done this in Fig. 5. We have taken $d\bar{\mu}/dc=-3\mu_B$, $-4.5\mu_B$, and $-5.5\mu_B$ for Ni-Al, Ni-Cr and Ni-V, respectively. The 5.3% Ni-Cr has been plotted directly. We have then plotted the 5.5%-Ni-V and 5.2%-Ni-Al spectra by first expanding the frequency scale around 28.5 MHz by 4.5/3 in the Al case and contracting it by 4.5/5.5 in the V case. The resulting curves enable a comparison of the Ni-Cr, Ni-V, and Ni-Al results, all about 5%, normalized to the same $d\bar{\mu}/dc$. In the Ni-Cr case there is a fairly pronounced knee which we have related to Ni atoms in the nearest-neighbor shell to the solute atom, while the main peak was related to Ni atoms in more distant shells. The fact that in the Ni-Al and Ni-V cases the peak of the curve is shifted over relative to the knee or to the center of gravity means that the magnetic disturbance in more distant shells is more comparable to the disturbance in the nearest neighbor shells in these two systems. A similar scaling, using Van Elst's value of $d\bar{\mu}/dc=-6\mu_B$ for Ni-Cr, gave a very poor fit of the Ni-Cr with the Ni-Al and Ni-V curves, indicating that, at least for our samples, the data of Marian or Sadron are more applicable.

IV. CONCLUSION

As in the case of the Ni-Co system previously studied it has been found that the hyperfine field at the site of Ni nuclei in Ni-V, Ni-Cr and Ni-Al systems has two contributions. The major contribution is due to the moment on the parent atom and a smaller contribution is from moments on neighboring atoms. The greater delocalization of the magnetic disturbances in these three systems is in contrast to the localized behavior of the Ni-Co system. The magnetic disturbances seem to be spatially more widespread in the Ni-Al and Ni-V systems than in the Ni-Cr system. The spatial variation of the magnetization for the Ni-Cr system, as deduced from the resonance spectra, is in agreement with results obtained by Collins and Low by means of neutron scattering techniques.

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Relaxation Times for Metastable States in the Mean-Field Model of a Ferromagnet*

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Relaxation from metastable to stable states is considered for a mean-field model Ising ferromagnet in which each spin interacts equally with every other spin in the system. Spins are chosen at random and flipped over with probability given by a suitable Boltzmann factor. Approximate solutions to the stochastic equations, confirmed by computer calculations on small systems, indicate a relaxation time increasing exponentially with the size of the system (contrary to one's expectation for a system with short-range interactions).

I. INTRODUCTION

THE description of metastable states on a fundamental level is both an interesting and unsolved problem in statistical mechanics. The long lifetime (especially compared with times characterizing molecular processes) observed for many such states suggests that an elementary extension of well-established procedures in the statistical mechanics of stables states might serve to cover metastable states as well.

In fact, metastable states are fairly easily defined in certain model systems of magnets or fluids with an attractive potential whose range is permitted to become infinite (the magnitude simultaneously going to zero) at some point in the calculation. Probably the simplest of these is the mean-field (molecular-field or Weiss) model of a ferromagnet. The mean-field theory is often considered an approximate method for solving the Heisenberg or Ising model with nearest-neighbor interactions.[1] It may also be regarded as the exact solution (in the limit of a large system) for a model in which each atom interacts equally with every other atom through an Ising exchange potential.[2] We shall adopt the latter point of view in this paper and investigate the following question in the case of atoms of spin-$\frac{1}{2}$: if such a ferromagnet is at some particular time in a

* Research supported in part by the National Science Foundation.

[1] J. S. Smart, *Effective Field Theories of Magnetism* (W. B. Saunders Company, Philadelphia, Pennsylvania, 1966).
[2] F. Bitter, *Introduction to Ferromagnetism* (McGraw-Hill Book Company, Inc., New York, 1937), p. 153. The analogous model for a lattice gas was discussed by K. Husimi at a meeting of the Physical Society of Japan in May, 1953 (unpublished) and by H. N. V. Temperley, Proc. Phys. Soc. (London) **A67**, 233 (1954)

metastable state, how long will it take to relax to the stable state?

