Methods for estimating entropy with computer simulation: the simple cubic Ising lattice

1983 J. Phys. A: Math. Gen. 16 839

(http://iopscience.iop.org/0305-4470/16/4/020)

J. Phys. A: Math. Gen. **16** (1983) 839–848. Printed in Great Britain

Methods for estimating entropy with computer simulation: the simple cubic Ising lattice

Hagai Meirovitch

Chemical Physics Department, Weizmann Institute of Science, Rehovot 76100, Israel

Received 4 March 1982

Abstract. An approximate method for estimating entropy with computer simulation, suggested recently, is applied here, together with a new method, to the Metropolis Monte Carlo (MC) simulation of the simple cubic Ising lattice. Beyond the critical temperature T_c, the accuracy of our best results for the entropy and the free energy is estimated to be better than 0.07% and 0.05% and at T_c itself, it is approximately 1% and 0.2% respectively. These results are in very good agreement with results obtained with the 'stochastic models' method, which is a computer simulation technique, alternative to the conventional MC, and with series expansion estimates. Our results for the entropy are significantly more accurate than results obtained with the commonly used reversible thermodynamic integration.

1. Introduction

An approximate method for estimating entropy with computer simulation techniques has been suggested recently (Meirovitch 1977a) and applied very successfully to the Metropolis Monte Carlo (MC) simulation (Metropolis *et al* 1953, Fosdick 1963) of the square lattice gas model (Meirovitch and Alexandrowicz 1977b) and the hard-square lattice gas (Meirovitch 1983). The method is based on an approximate formula for the entropy in which the entropy is expressed as a function of the frequency of occurrence of certain local states. These frequencies are calculated from a *single* MC run, which makes the method substantially more efficient than the commonly used reversible thermodynamic integration (Hansen and Verlet 1969). Also, in contrast to the 'multistage sampling' (Valleau and Card 1972) and Salsburg's method (Salsburg *et al* 1959), the accuracy of our method improves with increasing system size. The method is also more accurate than other methods for estimating entropy (Alexandrowicz (1976), and methods reviewed in Binder (1979)).

The formula for the entropy and the definition of the local states are based on the concepts of the stochastic models (SM) method, which is a computer simulation technique independent of the commonly used MC procedure (Alexandrowicz 1971, 1972, Meirovitch and Alexandrowicz 1977a). Understanding these concepts is therefore essential for applying our method to various systems. So far it has been applied to two-dimensional models only. In the present work we extend it to the simple cubic (SC) Ising lattice. We test several sets of local states, which represent different approximations for the entropy, in the vicinity of the critical temperature T_c and at T_c itself. The results are compared with MC results for the entropy obtained by reversible thermodynamic integration (Binder 1972), with results obtained by the SM

method (Meirovitch and Alexandrowicz 1977a) and with series expansion estimates. We also develop and test a new method for estimation of the entropy and discuss its advantages. This method is based on a new formulation of the SM method recently suggested (Meirovitch 1982).

2. Theory

2.1. The simple cubic Ising lattice

Consider a SC lattice with $N = L \times L \times L$ sites where at each site k a spin variable σ_k is defined, $\sigma_k = \pm 1$. Neighbour spins m and l interact with energy $-J\sigma_m\sigma_l$ ($J > 0$) and the microscopic energy E_i of lattice configuration i is therefore

$$E_i = -J \sum_{kl} \sigma_k \sigma_l \tag{1}$$

where k, l denote nearest-neighbour spins. The Boltzmann probability P_i^{B} of configuration i is given by

$$P_i^{\mathrm{B}} = Z^{-1} \exp(-E_i/k_{\mathrm{B}}T) \tag{2}$$

where Z is the partition function, k_{B} the Boltzmann constant and T the absolute temperature. The average energy can be estimated by sampling n configurations with P_i^{B} and calculating E_n

$$E_n = n^{-1} \sum_{t=1}^{n} E_{i(t)} \tag{3}$$

where $i(t)$ is configuration i obtained at time t of the process.

