered to be exact within the error bars) by no more than 0.3%.

It should be pointed out that while the *statistical* reliability of S^A increases with increasing system size, S^B becomes less reliable statistically, with efficiency comparable to that of importance sampling (eq 4). Therefore, the entropy of Mansfield's systems cannot be estimated reliably by S^M while S^A is expected to lead to significant overestimation of S. This conclusion is very clear from ref 7, and it is therefore surprising that Mansfield has decided to apply HSM to his systems in the first place. He calculated several approximations for S^A for increasing values of b (m in his notation), without realizing that his results increase, i.e. *worsen*, with increasing b (Figure 9 of ref 1), which means that his extrapolation to infinite b is meaningless. Defining better approximations for S^A would require the use of several values of b, as discussed previously for the scanning method. Finally, it should be noted that it was found[17] that differences of S^A can provide reliable estimates for differences in S, even in cases where S^A deviates considerably from S. The results for the simple cubic lattice demonstrate approximately this behavior. In summary, HSM is not applicable to highly dense many chain systems; however, it has led to extremely accurate results for a variety of relatively large systems such as single chains, nondense many chain models, and Ising models. Therefore, Mansfield's conclusion, that the method is not trustworthy for large systems with long-range interactions of correlations, is unwarranted.

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