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Magnetisation probabilities and metastability in the Ising model†

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Abstract. Let $P(m)$ be the equilibrium probability that a two-dimensional Ising model with nearest-neighbour interactions on an $N \times N$ lattice be found to have magnetisation m. We calculate $P(m)$ for $T < T_c$ and find it to agree with certain expectations. Difficulties in the use of $P(m)$ for interpretation of metastability for a system in an external field are stressed. $-\log P(m)$ is used as a potential in a Fokker–Planck equation for the diffusion of m under stochastic dynamics and, to the extent that that equation describes the physical system, a formula is derived for the lifetime of metastable states.

1. Introduction

Let the magnetisation m of a system of V spins be defined by $m = \Sigma_i \sigma_i / V$. A fundamental quantity for the statistical mechanics of these spins is $P(m)$, the equilibrium probability that the system has magnetisation m. Although one would have thought the properties of $P(m)$ for the two-dimensional Ising model to have been known since the earliest work in the field, it would appear that it has not actually been studied in any detail, although related quantities have received attention.

Our interest in $P(m)$ arises from trying to understand metastability and in examining the limitations of the commonly held view that metastability has something to do with a secondary peak in $P(m)$ (the largest peak corresponding to the stable state). For dynamical views of metastability too the logarithm of the equilibrium distribution is in some sense a potential in which m moves stochastically.

We restrict attention to the nearest-neighbour two-dimensional Ising model, although the results are expected to have wider applicability. Let the system configuration be denoted by $\mu = (\sigma_1, \ldots, \sigma_V)$, $\sigma_i = \pm 1$, and the energy by

$$E(\mu) = -\sum_{\substack{\text{n.n.} \\ \text{pairs}}} \sigma_i \sigma_j - h \sum_{i=1}^{V} \sigma_i, \tag{1}$$

where each nearest-neighbour pair appears in the sum once. Periodic boundary conditions are taken on the $N \times N$ lattice ($N^2 = V$). The zero-field constrained free energy is defined by

$$\exp(-\beta F(m)) = \sum_{\substack{\mu \\ \sum \sigma = mV}} \exp\Big(\beta \sum_{\text{n.n.}} \sigma_i \sigma_j\Big), \tag{2}$$

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where the sum over configurations μ includes only those having magnetisation m. β, the inverse temperature, will throughout this paper be taken larger than $\beta_c \simeq 0{\cdot}44$, so there is a first-order transition. For $h \neq 0$ the constrained free energy merely picks up a factor $\exp(\beta h V m)$, since the factor $\exp(\beta h \Sigma \sigma)$ is the same for all μ having the same m. The partition function as a function of h is

$$Z(h) = \sum_{k=0}^{V} \exp(-\beta F(m_k) + \beta h V m_k) \equiv \exp(-\beta \mathcal{F}_h), \tag{3}$$

where m_k is the magnetisation when k spins are 'down', i.e.

$$m_k = (V - 2k)/V. \tag{4}$$

Equation (3) also defines the total free energy $\mathcal{F}_h$.

In equilibrium the probability of finding the magnetisation with the value m with an external field h is

$$P_h(m) = \exp(-\beta F(m) + \beta h m V)/Z(h). \tag{5}$$

The apparently trivial h dependence in the numerator is deceptive and for metastability in some sense false, the issue being what states μ should enter the sum in (2). For the present we avoid this murky issue and use the licence suggested by (5) to concentrate on P_0, the zero-field distribution.

P_0 will be calculated by three methods:

(i) Heuristically, arguing in terms of droplets, large and small, to identify the largest contributions in the sum (2).

(ii) Doing the sum in (2) exactly for m_k, $0 \leqslant k \leqslant 6$ (and $0 \leqslant V - k \leqslant 6$). (This sum, for $k \leqslant 3$, is in fact the only work we have been able to find on $P(m)$ in the literature (Siegert 1955). An exact calculation of a quantity related to P, but not equivalent to it, is to be found in Gaunt and Baker (1970).)

(iii) A Monte Carlo technique, applicable for all m, which looks at virtual changes in m and computes $P(m)$ from the transition probability and the principle of detailed balance.

A stochastic evolution can be assigned to the Ising model, and the associated master equation can, with rather strong assumptions, be projected to give a Fokker–Planck equation for the diffusion of the quantity m. The potential in which m diffuses is essentially $-\log P(m)$, and the Fokker–Planck equation turns out to yield the Arrhenius formula for the lifetime of the metastable state.

Throughout the paper, and in particular towards the end, we point out the pitfalls of trying to understand metastability in terms of probability peaks. Notwithstanding the derivation of the quite reasonable Arrhenius formula, our overall conclusion is that this is not the best approach to metastability.

2. Heuristic calculation

Suppose $T(=1/\beta)$ is well below T_c and $h = 0$. For the infinite system there are two values of spontaneous magnetisation, and for the finite system we expect P_0 to have maxima near $\pm m_s$, the values of the spontaneous magnetisation (corresponding to some $k_s = \frac{1}{2}N^2(1 - m_s)$).