2.2. Approximate formulae for the entropy

Two approximate formulae for the entropy, based on the so-called local states, have been derived for the square Ising lattice (Meirovitch 1977a). These formulae are generally valid, but a suitable set of local states should be defined for each system. Let us now briefly describe the SM method procedure, as applied to the SC lattice, and this will enable us to define the particular sets of local states for this model and obtain the two formulae. With this method (Alexandrowicz 1971, Meirovitch and Alexandrowicz 1977a) a configuration is obtained by filling an initially empty lattice with spins with the help of a model stochastic process. At the kth step of the process, sites $k' = 1 \ldots k-1$ have already been filled with spins and the spin orientation at site k should be determined. It can be shown (Meirovitch 1982) that the *exact* transition probability (TP) for σ_k depends on *all* the spins of the surface between the filled and the empty regions of the lattice. This surface (illustrated in figure 1) consists of the as yet 'uncovered' spins of layer $l-1$ and the spins of layer l. Approximate TP can be defined by taking into account a limited number of surface spins, neighbours to site k. For example, as a first approximation one would consider only the three nearest-neighbour spins to site k on sites $k-1$, $k-L$ and $k-L^2$ (see figure 1). These three spins define $m = 2^3 = 8$ distinct local states which are labelled I. One can also define a wider set of local states $I,+$ and $I,-$ by also taking into account the two possible spins at site k, $\sigma_k = 1$ and $\sigma_k = -1$ respectively. Two TP $p_x(+|I)$ and $p_x(-|I)$,

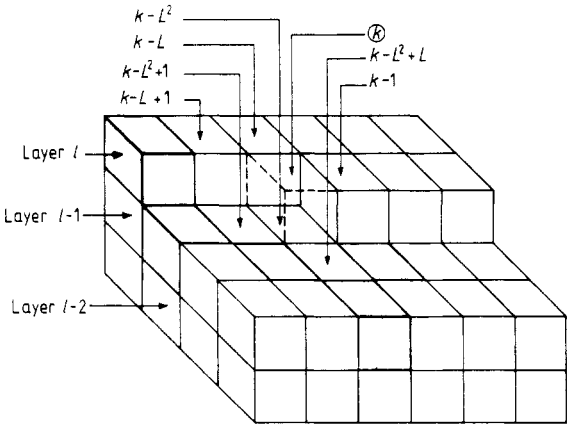

Figure 1. A diagram illustrating the surface between the filled and empty regions of the simple cubic Ising lattice at step k of the SM method construction. The small cubes denote lattice sites which have already been filled with spins in the previous steps of the process. The site to be filled, k, is denoted by a cube drawn with broken lines. The shaded cubes denote lattice sites with a distance of three lattice bonds (measured on empty lattice sites) from site k.

for fixing $+1$ or -1 respectively, correspond to each local state I, and they also depend on a set of parameters $\boldsymbol{x}$. The spin at site k is determined by a lottery according to $p_{\boldsymbol{x}}(+|I)$, and hence the probability $P_i(\boldsymbol{x})$ of lattice configuration i constructed with this process is given by the product of the N sequential TP with which the N spins have been chosen. The TP define therefore a probability distribution on phase space and hence, a free energy functional $F(\boldsymbol{x})$ can also be defined.

With the SM method, the 'best' probability distribution and free energy $F(\boldsymbol{x}^*)$ are obtained by minimising $F(\boldsymbol{x})$ with respect to $\boldsymbol{x}$ where $\boldsymbol{x}^*$ is the optimal set of parameters. According to the minimum free energy principle, $F(\boldsymbol{x}^*)$ is never smaller than the true free energy F, defined with the Boltzmann probability (equation (2)). In this context, it should also be pointed out that F has zero fluctuation, i.e.

$$\langle \Delta^2 F \rangle = 0, \tag{4}$$

whereas $\langle \Delta^2 F(\boldsymbol{x}) \rangle$ is generally larger than zero (where the same notation $\langle\,\rangle$ is used here for the statistical averages with P_i^{B} and $P_i(\boldsymbol{x})$). However, a strong positive correlation has been found between $F(\boldsymbol{x})$ and $\langle \Delta^2 F(\boldsymbol{x}) \rangle$ (Meirovitch and Alexandrowicz 1976) which will be used later as an optimisation criterion.

