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Complex Free Energies and Metastable Lifetimes

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For two simple models we consider the analytic continuation of the free energy across a first-order phase transition. For each system we also study an associated stochastic dynamics and decay rates for passage to the stable equilibrium. We then investigate the relation between the imaginary part of the free energy and the decay rate per unit volume.

KEY WORDS: Metastability; complex free energy; lifetimes; stochastic dynamics.

1. INTRODUCTION

That an analytic continuation of the free energy has something to do with metastable states is an idea one encounters with his very first acquaintance with the van der Waals equations of state. For more realistic models (i.e., with short-range forces) one believes that the free energy acquires an imaginary part in the metastable domain, and a natural interpretation of this imaginary part is as a decay rate. (Why this interpretation is "natural" probably has to do with familiarity with the formalism of quantum mechanics. There a negative imaginary part for the energy leads to decay.)

In this paper we consider some models whose free energy can be analytically continued and to which we can also assign a stochastic dynamics and deduce a decay rate. We find that near the transition point the imaginary part of the continued free energy is proportional to the decay rate with a proportionality factor given by Langer[1] in his work on metastability. Consequently, our models, though highly simplified, are able to provide rigorous examples of a relation between analytic continuation and metastable decay rates.

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By working with solvable models we are also able to see the interplay of infinite-volume limits, vanishing lifetimes, and continued free energies for metastable systems.

One of the models considered in this paper, the Curie–Weiss model, involves discrete spins all interacting with each other. A stochastic dynamics for this model has been considered before.[2] We provide a rigorous upper bound on the decay rate in the metastable region and exact infinite-volume limits for the decay rate per unit volume in the "transpinodal" region, where the external field is too large for a metastable state to persist. Our method can also be generalized to a stochastic dynamics where several "spin flips" are allowed (see below for details) and our conclusions are not altered. Since one of the questions that should be considered when assigning some spin flip dynamics to a spin model is the extent to which one's results depend on the details of the dynamics, the fact that one can also handle a slight generalization of the usual dynamics is of some interest. We also study a one-dimensional model whose extreme simplicity makes it useful for the interpretation of the Curie–Weiss model.

2. MODELS

We consider statistical mechanical systems with the following objects: a phase space P, a sequence of "finite-volume" Hamiltonians H_n defined on P, a fixed reference measure $\nu(dp)$ on P, a sequence of partition functions

$$Z_n = \int_P \exp(-\beta H_n)\, \nu(dp)$$

and an infinite-volume free energy

$$f = \lim_{n\to\infty} f_n = \lim_{n\to\infty} (-1/\beta n) \log Z_n \tag{1}$$

We also suppose that for each n there is a stochastic process defined with state space P which defines the (random) dynamics of the system in such a way that $\exp(-\beta H_n)\, \nu(dp)/Z_n$ is the unique invariant (initial) probability distribution for the process. The n dependence of the time scale for this process is chosen so that the relaxation time has a finite, nonzero limit as $n \to \infty$ corresponding to the infinite-volume relaxation time.

Suppose H_n depends on a parameter h and the system undergoes a first-order phase transition as h passes through some value (say $h = 0$) so that metastability can occur. Our interest is in discussing the relation between two distinct views of metastability: one in terms of the analytic continuation properties of f around $h = 0$; the other in terms of the existence of initial distributions on P which have anomalously large (n-dependent) lifetimes

before decaying by the random dynamics to the equilibrium distribution $\exp(-\beta H_n)\, v(dp)/Z_n$. In particular, we are interested in whether and how the metastable lifetime defined by the stochastic dynamics is related to the imaginary part of the analytic continuation of $f(h)$.

The following systems are of the above type.

A. Nearest Neighbor, d-Dimensional, Spin-1/2 Ising Model

In this model

$$\begin{aligned} P &= \{\sigma_i: \quad i = (i_1,\ldots, i_d) \in \mathbb{Z}^d, \quad \sigma_i = \pm 1\} \\ v &= \prod_i [\delta(\sigma_i + 1) + \delta(\sigma_i - 1)] \\ H_n &= -J \sum_{i \in B_n} \sum_{j \ni \|j-i\| = 1} \sigma_i \sigma_j - h \sum_{i \in B_n} \sigma_i \end{aligned} \tag{2}$$

where

$$B_n = \{i = (i_1,\ldots, i_d) \in \mathbb{Z}^d: \quad |i_l| \leqslant (\tfrac{1}{2}n)^{1/d}, \quad l = 1,\ldots, d\}$$

is the cube of volume n in $\mathbb{Z}^d$ and $\|i\|$ denotes the Euclidean length of i.