Consider $P_0(m)$ for $m = m_s + \epsilon$, ϵ being a fixed small positive number. A configuration contributing to this probability represents a fluctuation away from the most likely configurations. The most likely configurations (at a given T) have some distribution of spin-down clusters, and a configuration with $m = m_s + \epsilon$ will have fewer and smaller clusters. If the probability of such a fluctuation occurring in some large volume is p then the probability of its occuring in twice the volume is p^2. Hence $-\log(P_0(m_s+\epsilon)/P_0(m_s))$ is proportional to V. In terms of free energy this says (approximately) that $F(m_s+\epsilon) - \mathscr{F}_0$ is proportional to V. $\mathscr{F}_0$ itself is also proportional to V.

Now consider $P_0(m)$ for $m = m_s - \epsilon$. A magnetisation below m_s can be obtained by a homogeneous fluctuation throughout the volume, and configurations of this sort give contributions (in the sum (2)) which decrease with increasing V, exactly like those in $P_0(m)$ for $m > m_s$. However, for ϵ not too small there is a cheaper fluctuation (in free energy currency) to reduce m. Most of the volume is left at the equilibrium value of m (i.e., m_s) while a small part is at $m = -m_s$, a condition in which its free energy is just as low as the $+m_s$ state. The only free energy cost comes from the interface. If a volume V_1 is in the $-m_s$ phase, we have

$$mV = (m_s - \epsilon)V = m_s(V - V_1) + (-m_s)V_1. \tag{6}$$

The length of the interface is $\sqrt{V_1}$ times a geometrical factor g. Solving for V_1 from (6) and letting σ be the surface tension (free energy/length),

$$F(m) - \mathscr{F}_0 = (g\sigma/\sqrt{2m_s})\sqrt{V}\sqrt{m_s - m}. \tag{7}$$

For m well away from m_s and near zero, the 'droplet' stretches from one end of the system to the other and the length of the interface is just $2N$, independent of m. For such m we expect

$$F(m) - \mathscr{F}_0 = 2N\sigma. \tag{8}$$

What stands out in equations (7) and (8) is that $F(m) - \mathscr{F}_0$ behaves as $\sqrt{V}$ rather than V. Consequently, for large enough V two phase contributions to the free energy are more important than homogeneous fluctuations. The depth of the minima at $\pm m_s$ for $h = 0$ is therefore $O(\sqrt{V})$. Turning on a magnetic field introduces a contribution $hmV = O(V)$. For large enough V the magnetic field triumphs and the local minimum shrinks to insignificance. This is an important limitation on the idea that a metastable state is a local peak in the probability distribution (or local minimum of free energy). Note that this limitation would persist had we taken the surface contribution to be V^σ with any $\sigma < 1$ (not just $\frac{1}{2}$), as suggested by some droplet models. One can also see at this stage why metastability can be more easily defined for long-range forces, since the definition of an interface, essential to the derivation of the $\sqrt{V}$ factor, can only be made with forces that decrease sufficiently rapidly with distance.

3. Exact calculation of $P_0(m_k)$, $k \leq 6$

The sum to be evaluated is given in equation (2). (Note that we are actually calculating $F(m)$, not P.) For $k = 0, 1, 2, 3$ the probabilities have been calculated by Siegert (1955) and Yang. With increasing k the numbers and kinds of configurations increase rapidly. What must be determined, for each k, is the number of reversed bonds. With the help of a computer we have evaluated these numbers and our results are presented in table 1.

Table 1. Values of $\exp(-\beta F(k))$ for $k<N=\sqrt{V}$ on the $N\times N$ Ising lattice. $Q\equiv \exp(-4/T)$. Let $\exp(-\beta F(k))=VQ^{V/2}H(k)$. Then we further define

$$H(k)=\sum_{i=0}^{2k} Q^{2k-i}G_{ki}.$$

Listed below are all non-zero G_{kl} for the given k.

$k=0$: $G_{00}=1/V$
$k=1$: $G_{10}=1$
$k=2$: $G_{20}=(V-5)/2$, $G_{21}=2$
$k=3$: $G_{30}=(V^2-15V+62)/6$, $G_{31}=2V-16$, $G_{32}=6$
$k=4$: $G_{40}=\{V[V(V-30)+323]-1254\}/24$, $G_{41}=V^2-21V+118$, $G_{42}=8V-85$, $G_{43}=18$, $G_{44}=1$
$k=5$: $G_{50}=(V^4-50V^3+995V^2-9370V+35424)/120$, $G_{51}=V^3/3-13V^2+536V/3-872$, $G_{52}=5V^2-132V+926$, $G_{53}=30V-400$, $G_{54}=V+43$, $G_{55}=8$
$k=6$: $G_{61}=(V^4-62V^3+1511V^2-17242V)/12+6520$, $G_{62}=2V^3-189V^2/2+3129V/2-9144$, $G_{63}=67V^2/3-711V+17978$, $G_{64}=V^2/2+189V/2-1651$, $G_{65}=10V+30$, $G_{66}=40$, $G_{67}=2$, $G_{60}=\frac{1}{V}\binom{V}{6}-\sum_{l=1}^{7}G_{6l}$

4. Stochastic evaluation of $P_0(m)$

This is a variant of the Monte Carlo technique, one of whose first uses was the evaluation of the partition function for the Ising model (Fosdick 1963). We also use a process in which two spins are flipped, conserving magnetisation (see Kalos *et al* 1978). One can interpret these spin flips as dynamics or as a way of finding the principle contribution to the sum (2).