The fact that $P_i(\boldsymbol{x}^*)$ is provided by the SM procedure enables one to derive two general formulae for the entropy (Alexandrowicz 1971, Meirovitch 1977a),

$$S/k_{\mathrm{B}}N \cong \sum_{I=1}^{m} \nu_{I,+} \log p(+|I) + \nu_{I,-} \log p(-|I), \tag{5}$$

$$S/k_{\mathrm{B}}N \cong \sum_{I=1}^{m} \nu_{I,+} \log(\nu_{I,+}/\nu_I) + \nu_{I,-} \log(\nu_{I,-}/\nu_I), \tag{6}$$

$$\nu_I = \nu_{I,+} + \nu_{I,-}. \tag{7}$$

In these equations m denotes the number of local states I and ν_I, $\nu_{I,+}$ and $\nu_{I,-}$ stand for the frequencies of occurrence of local states I, $I,+$ and $I,-$ respectively. In

equation (5), $p(+|I)$ and $p(-|I)$ denote the optimal set of TP. In equation (6), however, these TP are expressed in terms of the ν's which are a typical property of the lattice at equilibrium. In this sense, equation (6), although derived on the basis of the SM method considerations, constitutes a general expression for the entropy. We shall simulate the SC Ising lattice with the MC procedure, estimating $\nu_{I,+}$ (and $\nu_{I,-}$) by $\bar{\nu}_{I,+}$ from a sample of n configurations,

$$\bar{\nu}_{I,+} = (nN)^{-1} \sum_{t=1}^{n} N_{I,+}[i(t)] \tag{8}$$

where $N_{I,+}[i(t)]$ is the number of times the local state $I,+$ appears in configuration i sampled at time t. The entropy is then calculated by substituting the $\bar{\nu}$'s in equation (6). Alternatively, we will show that a set of approximate TP can be calculated independently of the MC run and thus the entropy can also be estimated with equation (5).

2.3. Definition of local states

In this section, we define four sets of local states, which define four approximations for the entropy via equations (6) and (7). The first set (set I, which consists of the three nearest-neighbour spins to site k), has already been described in § 2.2. In addition to these three spins, set II also takes into account the three next-nearest-neighbour spins to site k, on sites $k-L+1$, $k-L^2+1$ and $k-L^2+L$ (see figure 1); it consists therefore of $m=2^6=64$ local states of type I. Set III also takes into account the five spins with a distance of three lattice bonds from site k (measured on empty lattice sites). These sites are represented by shaded cubes in figure 1. For this set $m=2^{11}=2048$. Set IV also considers, in an approximate way, the ten spins, with a distance of four lattice bonds, from site k. Instead of taking into account all their 1024 possible local states, we define only three local states according to whether their magnetisation g satisfies $-10 \leqslant g < -2$, $-2 \leqslant g \leqslant 2$ or $g > 2$. Therefore, for this set $m = 2048 \times 3 = 6144$.