The Hamiltonian for the mean-field model is introduced in Sec. II together with an assumed time dependence described by a Markoff process. The approximate solutions to the stochastic equations obtained in Sec. III are in fair agreement with computer calculations for small systems. They predict a relaxation time from metastable to stable states, for a given temperature and external magnetic field, increasing exponentially with the number of spins for a large system. This result, discussed in Sec. IV, is in marked contrast with what one would predict on physical grounds for a system with forces of finite range and lends support to the conjecture (by no means new) that characterization of a metastable state in a real system is far more subtle than the simplest models (including the van der Waals model for a fluid) would suggest.

II. MEAN-FIELD MODEL

Consider the Hamiltonian

$$\mathcal{H}=-(J/N)\sum_{i<j}\sigma_i\sigma_j-\mu H\sum_i\sigma_i-\tfrac{1}{2}J \tag{1}$$

for N Ising spins $\sigma_i=\pm1$ in an external magnetic field H. For convenience we set the constants J and μ equal to 1. Let

$$n=\tfrac{1}{2}(N+\textstyle\sum_i\sigma_i) \tag{2}$$

be the number of spins pointing "up" and let us write (1) in the form

$$\mathcal{H}=U(n)=-(2n-N)^2/2N-H(2n-N)\,. \tag{3}$$

If the system is in equilibrium at a temperature (in energy units) $T=\beta^{-1}$, the probability of finding n spins "up" is

$$P_e(n)=Z^{-1}\binom{N}{n}e^{-\beta U(n)}=Z^{-1}e^{-N\beta a_N(T,x)}\,, \tag{4}$$

where

$$Z=\sum_n\binom{N}{n}e^{-\beta U(n)} \tag{5}$$

is the partition function. The "free energy" per spin a_N as a function of the quasi-continuous variable

$$x=N^{-1}\textstyle\sum\sigma_i=N^{-1}(2n-N) \tag{6}$$

(the average magnetization per spin) approaches a limit $a(x)$ for large N. For $T>T_c=1$, the Curie temperature $a(x)$ has one minimum and for $T<T_c$ two minima, shown schematically in Fig. 1 for the case $H=0$. In a small magnetic field $H>0$ the curve $a(x)$ for $T<T_c$ as sketched in Fig. 2. Both minima move to the right; the one on the right becomes deeper, the one on the left more shallow. The former is naturally associated with the stable and latter with the metastable state.

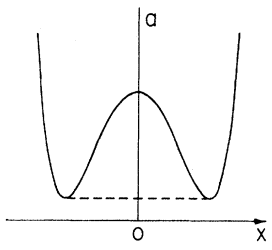

FIG. 1. The function $a(x)$ for a temperature $T<T_c$ and field $H=0$.

We remark that no such simple characterization of the metastable state is possible for a system with a short-range Ising interaction. The function $a(x)$ is convex downwards[3] for this case and may possess a "flat bottom" (as shown by a dotted line in Fig. 1), but never two distinct minima.

We introduce time dependence as follows. When $\tau=0$, a spin is chosen at random and either flipped over ($\sigma_i=+1$ going to -1 or vice versa) or not flipped over, with a probability depending on the change in total energy (3). The process is repeated at $\tau=1, 2, 3, \cdots$. The probability $P_\tau(n)$ of finding n "up" spins in the τth interval satisfies the difference equation

$$P_{\tau+1}(n)=\sum_{m=n-1}^{n+1}P_\tau(m)T_{m,n} \tag{7}$$

with

$$\begin{aligned}
&T_{n,n+1}=\alpha N^{-1}(N-n)\exp\{-\tfrac{1}{2}\beta[U(n+1)-U(n)]\}\,,\\
&T_{n,n-1}=\alpha N^{-1}n\exp\{-\tfrac{1}{2}\beta[U(n-1)-U(n)]\}\,,\\
&T_{n,n}=1-T_{n,n+1}-T_{n,n-1}\,,
\end{aligned} \tag{8}$$