For given k (or m) and a (randomly selected) initial configuration we consider the configuration generated by flipping one up-spin down and one down-spin up. The selection of spin flip candidates is random. If the (double) flip lowers the energy, the configuration is so changed. If the flip raises the energy, it is implemented with probability $\exp(-\Delta E/T)$. The system then relaxes to those configurations figuring most prominently in (2). (For some k and T relaxation may be slowed by the kind of metastability considered by Kalos *et al* (1978). We did not study this phenomenon.)

Next we consider the outcome of a virtual spin flip. That is, we randomly select a single spin and evaluate ΔE if it were to be flipped. If $\Delta E<0$, we record the virtual occurrence of a transition. If $\Delta E>0$, the virtual transition is recorded with probability $\exp(-\Delta E/T)$.

None of these transitions $k\to k\pm 1$ takes place. The system remains with k spins down and only the double spin flips actually change its configuration. A record is kept of the number of $k\to k\pm 1$ flips which *would have occurred* had the single-flip transition been implemented. Then, allowing for the variation in the numbers of available up and

down spins for different k, we obtain the ratio of transition probabilities $k \to k+1$ and (starting with the $k+1$ states) $k+1 \to k$.

By the principle of detailed balance (which has been built into the microscopic stochastic dynamics), transition probabilities and the equilibrium distribution are related by

$$P_0(k)\,W(k \to k+1) = P_0(k+1)\,W(k+1 \to k), \tag{9}$$

where $W(k \to j)$ is the transition probability for going from k spins down to j spins down. All that our double stochastic process obtains, and indeed all that we need, are the ratios

$$W(k \to k+1)/W(k+1 \to k) = P_0(k+1)/P_0(k). \tag{10}$$

Having obtained this ratio for all k, we normalise with the condition

$$\sum_{k=0}^{V} P_0(k) = 1. \tag{11}$$

5. Results of the calculations

The forthcoming results represent a combination of the exact and stochastic methods. For $k \leqslant 6$ exact results were used, at the same time checking that the stochastic method probability ratios came out reasonably near to the exact values (see table 2). For $k \geqslant 7$ stochastic ratios were used. In figure 1 is a typical graph of $-\log P_0$ against k at $T = 2{\cdot}0$ and $N = 19$. The minimum value is approximately $\log 2N$, and the curve flattens towards $m \sim 0$ as expected. The minimum occurs at m values just a bit larger than m_s.

Table 2. Comparison of exact and stochastic probability ratios for k from 0 to 6 spins down. Also given are the spontaneous magnetisation (m_s) as predicted by the calculated $P(k)$ and the exact theoretical value. The quantity listed is $Q(k) = \log(P(k+1)/P(k))$. Note that because a logarithm is tabulated it is the smallness of the difference between numbers that is significant rather than their ratio. In our units $T_c \simeq 2{\cdot}27$.

	$T = 2{\cdot}0, N = 19$		$T = 2{\cdot}0, N = 15$		$T = 2{\cdot}0, N = 13$	
k	Exact	Stochastic	Exact	Stochastic	Exact	Stochastic
1	1·26	1·31	0·827	0·832	0·572	0·552
2	0·919	0·949	0·517	0·582	0·289	0·268
3	0·691	0·752	0·320	0·386	0·116	0·158
4	0·526	0·519	0·183	0·204	0·003	0·012
5	0·400	0·373	0·085	0·040	−0·075	−0·013
m_s	0·911	0·910	0·911	0·914	0·911	0·914
	$T = 1{\cdot}8, N = 19$		$T = 1{\cdot}8, N = 15$		$T = 1{\cdot}8, N = 13$	
k	Exact	Stochastic	Exact	Stochastic	Exact	Stochastic
1	0·836	0·883	0·411	0·421	0·165	0·141
2	0·510	0·550	0·126	0·147	−0·088	0·001
3	0·298	0·404	−0·048	−0·048	−0·232	−0·226
4	0·145	0·062	−0·162	−0·149	−0·317	−0·348
5	0·038	0·011	−0·238	−0·252	−0·368	−0·280
m_s	0·956 86	0·958 36	0·956 86	0·956 43	0·956 86	0·956 64

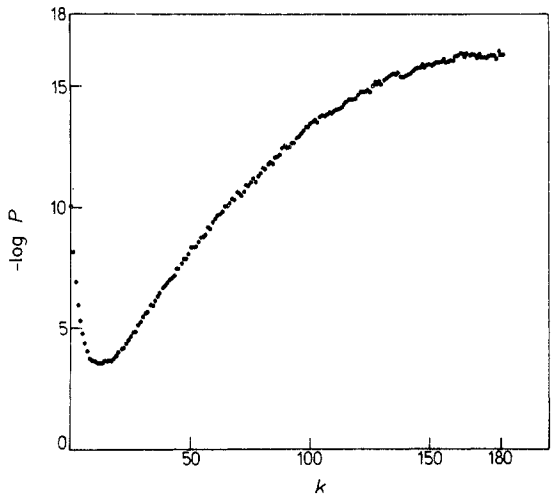

Figure 1. $-\log P_0$ against k (number of spins down) for $T = 2{\cdot}0$, $N = 19$.