2.4. Definition of TP for equation (5)

A new method has recently been developed for calculating approximate TP for the SM procedure of the square Ising lattice which depends on a mean field parameter A only (Meirovitch 1982). Similar TP can also be defined for the SC lattice. Assume, again, that we are in the kth step of the SM procedure, and let us consider the eleven spins that define set III. 'Above' these spins we define a 'box' of empty lattice sites in the following way: 'above' site k we include in the box the empty sites $k+L^2$, $k+2L^2$ and $k+3L^2$, which reside on layers $l+1$, $l+2$ and $l+3$, respectively. In the same way, three empty sites for the box are defined above each of the other four spins of layer l ($k-1$, $k-L$, $k-L+1$ and $k-L+2$). However, above the six spins of layer $l-1$ one should also include in the box empty sites which belong to layer l, and therefore $5\times3+6\times4=39$ empty lattice sites define this box. The TP for having a spin σ at site k is proportional to the conditional partition function $Z(\sigma, I, A)$ (see Meirovitch 1982, § 3.2),

$$Z(\sigma, I, A) = \sum_{\text{all } j} \exp\{(k_B T)^{-1}[E(j)+E(I, J_j)+E(\sigma, \sigma')+E(j, A)]\} \tag{9}$$

where j runs over all the possible spin configurations of the empty box which can be obtained in future steps of the process. These as yet undetermined spins should be distinguished from the $k-1$ already fixed ones, and therefore we call them the future spins. $E(j)$ is the microscopic energy of future box configuration j. J_j denotes the configuration of the eleven future spins of the bottom of the box. J_j interacts with I and $E(I, J_j)$ is the interaction energy. $E(\sigma, \sigma')$ denotes the interaction energy of σ with its six nearest-neighbour σ' and $E(j, A)$ stands for the interaction energy of the future spins located on the surface of the box with the mean field parameter A. (A future spin σ of the surface contributes a factor $-JA\sigma$ to $E(j, A)$ where J is the interaction constant.) The normalised approximate TP is

$$p(\sigma, I, A) = Z(\sigma, I, A)/[Z(\sigma, I, A) + Z(-\sigma, I, A)]. \tag{10}$$

This set of TP (which is independent of the MC simulation) enables one to estimate the entropy using equation (5). However, one should also optimise the parameter A, and this cannot be achieved with the minimum free energy principle criterion since the energy (in contrast to the SM method) is independent of A. We rely therefore on the strong positive correlation found between $F(A)$ and $\langle \Delta^2 F(A) \rangle$ (Meirovitch and Alexandrowicz 1976) and seek the optimal parameter A^* which minimises $\langle \Delta^2 F(A) \rangle$. In practice, five sets of TP with different values of A are calculated prior to the MC run. $\langle \langle \Delta^2 F(A) \rangle \rangle$ is estimated from the simulation and thus A^* can be determined. To save computer time, a crude value of A^* is initially determined from a short MC run.

Estimation of the entropy might be more practical with equation (5) than with equation (6) for systems with many degrees of freedom, which require a huge computer memory for storing the vector of the ν's. In that case, computing the TP (equation (10)) in each step of the MC run requires less computer memory; however, much more computer time is needed.

3. Results and discussion

Using the 'symmetric' Metropolis procedure with periodic boundary conditions (Yang 1963), we have carried out MC runs of $n = 10^4$ lotteries per spin (lps) at several reciprocal temperatures $K = J/k_B T$, above and below the critical temperature K_c; lattice sizes of $L = 30$ and $L = 25$ have been used close to and far from K_c, respectively. At the best estimate for the critical temperature $K_c = 0.22169$ (Sykes *et al* 1972), we have performed longer MC runs, of $n = 15000$ lps, for smaller lattices, of size $L = 16$ and $L = 20$. In order to exclude the relaxation to equilibrium (from initial random distribution), the averaging was started after 1000 lps. The MC results for the entropy S, the free energy F and the energy E_{MC} are summarised in table 1, together with results obtained with the SM method (Meirovitch and Alexandrowicz 1977a) and with series expansion techniques. E_{MC} has been calculated with equations (1) and (3) and S_1–S_4 with equations (6) and (7), using the sets of local states I–IV (defined in § 2.3), respectively. F_i, $1 \leqslant i \leqslant 4$, are the corresponding free energy estimates

$$F_i = KE_{MC} - S_i. \tag{11}$$

In the hot region ($K < K_c$) the series expansion results are based on an approximate formula, of relatively high accuracy, for the specific heat (Sykes *et al* 1972), and therefore will be used here as references for estimating the accuracy of the MC results.