where the constant $\alpha>0$ is chosen small enough so that $T_{n,n}$ is positive for any n. The $T_{m,n}$ are chosen so that $P_{\tau+1}=P_\tau=P_e$ satisfies (7). In a real magnetic system the number of times per second a particular spin flips over should be roughly independent of the size of the system. So that this condition is satisfied in our model we introduce the "physical" time scale by

$$t=\tau/N\,. \tag{9}$$

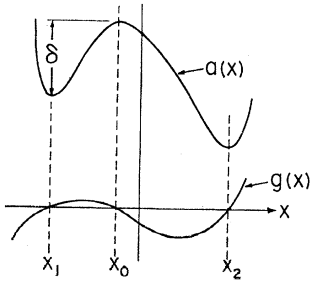

FIG. 2. The functions $a(x)$ and $g(x)$ for a temperature $T<T_c$ and a small positive field H.

[3] This result has been proved for the analogous problem in fluids by D. Ruelle, Helv. Phys. Acta 36, 183, 789 (1963) and may be derived for spin systems by similar methods. [See also R. B. Griffiths, J. Math. Phys. 5, 1215 (1964) and 6, 1447 (1965).]

III. TIME DEPENDENCE OF THE MODEL

A. Short-Term Behavior

Consider the probability $P_\tau(n)$ expressed in terms of the quasi-continuous variables x, t by

$$p(t,x)=P_{Nt}(\tfrac{1}{2}N[x+1]). \tag{10}$$

Our problem is to find the time dependence of p given that x has a definite value at $t=0$. It seems reasonable to replace the difference equation (7) by a corresponding partial differential equation. But one must proceed with care, since for large N even $p_e(x)$ [corresponding to $P_e(n)$] is, by (4), a rapidly varying function of x. However, $\phi(t,x)$ defined by

$$p(t,x)=e^{N\phi(t,x)} \tag{11}$$

should be less rapidly varying. If we insert the approximations

$$\begin{aligned}\phi(t,\,x+2N^{-1})&\simeq\phi+2N^{-1}\phi_x,\\ \phi(t+N^{-1},\,x)&\simeq\phi+N^{-1}\phi_t\end{aligned} \tag{12}$$

(subscripts denote partial derivatives) in (7) [via (10) and (11)] and drop certain terms of order N^{-1}, we obtain

$$\begin{aligned}\alpha^{-1}[e^{\phi t}-1]=&\tfrac{1}{2}(1-x)e^{\beta(x+H)}(e^{-2\phi x}-1)\\ &+\tfrac{1}{2}(1+x)e^{-\beta(x+H)}(e^{2\phi x}-1).\end{aligned} \tag{13}$$

Clearly the equation makes no sense for very short times, since $p(0,x)$ is zero and hence $\phi=-\infty$ for most values of x at $t=0$, but it should describe the state of affairs in some approximation for $t\gtrsim 1$ when all $P_\tau(n)$ are positive.

Suppose that ϕ has a smooth maximum in x at some $x_m(t)$. Very near the maximum ϕ_x and [by (13)] ϕ_t should be small, making possible a linear approximation to (13):

$$\phi_t=\alpha g(x)\phi_x, \tag{14}$$

$$g(x)=2x\cosh\beta(x+H)-2\sinh\beta(x+H). \tag{15}$$

Along the curve $x_m(t)$ in the x, t plane ϕ_x vanishes and thus

$$0=d\phi_x=\phi_{xx}dx+\phi_{xt}dt=\phi_{xx}dx+g(x)\phi_{xx}dt, \tag{16}$$

where we have used (14) and the condition $\phi_x=0$ to evaluate ϕ_{xt}. Thus $x_m(t)$ satisfies the equation

$$dx_m/dt=-\alpha g(x). \tag{17}$$

The situation for $T<T_c$ and H positive but small is shown schematically in Fig. 2. The points x_0, x_1, x_2 where g is zero are the extreme points for $a(x)$, the last two corresponding to the metastable and stables states, respectively. Clearly if x_m is initially anywhere to the right of x_0, (17) implies that it approaches x_2, the stable state; whereas starting to the left of x_0 it approaches the metastable position x_1. This behavior is confirmed qualitatively by computer calculations (see below) for finite N. The time scale for this approach to the stable or metastable state is of order 1, in contrast with the result we shall obtain below for relaxation from the metastable to the stable state. For $T>1$, $g(x)$ has but one zero, which is, of course, the limit of x_m as $t\to\infty$.