To check the heuristic assertions of § 2 we first note table 3. There we study the N dependence of the height of the maximum at $m \sim 0$. We think the case is good for that difference behaving as $N(=\sqrt{V})$ rather than N^2. In figure 2 is a plot of $(\log P_0)^2$ against m (again $T = 2{\cdot}0$, $N = 19$). By equation (7), for $m > m_s$ and until the curve flattens, $(\log P_0)^2$ should be a straight line, and indeed the fit to a straight line seems good. Moreover, for various N, values of $g\sigma$ can be deduced from the straight-line fit. An estimate of σ alone can be obtained from table 3 and formula (8). Thus at $T = 2{\cdot}0$, σ is about 0·7. For lower temperatures σ is found to rise (data not in table 3), and at $T = 1{\cdot}0$ approaches 2·0, which is the energy cost of a broken bond, showing essentially no entropy contribution at this low temperature.

Finally we check that, for $|m| > m_s$, $\log P_0$ does indeed scale as $N^2 = V$. In figure 3 is plotted $[-\log P_0 - (\log P_0)_{\min}]/N^2$ for various N at $T = 2{\cdot}0$. The constant is put in to take care—approximately—of overall normalisation. The curves are seen to be

Table 3. Probability of $m = 0$ for systems with spontaneous magnetisation ($T < T_c$) as a function of system size. Listed below is $\Delta F \equiv T[(-\log P)_{\max} - (-\log P)_{\min}]$ for various N (on an $N \times N$ lattice), where the maximum occurs near $m = 0$ and the minimum at m near m_s, the spontaneous magnetisation.

	$T = 2{\cdot}0$			$T = 1{\cdot}8$		
N	ΔF	$\Delta F/N$	$\Delta F/N^2$	ΔF	$\Delta F/N$	$\Delta F/N^2$
7	12·9	1·84	0·26	15·2	2·17	0·31
9	13·9	1·55	0·17	19·9	2·21	0·25
10	14·4	1·44	0·14	21·4	2·14	0·21
12	16·5	1·37	0·11	25·3	2·10	0·18
14	19·7	1·4	0·10	27·6	1·97	0·14
15	19·8	1·32	0·08	28·8	1·92	0·13
17	23·0	1·35	0·08	33·1	1·95	0·11
19	25·5	1·34	0·07	38·9	2·04	0·11

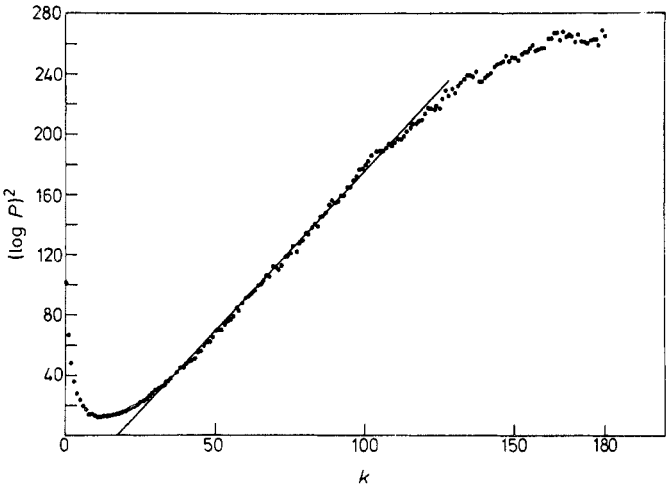

Figure 2. $(\log P_0)^2$ against k for $T = 2{\cdot}0$, $N = 19$.

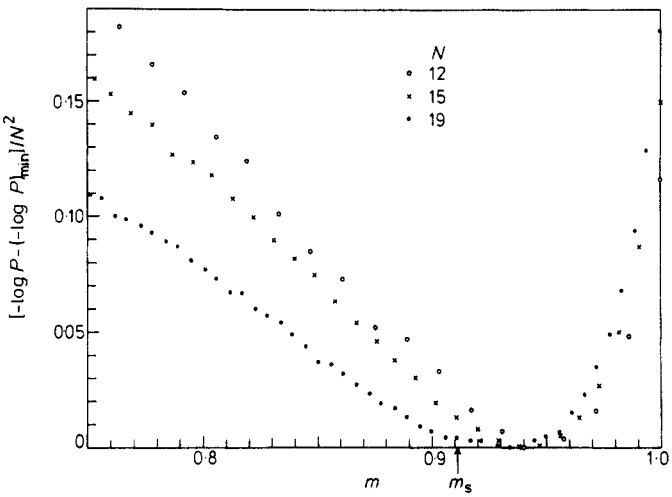

Figure 3. $-\{\log P_0)/N^2$ against m for $T = 2{\cdot}0$, various N.

reasonably parallel to one another for $m > m_s$ while for $m < m_s$ the incorrectness of the $1/N^2$ scaling causes them to separate.