Table 1. MC results (per spin) for the entropy S (per k_B), the free energy F (per k_BT) and the energy E (per J) for the simple cubic Ising lattice at reciprocal temperatures $K = J/k_BT$. $K_c = 0.22169$ is the best series expansion estimate for the critical temperature (Sykes *et al* 1972). E_{MC} has been obtained with equations (1) and (3). S_i, $1 \leq i \leq 4$, are four approximations for the entropy obtained with equations (6) and (7) and F_i, $1 \leq i \leq 4$, are the corresponding free energy results (equation (11)). S_p has been obtained with equation (5) by optimising the parameter A and F_p is the corresponding free energy. E_{SM}, S_{SM} and F_{SM} have been obtained with the SM method (Meirovitch and Alexandrowicz 1977a). E_{SER}, S_{SER} and F_{SER} have been obtained by performing a thermodynamic integration over C/T where C is the series expansion estimate for the specific heat. For $K > K_c$, C is obtained by a Padé approximant (Baker 1963) and for $K < K_c$ with an approximate formula (Sykes *et al* 1972). The series expansion results at K_c are taken from Sykes *et al* (1972). L is the lattice size. The statistical error of the last decimal place appears in parentheses e.g., $0.561(2) = 0.561 \pm 0.002$.

K	0.210 $L = 25$	0.213 $L = 25$	0.217 $L = 30$	0.221 69 $L = 16$	0.221 69 $L = 20$	0.226 $L = 30$	0.230 $L = 25$	0.235 $L = 25$
S_1	0.5973 (1)	0.5919 (1)	0.5835 (1)	0.560 (2)	0.561 (2)	0.5097 (3)	0.4730 (2)	0.4347 (1)
S_2	0.5927 (1)	0.5867 (1)	0.5778 (1)	0.553 (2)	0.553 (2)	0.5060 (3)	0.4702 (2)	0.4327 (1)
S_3	0.5919 (1)	0.5859 (1)	0.5767 (1)	0.550 (2)	0.552 (2)	0.5054 (3)	0.4698 (2)	0.4324 (1)
S_4	0.5917 (1)	0.5856 (1)	0.5764 (1)	0.550 (2)	0.552 (2)	0.5052 (3)	0.4697 (2)	0.4324 (1)
S_p	0.5921 (1)	0.5860 (1)	0.5769 (1)	0.550 (2)	0.552 (2)	0.5055 (3)	0.4699 (2)	0.4325 (1)
S_{SM}	0.592	0.586	0.579	0.554	0.557	0.506	0.467	0.431
S_{SER}	0.5916	0.5856	0.5760	0.558	0.558	0.497	0.465	0.429
$-F_1$	0.7730 (1)	0.7762 (1)	0.7810 (1)	0.789 (1)	0.788 (1)	0.7877 (2)	0.7914 (1)	0.7979 (1)
$-F_2$	0.7684 (1)	0.7711 (1)	0.7752 (1)	0.781 (1)	0.781 (1)	0.7839 (2)	0.7886 (1)	0.7959 (1)
$-F_3$	0.7676 (1)	0.7703 (1)	0.7741 (1)	0.780 (1)	0.779 (1)	0.7833 (2)	0.7882 (1)	0.7956 (1)
$-F_4$	0.7674 (1)	0.7700 (1)	0.7738 (1)	0.779 (1)	0.779 (1)	0.7832 (2)	0.7882 (2)	0.7956 (1)
$-F_p$	0.7677 (1)	0.7704 (1)	0.7744 (1)	0.779 (1)	0.779 (1)	0.7835 (2)	0.7884 (1)	0.7957 (1)
$-F_{SM}$	0.767 28	0.769 82	0.773 34	0.777 82	0.777 77	0.782 61	0.787 88	0.795 22
$-F_{SER}$	0.767 39	0.769 94	0.773 49	0.777 87	0.777 87	0.782 48	0.787 82	0.795 20
$-E_{MC}$	0.8366 (2)	0.866 (1)	0.910 (1)	1.03 (1)	1.025 (5)	1.230 (2)	1.385 (1)	0.545 (1)
$-E_{SM}$	0.836	0.863	0.897	1.006	0.997	1.226	1.393	1.550
$-E_{SER}$	0.8369	0.8653	0.910	0.992	0.992	1.262	1.403	1.559