B. Long-Term Behavior

Equation (13) is inadequate to describe the relaxation from the metastable to the stable state; so we adopt an alternative approach. The functions Q and q, defined by

$$P_\tau(n)=Q_\tau(n)P_e(n) \tag{18}$$

$$q(t,x)=Q_{Nt}[\tfrac{1}{2}N(1+x)], \tag{19}$$

should approach 1 as t (or τ) becomes very large. Thus for large times it should be possible to approximate the difference equation [completely equivalent to (7)]

$$\begin{aligned}&q(t+N^{-1},\,x)-q(t,x)\\ &=\alpha'\{\tfrac{1}{2}(1+x)e^{-\beta(H+x)}q(t,\,x-2N^{-1})\\ &\quad+\tfrac{1}{2}(1-x)e^{\beta(H+x)}q(t,\,x+2N^{-1})\\ &\quad-[\tfrac{1}{2}(1-x)e^{\beta(H+x)}+\tfrac{1}{2}(1+x)e^{-\beta(H+x)}]q(t,x)\},\end{aligned} \tag{20}$$

where

$$\alpha'=\alpha e^{\beta/N} \tag{20a}$$

by the differential equation

$$q_t=\alpha'[-g(x)q_x+N^{-1}h(x)q_{xx}] \tag{21}$$

with g defined in (15) and

$$h(x)=2\cosh\beta(H+x)-2x\sinh\beta(H+x). \tag{22}$$

For large N the q_{xx} term in (21) should be important only near points where $g(x)$ vanishes. In particular let us look for a static solution $q=f(x)$ to (21) very near $x=x_0$ (Fig. 2), using lowest order linear approximations for g and h:

$$N^{-1}h(x_0)f''(x)=(x-x_0)g'(x_0)f'(x). \tag{23}$$

The general solution to (23),

$$\begin{aligned}&f(x)=A+B\,\mathrm{erf}[(Nr)^{1/2}(x-x_0)],\\ &\mathrm{erf}(t)=2\pi^{-1/2}\int_0^t\exp(-y^2)dy,\end{aligned} \tag{24}$$

$$r=-g'(x_0)/2h(x_0)>0, \tag{25}$$

where A and B are arbitrary constants, is sketched in Fig. 3. Provided $|x-x_0|\geq O(N^{-1/2})$, f is essentially constant and therefore also (approximately) a static solution to (21), even for x not near x_0. This form for $f(x)$ implies that the probability distribution on either side of x_0 is essentially at its equilibrium value apart from a constant factor, whereas in the immediate vicinity of x_0 there is a strong departure from equilibrium, indicating a "flow" of probability from one side to the other. A mechanical analogy would be two large tanks of water filled to different levels and con-

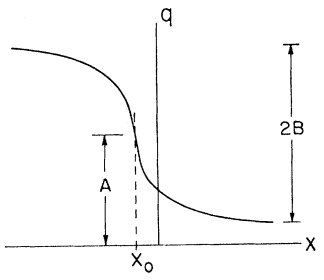

FIG. 3. The function $q(x)$ defined by Eq. (26).

nected by a narrow pipe. Thus, for large values of t, a good approximation to the solution of (20) should be

$$q(t,x)=A(t)+B(t)\ \mathrm{erf}[(Nr)^{1/2}(x-x_0)] \quad (26)$$

with the (very slow) time dependence of A and B determined by the rate at which probability "flows" past x_0. This rate is easily calculated.