There is one significant, if puzzling, feature of figure 2 to which we call attention. Note that the straight-line fit to $(\log P_0)^2$ seems to pass through 0 at $m = m_s$ rather than through $\log N$. This feature is borne out by other graphs (at other T and N) not reproduced here. Of course it is only the extrapolation of the line that hits zero, as the form (7) does not hold so close to m_s. We remark that this property does not arise because of any confusion of k versus m dependence, as the graphs in question have the same normalisation for all values of k (i.e. equation (11)). It may seem strange to worry about $\log N$ terms, but in the next section this will be seen to be crucial for the recovery of the Arrhenius formula.

We summarise our results for P_0, expressed in terms of the function $F(m)$:

(a) For $m > m_s$,

$$F(m) = N^2\phi(m) + \beta^{-1}\log N + \mathscr{F}_0. \tag{12}$$

Equation (12) defines ϕ as a function independent of N but depending on T and m. We take $\phi(m_s) = 0$.

(b) For $m_s - \epsilon > m > m_s(1 - 8/g^2) \sim \frac{1}{2}m_s$ (ϵ to be specified below),

$$F(m) = (g\sigma N/\sqrt{2m_s})\sqrt{m_s - m} + \mathscr{F}_0. \tag{13}$$

(c) For $0 \leqslant m \leqslant m_s(1 - 8/g^2)$,

$$F(m) = 2N\sigma + \mathscr{F}_0. \tag{14}$$

For $m < 0$, $F(-m) = F(m)$. An overall constant may be added to all terms to allow for Σ_k or $\int dm$ normalisation.

For $h \neq 0$, defining $F_h(m)$ in the obvious way,

$$F_h(m) = F(m) - hmN^2 + (\mathscr{F}_h - \mathscr{F}_0). \tag{15}$$

There is a small but important range, $m_s - \epsilon < m < m_s$, within which we have not given $F(m)$, nor have we given a precise estimate of ϵ. Within this range the single large droplet competes with the volume distribution of smaller droplets as major contributions to P_0. An estimate of the size of the region can be obtained by postulating that $F(m)$ of (12) extends below m_s and seeing where the competing terms of (12) and (13) are equal. We shall show below that $\phi'(m_s) = 0$, and we therefore set

$$\tfrac{1}{2}N^2\phi''(m_s)(m_s - m)^2 + \log N = g\sigma N\sqrt{m_s - m}/\sqrt{2m_s}. \tag{16}$$

Neglecting terms $O((\log N)/N)$, this yields for the value of m at which surface energy begins to dominate (coming from above)

$$\varepsilon = m_s - m = \left(\frac{2g\sigma}{\phi''(m_s)\sqrt{2m_s}}\right)^{2/3}\frac{1}{N^{2/3}}. \tag{17}$$

We have in effect continued the function ϕ to a region below m_s, a region whose size shrinks to zero with increasing N. There is reason to believe that in the thermodynamic limit ϕ cannot be continued to real m below m_s, and equation (17) therefore seems quite reasonable. We do not have any simple form for $F(m)$ in the range $m_s - \epsilon < m < m_s$, and we shall keep further developments independent of F in that range.

The function $\phi(m)$ has thermodynamic significance. In general the expectation of m at non-zero h is given by

$$\langle m(h)\rangle = \int dm\, m \exp(-\beta F_h(m)) \Big/ \int dm \exp(-\beta F_h(m)). \tag{18}$$

Since $F_h(m)$ grows with N, for sufficiently large N the integral is dominated by that m for which $F_h(m)$ is a minimum. From the condition $\partial F_h(m)/\partial m = 0$ we have

$$\partial\phi(m)/\partial m = h, \tag{19}$$

which is an implicit equation for $m(h)$ as a function of h. Note that, as $h \downarrow 0$, m approaches m_s, and $\partial\phi(m_s)/\partial m$ is zero as claimed earlier. The significance of the

function ϕ is therefore that the inverse function of its derivative is the magnetisation as a function of h. Similarly

$$\partial^2\phi/\partial m^2 = 1/\chi, \tag{20}$$

with χ the susceptibility.

6. The Fokker–Planck equation and the Arrhenius formula

Let there be given some stochastic evolution for the Ising model and let $p(\mu, t)$ be the probability that the system be found in configuration μ at time t. Then p satisfies a master equation

$$\frac{\mathrm{d}p\ (\mu, t)}{\mathrm{d}t} = \sum_{\mu'} p(\mu', t) W(\mu' \to \mu) - \sum_{\mu'} p(\mu, t) W(\mu \to \mu')$$

$$\equiv -\mathscr{H}p = -\sum_{\mu'} \mathscr{H}(\mu, \mu') p(\mu', t), \tag{21}$$

where $W(\mu \to \mu')$ is the transition probability from μ to μ', and $\mathscr{H}$ is a $2^{N^2} \times 2^{N^2}$ matrix. By virtue of the detailed balance condition (which we assume for the process) relating W to the equilibrium distribution $\bar{p}(\mu)$ $(= \exp(-\beta E(\mu))/Z)$, equation (21) has a stationary state, namely $\bar{p}(\mu)$ itself.