For $K = 0.210$ and $K = 0.213$, S_4 equals S_{SER} and F_4 equals F_{SER} within the statistical errors 0.017% and 0.013%, respectively. These errors therefore measure the accuracy of S_4 and F_4. For $K = 0.217$ the accuracy of S_4 and F_4 is determined by their deviation—0.07% and 0.04%, respectively, from the corresponding series expansion values. In the cold region ($K > K_c$) the series expansion results have been obtained from a Padé approximant for the specific heat (Baker 1963). However, they seem to become inaccurate close to K_c, which can be deduced from the significantly lower values obtained for E_{SER} than for both E_{MC} and E_{SM} (the largest deviation is ~3% at $K = 0.226$), and also from the fact that $F_{SER} > F_{SM}$, which means that F_{SER} is less accurate than F_{SM} (since always $F_{SM} \geqslant F_{Exact}$). Therefore, in the cold region, we shall not determine the accuracy of the MC results by comparing them with the series expansion estimates, but in a different way. It should be pointed out that for all temperatures S_i decreases monotonically with increasing i. In the cold region, S_3 equals S_4 within the statistical error. Therefore, if we assume that a better approximation for S would not lower the entropy to a detectable extent (i.e. beyond the statistical error), the statistical error can constitute a measure for the accuracy of S_4. According to this criterion, the accuracy of S_4 is better than 0.03%, 0.05% and 0.06% for $k = 0.235$, $k = 0.230$ and $k = 0.226$ respectively. A similar consideration can be used for estimating the accuracy of F_i (which increases monotonically with i), and we obtain 0.02%, 0.03% and 0.03% for temperatures 0.235, 0.230 and 0.226, respectively. The results for S_4 and F_4 therefore have comparable accuracy in the hot and the cold regions. It should be pointed out that the results for S_4 in the cold region are also comparable in accuracy to results obtained with the same method in the cold region of the square Ising lattice (Meirovitch 1977a), which supports the present estimation of the accuracy. It should also be noted that the entropy of relatively small SC lattices ($L \leqslant 12$) with 'free' boundary conditions has been calculated by Binder (1972) by thermodynamic integration of the MC estimates for the specific heat and the energy. From the scale of his graph, it can be deduced that the error is not smaller than 2%, which is significantly larger than our error. It should be pointed out that, in general, our method is also much more efficient since the entropy is estimated from a *single* MC run, whereas for a thermodynamic integration many MC runs, at different temperatures, are required. In particular, in the critical region, where the specific heat diverges, more and longer runs are necessary.

It is more difficult to determine the accuracy of the results obtained at K_c since the series expansion values describe the thermodynamic limit, whereas the SM and the MC methods simulate relatively small lattices with different boundary conditions. It should be noticed however, that, as expected, both S_{SM} and S_{MC} become closer to S_{SER} when lattice size is increased from $L = 16$ to $L = 20$, and the same tendency occurs for E_{SM}, E_{MC} and E_{SER}. For $L = 20$, S_4 deviates from S_{SER} by ~1% and F_4 equals F_{SER}, within the statistical error, 0.13%. Obviously one would expect better agreement with the series expansion estimates by increasing lattice size and using larger (i.e. better approximations) sets of local states.