Let us denote by[4]

$$s(t)=\sum_{y<x_0} p(t,y)=\sum_{y<x_0} p_e(y)q(t,y) \quad (27)$$

the probability that x is less than x_0. This satisfies a difference equation [easily derived from (7)]:

$$s(t+N^{-1})-s(t)=\tfrac{1}{2}\alpha' p_e(x_0)(1+x_0)e^{-\beta(H+x_0)} \times[q(t,x_0)-q(t,\ x_0-2N^{-1})] \quad (28)$$

and approaches

$$s_e=\sum_{y<x_0} p_e(y) \quad (29)$$

as $t\to\infty$. If (28) is approximated by a differential equation and (26) inserted on the right-hand side, one obtains

$$s_t=B(t)[4Nr/\pi]^{1/2}\alpha'(1+x_0)e^{-\beta(H+x_0)}p_e(x_0). \quad (30)$$

On the other hand, upon inserting (26) in (27) and in

$$\textstyle\sum_y p(t,y)=\sum_y p_e(y)q(t,y)=1 \quad (31)$$

and taking the time derivatives of both expressions, we obtain

$$s_t=B'(t)[u_0-u_1 s_e], \quad (32)$$

where

$$u_0=\sum_{y<x_0} p_e(y)\ \mathrm{erf}[(Nr)^{1/2}(y-x_0)],$$
$$u_1=\textstyle\sum_y p_e(y)\ \mathrm{erf}[(Nr)^{1/2}(y-x_0)]. \quad (33)$$

Combining (30) and (32) we have

$$B(t)=B_0e^{-\lambda t} \quad (34)$$

and

$$\lambda=\alpha'\{2N[\beta(1-x_0^2)-1]/\pi\}^{1/2}p_e(x_0)[s_eu_1-u_0]^{-1}, \quad (35)$$

[4] In the summations in Eqs. (27) to (33) it is understood that y has the discrete values prescribed by (6) with n an integer between 0 and N.

TABLE I. Results of computer calculations for long-time behavior of metastable states. Here λ_c is the numerical result for the exponent in (34) and λ_a is the prediction of (35).

N	β	βH	λ_c	λ_a
4	1.2	0	0.33	0.31
4	2.0	0	0.12	0.14
8	1.2	0	0.179	0.175
8	1.2	0.05	0.190	0.188
8	2	0	0.024	0.026
8	2	0.25	0.032	0.031
8	2	0.4	0.048	0.049
16	1.2	0	a	

[a] Value could not be obtained because of roundoff errors.

where the identity $g(x_0)=0$ has been used to simplify the expression for λ.

For $H>0$ and N large, $p_e(x)$ has two very sharp peaks, a large one at x_2 and a much smaller one at x_1. Under these conditions u_0 may be replaced by $-s_e$ and u_1, by 1, to a very good approximation. Also, s_e may be evaluated by using a Gaussian approximation to p_e near x_1. The result is

$$\lambda\simeq(\alpha'/\pi)[\beta(1-x_0^2)-1]^{1/2}[(1-x_1^2)^{-1}-\beta]^{1/2}e^{-N\delta\beta}, \quad (36)$$

where δ is the quantity indicated in Fig. 2, that is, the height of the potential barrier above the metastable minimum. For the case $H=0$ the right side of (36) must be increased by a factor of 2, since u_1 vanishes. Our whole derivation is only valid, of course, when β and H have such values that the curve $a(x)$ in Fig. 2 actually possesses two minima, and the result (36) should then be asymptotically correct for large N.

C. Direct Computation

The analytic results obtained above were checked by direct iteration of (20) on a computer for $N=4$, 8, and 16 and $\alpha=\frac{1}{2}$. Values of β and H are given in Table I. It was found that if the system started with a definite value of x less than or greater than x_0, the function q rapidly ($t=1$ to 2 times α^{-1}) approached a form closely resembling (24), with B less than or greater than zero, respectively, thus providing qualitative confirmation of (17). After this distribution was achieved the changes in A and B were comparatively slow and a decay constant λ_c could be obtained from the numerical results. Table I gives this "experimental" value together with the approximate value λ_a predicted by (35). For $N=16$ the decay was so slow that roundoff errors in the computation made a reliable determination of λ_c impossible. The agreement between the two values for λ is certainly as good as could be expected for small N, considering the approximations used to obtain (35). We are therefore reasonably confident that (35) and the asymptotic form (36) give the correct long-time behavior, and in particular the relaxation time increases exponentially with the size of the system.