This suggests a definition of the metastable state as an eigenstate of $\mathscr{H}$ with small positive eigenvalue. (From detailed balance it is not hard to prove that all eigenvalues of $\mathscr{H}$ are non-negative and for ergodic transition elements the ground state is non-degenerate.) We consider this suggestion promising, although in the form just stated it is untenable, at least in the thermodynamic limit. Even for finite systems there is still a problem of interpretation, since the orthogonality of this excited state to the ground state requires that the 'metastable probability distribution' assume negative values for some μ.

Let $P(m, t)$ be the probability that the system has magnetisation m (in this section the equilibrium distribution will be indicated by putting a bar over P). It satisfies $P(m, t) = \Sigma\, p(\mu, t)$, the sum being over those μ with magnetisation m. To get a dynamical equation for P by projecting from that for p (equation (21)), some rather restrictive assumptions must be made.

In particular, products $p(\mu', t) W(\mu' \to \mu)$ are replaced by $P(m, t) W(m \to m \pm \mathrm{d}m)$, thereby neglecting microscopic correlations. The projection can then be carried out in a straightforward manner and the result is the Fokker–Planck equation for the probability distribution $P(m, t)$,

$$\Gamma\, \partial P(m, t)/\partial t = \partial^2 P/\partial m^2 + \partial(U'P)/\partial m, \tag{22}$$

where $U(m) = F_h(m)$ and the prime is $\partial/\partial m$. If time is measured in units such that there are N^2 spin flip attempts per second (corresponding to each spin interacting once per second), then $\Gamma = \mathrm{O}(N^2)$.

The outstanding feature of equation (22) is the fact that the function $U = \beta F_h(m)$ that enters is just the same as that calculated above. Interpreting (22) as a diffusion equation, U is the potential in which the stochastic collective variable $m = \Sigma\, \sigma/N^2$ diffuses.

Let

$$HP = -\partial^2 P/\partial m^2 - \partial(U'P)/\partial m; \tag{23}$$

then the spectrum of H is non-negative and has 0 as a non-degenerate eigenvalue for the eigenvector $\bar{P}_h(m) = \exp(-U(m))$, which is the equilibrium distribution, up to normalisation.

In this context too it is natural to propose that higher eigenvectors of H correspond to the metastable state, and indeed such a suggestion has been put forth in the literature by Tomita *et al* (1976). (Tomita *et al* assume, however, that the maximum in U between its two minima is high enough that increasing N leaves it unscathed even with non-zero h. Since this property holds only for infinite-range forces, their calculations do not cover the case of short-range forces.)

We next apply a similarity transformation (van Kampen 1977) to equation (23), defining $K = QHQ^{-1}$ and $\phi = QP$ with Q the multiplication operator by the function $\exp(-U(m)/2)$. Then

$$K = -\partial^2/\partial m^2 + V, \qquad \text{with} \quad V = (U'/2)^2 - U''/2, \tag{24}$$

and the spectrum of K is the same as that of H. To verify that $\Gamma = O(N^2)$ gives the appropriate time scale, as stated after equation (22), we can consider m near the stable minimum, near which $U = \frac{1}{2}\alpha N^2(m-\tilde{m})^2$ with $\alpha = O(1)$. This makes K essentially the Hamiltonian of a harmonic oscillator of frequency αN^2, so that the energy of the first excited state localised near $\tilde{m}$ is just αN^2. For $\Gamma = O(N^2)$ this says that the relaxation time for states near equilibrium is independent of size, which is appropriate for systems in which the heat bath and the external field are assumed to permeate the lattice. (In general the relaxation rate from a state ν with eigenvalue E_ν is $(E_\nu - E_0)/\Gamma$. E_0 is 0.)

Now consider the use of equation (23) for metastability. Before going to the detailed form of U derived above, we argue generally. The assumed form of U is shown in figure 4. The locations of the right and left minima of U are denoted m_R and

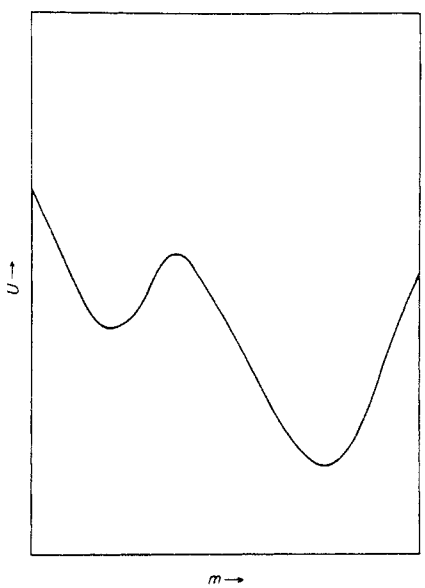

Figure 4. General form of $U(m)$.

m_L respectively, and m_0 is the position of the maximum between them. Corresponding values of U and its derivatives at these points are denoted U_R, U'_R, etc.