It should be pointed out that the statistical error of F_{SM} is about an order of magnitude smaller than that of F_i, $1 \leqslant i \leqslant 4$. This stems from the fact that F_{SM} (but not F_i) is a result of a minimisation procedure which also minimises its fluctuation (Meirovitch and Alexandrowicz 1976, see discussion in § 2.2).

It is of interest to remark that even S_1, the crudest approximation, provides relatively good estimates for the entropy which are larger than the corresponding values of S_4 by 0.5%–0.9% for $K > K_c$, and 0.9%–1.3% for $K < K_c$. The results for

S_2 and S_3 are already much closer to those of S_4. The results for S_3 and S_p (which both are based on set III of local states) are always equal, within the statistical error. Within this error, we found S_p and F_p to be insensitive to relatively large variation of the mean field parameter A, and therefore we were able to minimise the fluctuations of F_p with respect to A from a single MC run only.

4. Conclusions

We have tested several sets of local states for the SC lattice which define by equation (6) different approximations for the entropy. For $K \neq K_c$ we estimate the accuracy of our best approximation for the entropy and the free energy to be better than 0.07% and 0.04%, and at K_c approximately 1% and 0.2% respectively. These results are significantly more accurate than results obtained with reversible thermodynamic integration (Binder 1972).

For $K > K_c$ it is argued that our results for S are more accurate than series expansion estimates. We have also tested a new method for estimating the entropy, based on equation (5), which led to the same accuracy as our first method.

Our accurate methods for estimating the entropy and the free energy can be very useful for determining the transition point in MC studies of first-order phase transitions, where hysteresis loops occur (Meirovitch 1977b, Landau and Binder 1978). We also expect our methods to lead to very accurate estimates for the pressure of three-dimensional lattice gas systems (Meirovitch and Alexandrowicz 1977b, Meirovitch 1983).

Acknowledgment

This work has been supported by the Sir Charles Clore–Weizmann Fund Post Doctoral Fellowships. I would like to thank Professor Zeev Alexandrowicz for helpful comments regarding this manuscript.

References

Alexandrowicz Z 1971 *J. Chem. Phys.* **55** 2765–79
—— 1972 *J. Stat. Phys.* **5** 19–34
—— 1976 *J. Stat. Phys.* **14** 1–9
Baker G A Jr 1963 *Phys. Rev.* **129** 99–102
Binder K 1972 *Physica* **62** 508–26
Binder K (ed) 1979 in *Monte Carlo Methods in Statistical Physics* (Berlin: Springer)
Fosdick L D 1963 in *Methods of Computational Physics* vol 1 (New York: Academic) pp 245–80
Hansen J P and Verlet L 1969 *Phys. Rev.* **184** 151–61
Landau D P and Binder K 1978 *Phys. Rev.* B **17** 2328–42
Meirovitch H 1977a *Chem. Phys. Lett.* **45** 389–92
—— 1977b *Chem. Phys.* **21** 251–6
—— 1982 *J. Phys. A: Math. Gen.* **15** 2063–75
—— 1983 *J. Stat. Phys.* in press
Meirovitch H and Alexandrowicz Z 1976 *J. Stat. Phys.* **15** 123–7
—— 1977a *J. Stat. Phys.* **16** 121–38
—— 1977b *Molec. Phys.* 1027–35

Metropolis N, Rosenbluth A W, Rosenbluth M N, Teller A H and Teller E 1953 *J. Chem. Phys.* **21** 1087–92
Salsburg Z W, Jacobson J D, Ficket W and Wood W W 1959 *J. Chem. Phys.* **30** 65–72
Sykes M F, Hunter D L, McKenzie D S and Heap B R 1972 *J. Phys. A: Gen. Phys.* **5** 667–73
Valleau J P and Card D V 1972 *J. Chem. Phys.* **57** 5457–61
Yang C P 1963 *Proc. Symp. Appl. Math.* **15** 351–65