IV. DISCUSSION OF RESULTS

The exponent in the last factor in (36) is just the height of the total free-energy barrier (N times the barrier per spin) separating the metastable from the stable state, divided by the temperature, a result not dissimilar to one obtained by Kramers[5] for the escape of a particle from a potential well under the influence of random forces (Brownian motion). A similar exponential factor appears in the calculation of Becker and Döring[6] for the relaxation rate of a metastable state in the droplet model[7] of condensation; only in this case the free-energy barrier is the isothermal work required to form a droplet of sufficient size to provide a nucleus for condensation, and thus is not proportioned to the volume for a large system.

In fact, on physical grounds the "droplet" model appears more realistic than a long-range force model in describing condensation in systems with forces of reasonably short range. At low temperatures and a low degree of supersaturation one expects the condensation of a vapor to proceed through the random formation of nuclei ("spontaneous nucleation") which then grow in size.[8] An analogous result should hold true in, for example, the Ising model with nearest-neighbor forces. As the probability of spontaneous nucleation is proportional to the volume, one expects the relaxation time to decrease with the size of the system, or at least not increase, in contrast to our mean-field model.

We suspect, in fact, that the reason metastable states are so easily defined in the infinite-range force models—the isotherm in the metastable region is simply the analytic continuation of the isotherm in the single-phase region—is that the relaxation time in the thermodynamic limit of infinite volume becomes infinitely long; that is, the metastable state becomes in fact a stable state. In contrast, the droplet model of condensation provides a less definite prescription for defining the metastable state (one must arbitrarily exclude from the partition sum configurations containing droplets greater than the critical size) and also predicts that the pressure-volume (or field-magnetization) isotherms possess an essential singularity at the condensation point.[9] This singularity does not preclude a smooth (all derivatives continuous) extension of the isotherm into the metastable region and would presumably be very hard to detect experimentally. Nonetheless, the presence or absence of such a singularity in more realistic models is an important problem in our understanding of phase transitions.

Recent work[10] has shown that the mean-field results (and their analogs in fluids) may be obtained by use of a "Kac potential" with a long but finite-range,[11] γ^{-1} provided that the range is allowed to become infinite ($\gamma \to 0$) after the thermodynamic (infinite volume) limit. Our considerations do not, of course, apply directly to these systems.[12] However, if one adopts the "nucleation" picture of relaxation from the metastable to the stable state, our calculation suggests that the probability per unit volume of forming a nucleation center probably decreases exponentially as some factor times γ^{-3}, or perhaps even more rapidly for small γ. The point is that within a volume of order γ^{-3} the interaction of one spin with any other is, to a first approximation, of the form (1). Thus the required "critical nucleus" will involve a number of spins at least of order γ^{-3} and the time required for its formation should be (very roughly) comparable to, or larger than, that computed above for $N=\gamma^{-3}$, going to infinity as γ approaches zero.

The problem remains of characterizing metastable states in more realistic models for which the relaxation time is probably finite. Although the aforementioned droplet model seems a step in the right direction, it would be of interest to obtain a characterization of metastable states and an estimate of relaxation times in, for example, the Ising model with nearest-neighbor attractive forces.

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[10] One-dimensional fluids were discussed in the series of papers by M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, J. Math. Phys. **4**, 219, 229 (1963); **5**, 60 (1964). One- and two-dimensional Ising ferromagnets were considered by M. Kac and E. Helfand, J. Math. Phys. **4**, 1078 (1963). J. Lebowitz and O. Penrose, J. Math. Phys. **7**, 98 (1966), have obtained very general results for fluids in any number of dimensions, and E. Lieb [J. Math. Phys. (to be published)] has recently extended the argument to quantum fluids. J. Lebowitz, Proceedings of the Eastern Theoretical Physics Conference, Stony Brook, New York, 1965 (to be published) has discussed the definition of metastable states.

[11] We use "range" in a loose sense; the potentials employed are not of strictly finite range, but are characteristically of the form $e^{-\gamma r}$, where r is the distance between atoms.

[12] Since, in the simple mean-field model, the range of the potential is permitted to become infinite simultaneously with the volume.