The metastable state is assumed to be the lowest excited state of H; we call its energy E_{ms}. For the operator K, E_{ms} satisfies the variational principle

$$E_{ms} \leqslant \left(\int \phi^* K \phi \, dm\right) \Big/ \int \phi^* \phi \, dm$$

for all ϕ orthogonal to the ground state ($\phi_0 = \exp(-U/2)$). In terms of H (which is not Hermitian) this implies

$$E_{ms} \leqslant \int e^U P^*(m) H P(m) \, dm \Big/ \int e^U P^*(m) P(m) \, dm \tag{25}$$

for all P such that

$$\int P(m) \, dm = 0. \tag{26}$$

Guessing that, for $m < m_0$, P should resemble an equilibrium state, we take as a trial wavefunction

$$P(m) = \theta(m) \, e^{-U(m)}, \tag{27}$$

where θ is expected to be about 1 for $m < m_0$. We further assume *a priori* that θ is nearly constant except near m_0, and that for $m > m_R$ and $m < m_L$ it is precisely constant. Substituting in equation (26) and using Laplace's method yields

$$0 = (1/\sqrt{U''_L})\theta(m_L) \, e^{-U_L} + (1/\sqrt{U''_R})\theta(m_R) e^{-U_R}. \tag{28}$$

Taking $\theta(m_L)$ to be 1 (so that P is not normalised to 1) we get

$$\theta(m_R) = -\sqrt{U''_R/U''_L} \, e^{-(U_L - U_R)}. \tag{29}$$

For any non-zero h, $U_L - U_R$ is proportional to N^2 ($= V$), showing that $\theta(m_R)$ is extremely small.

The interesting calculation arises when (27) is substituted into (25). The integral in the denominator is evaluated using Laplace's method:

$$\int e^U P^2 = \int \theta^2 e^{-U} \sim \sqrt{\frac{2\pi}{U''_L}} e^{-U_L} + \sqrt{\frac{2\pi}{U''_L}} e^{-U_L} \sqrt{\frac{U''_R}{U''_L}} e^{-(U_L - U_R)}, \tag{30}$$

and the second term in the sum is negligible.

For the numerator,

$$\int e^U PHP = -\theta\theta' e^{-U} \Big|_{-1}^{1} + \int e^{-U} (\theta')^2. \tag{31}$$

The integrated term vanishes, since by assumption $\theta' = 0$ at $m = \pm 1$. The variational principle has thus been reduced to minimising the integral

$$\int e^{-U} (\partial\theta/\partial m)^2 \, dm \tag{32}$$

subject to the boundary conditions at m_R and m_L. But this yields the equation of a

classical particle with non-constant mass. The solution is

$$\frac{\partial\theta}{\partial m} = c\, e^{U(m)}, \qquad c = -\left(\int_{m_L}^{m_R} e^{U}\right)^{-1} \sim -\sqrt{\frac{U_0''}{2\pi}}\, e^{-U_0}. \tag{33}$$

Collecting all our results yields

$$E_{ms} \leqslant (1/2\pi)\sqrt{-U_0'' U_L''}\, e^{-(U_0 - U_L)}. \tag{34}$$

Bearing in mind that U is βF, this shows a strong resemblance to the Arrhenius formula, and in fact for the U calculated above will yield that formula.

Tomita *et al* (1976) give a formula differing from (34) only in an overall factor using the WKB approximation. Because our formula provides a rigorous lower bound (subject to a single approximation), we thought it worthwhile to present its derivation. The sole approximation is the use of the Laplace method for a one-dimensional integral and, should one wish, it is not difficult to obtain error estimates for that method.

For the remainder of this paper the inequality of equation (34) will be treated as an equality, since both our physical considerations and the calculation of Tomita *et al* (1976) suggest that it is not very different.

It remains to use the results of our calculation of U to see the implications of (34) for the Ising model.

By equations (12)–(15), for some small positive h, U has the form shown in figure 4. We shall assume that m_0 falls in the region of $F_0(m)$'s square-root dependence. This is where the concept of a critical droplet is relevant. Thus m_0 is found by setting $\partial F_h/\partial m = 0$, using F_h as obtained from equations (13) and (15). This yields

$$m_0 = -m_s + (g\sigma/2\sqrt{2m_s})^2/h^2N^2. \tag{35}$$

Note that, for sufficiently large N, m_0 moves into the transition region defined by equation (17) (since N^{-2} must get smaller than constant $\times N^{-2/3}$).

Next we wish to use the form (12) for F in the region $m > -m_s$. This can only be valid for sufficiently small N, since (12) is based on the dominance of those fluctuations that take place throughout the volume. Using (12), m_L is given by

$$\phi'(m_L) = h \qquad \text{or} \quad m_L \simeq -m_s + 2h/\varphi'', \tag{36}$$

where in the second equation a quadratic approximation has been used for ϕ. Equation (36) also shows that the distance from $-m_s$ at which we wish to use (12) depends on h.

Also required are $U_0 - U_L$, U_L and U_0. For U'' at m_L we again use the form (12). Any error arising from this cannot affect our results very much, since U'' entered as an area arising from an integration (in normalising P), and even if $F_0(m)$ were suddenly to rise steeply to the right of $-m_s$ it could at most affect the area by a factor 2. Hence at m_L

$$U''(m_L) \simeq \beta N^2 \phi''(m_s) = \beta N^2/\chi, \tag{37}$$

with χ the susceptibility (equation (20)). For U_0 we take a second derivative of F_h at m_0 to obtain

$$U''(m_0) = -4N^4 h^3 m_s \beta/g^2\sigma^2. \tag{38}$$

Finally, we require

$$U(m_0) - U(m_L) \simeq U(m_0) - U(-m_s) = \beta g^2\sigma^2/4m_s h - \log N. \tag{39}$$

Both in (37) and more seriously in (39) m_L has been replaced by $-m_s$. Any better estimate would require information on the form of $F_0(m)$ to the right of $-m_s$, precisely

in the transition region. Hence our subsequent results are accurate only modulo this imprecision. Aside from this problem (39) has a very satisfying form. To see this we first substitute (37) and (38) into (34) to get

$$\text{rate} = \frac{E_{\text{ms}}}{\Gamma} \cong \frac{1}{\pi\Gamma} \frac{\beta N^3}{g\sigma} \sqrt{\frac{h^3 m_{\text{s}}}{\chi}} \exp(U_{\text{L}} - U_0). \tag{40}$$

At first sight this seems to give the strange result that rate $= O(N^3/\Gamma) = O(N) = O(\sqrt{V})$. However, the log N term in (39), whose appearance we found numerically but for which we had no theoretical explanation, puts things right and gives us a rate proportional to volume. To summarise,

$$\text{rate} = \frac{E_{\text{ms}}}{\Gamma} \cong V\left(\frac{V}{\Gamma}\right) \frac{\beta h^{3/2} m_{\text{s}}^{1/2}}{\pi g \sigma \chi^{1/2}} \exp\left(\frac{-\beta g^2 \sigma^2}{4 m_{\text{s}} h}\right), \tag{41}$$

which is the Arrhenius formula. The particular dependence of h in the denominator of the exponent has been noted on several previous occasions (Langer 1967, Capocaccia *et al* 1974, McCraw and Schulman 1978) and to some extent has motivated suggestions of an essential singularity at first-order phase transitions.

The foregoing discussion is unsatisfactory on a number of counts. In particular, with increasing N the range of validity with respect to h (cf equation (36)) shrinks to zero. Moreover, the spread of the 'metastable eigenstate' for $m > -m_{\text{s}}$ appears to be only $1/V$ rather than $1/\sqrt{V}$, as should be the case for a state resembling an equilibrium state.

Our feeling is that at least some of the above problems arise from the projection from microscopic configuration space $\{\mu\}$ to the single variable m. Hence there may be states with $\Delta m \sim \sqrt{V}$ which contribute to the metastable free energy and which do not contain critical or transcritical droplets. These are distinguished from states containing large droplets through the use of other variables (in effect one constrains the sum over states in ways beyond merely fixing m). Also the formula $\partial\varphi/\partial m = h$ would then carry over to finite values of h with the understanding that other variables in the argument of ϕ take values such that the equation is meaningful (through the exclusion of transcritical droplets). Unfortunately, we do not have a good candidate for the additional variables and so cannot improve on the admittedly flawed treatment given above.

7. Summary and concluding remarks

The calculated and stochastically computed probability distribution agrees quite well with what one expects on heuristic grounds. There is, however, a $\frac{1}{2}\log V$ term that enters the free energy for which we do not have an explanation.

The probability distribution for non-zero external field (h) is related in a simple way to that for $h = 0$. However, for h macroscopically different from zero, this simple form probably does not have much to do with metastability. Understanding metastability through probability distributions would seem to require a finer set of constraints than merely fixing m. Ideas of this sort have appeared in the literature, but they are not without problems. (The techniques of Penrose and Lebowitz (1971) would seem to apply only where the forces ultimately become infinite-range. Capocaccia *et al* (1974) effectively limit droplet size. But if the limitation is only for very large droplets, then transcritical droplet contributions will dominate the metastable free energy. If the limit

is of the order of the droplet size, the definition of the metastable state will be dependent on cut-off.)

The Arrhenius formula for the decay rate of a metastable state was derived with a specific prediction as to its dependence on surface tension, susceptibility and other quantities. The correct volume dependence was obtained only with the aid of the unexplained $\frac{1}{2}\log V$ term.

We observe finally that analytic continuation of the free energy from the stable to the metastable domain (done perhaps by the method of Newman and Schulman (1977)) would seem to avoid many of the pitfalls of approaches based on constrained probability distributions. Perhaps this approach, because it does not define the metastable state (as a probability distribution on microscopic configuration space), is less demanding and more able to succeed. The evidence of McCraw and Schulman (1978) suggests that the analytic continuation can be carried out. The off-axis branch points observed there are probably an artefact of the specific method of continuation and in a way analogous to the model studied by Schulman *et al* (1978) we expect to find that the free energy function itself has a branch cut only along the negative real h axis.

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† Quoting work by C N Yang. The notation of this paper differs from ours. Also in Siegert's expression for $P(3)$ (his equation (2.8)) there is a typographical error and 1/2! appears instead of the correct 1/3!