B. Curie–Weiss, Spin-1/2 Ising Model

For this model

$$\begin{aligned} P &= \{\sigma_i: \quad i \in \mathbb{Z}_+, \quad \sigma_i = \pm 1\} \\ v &= \prod_i [\delta(\sigma_i + 1) + \delta(\sigma_i - 1)] \\ H_n &= -\frac{1}{2n}\left(\sum_{i=1}^n \sigma_i\right)^2 - h \sum_{i=1}^n \sigma_i \end{aligned} \tag{3}$$

In both of the above examples, the stochastic process (for given n) is the usual stochastic "spin flip" dynamics (related to H_n) for the $\{\sigma_i: i \in B_n\}$ or $\{\sigma_i: i = 1,\ldots, n\}$ (see Refs. 2–4).

The next model is the simplest. It may be thought of as an approximation to the Curie–Weiss model above since by a standard Gaussian transform trick the Curie–Weiss partition function can be expressed as

$$Z_n = (n/2\pi\beta)^{1/2} \int e^{-nA(y)}\, dy \tag{4}$$

where $A(y) = (y - \beta h)^2/2\beta - \log\cosh y - \log 2$. For small y, $A(y) \approx y^4/12 + y^2(1/\beta - 1)/2 - yh + \beta h^2/2$.

C. One-Dimensional Model

Here $P = \mathbb{R} = \{x: -\infty < x < \infty\}$, $\nu(dp) = dx$, and $H_n = nG(x)$, with $G(x) = x^4/12 - x^2/2 - hx$. For simplicity, we set $\beta = 1$ in this example. An appropriate dynamics for this model is the (one-dimensional) diffusion process $X(t)$ whose Fokker–Planck equation for the probability density at time t, $g(x, t)$, is

$$\frac{\partial}{\partial t} g(x, t) = \varepsilon_n \left\{ \frac{\partial^2}{\partial x^2} g(x, t) + n \frac{\partial}{\partial x} [G'(x) g(x, t)] \right\} \tag{5}$$

where ε_n is an n-dependent time scale to be chosen so that the equilibrium relaxation time has a finite nonzero limit as $n \to \infty$. In some of the discussion below, we also let G depend on n through its dependence on h.

We now turn to a detailed analysis of the last two models.

3. THE ONE-DIMENSIONAL MODEL

Analyticity properties of $f(h)$ in the one-dimensional model are easily determined. For real h, we have

$$f(h) = \min_{-\infty < x < \infty} (x^4/12 - x^2/2 - hx) \tag{6}$$

There is a phase transition at $h = 0$ evidenced by a discontinuity in f':

$$f(h) = \begin{cases} f_+(h) = \min\limits_{x>0}(x^4/12 - x^2/2 - hx), & h > 0 \\ f_-(h) = \min\limits_{x<0}(x^4/12 - x^2/2 - hx), & h < 0 \end{cases} \tag{7}$$

Now $f_+(h)$ is analytic for $\operatorname{Re} h > 0$ and has an analytic continuation [which differs from $f_-(h)$] into the left half plane, $\operatorname{Re} h \leqslant 0$. The first singularity in the left half-plane occurs as a square root branch point along the negative real axis at the spinodal value $h = -2/3$. The natural analytic continuation past this branch point places a branch cut along $(-\infty, -2/3)$ and f then develops an imaginary part along this branch cut. For $h \in (-2/3, \infty)$, $f_+(h)$ is still given by the formula above, while for other values of h, one picks the appropriate root $\bar{x}_+(h)$ of

$$x^3/3 - x - h = 0 \tag{8}$$

and then defines $f_+(h) = (\bar{x}_+)^4/12 - (\bar{x}_+)^2/2 - h\bar{x}_+$. We note that for $h = -2/3 - z$ we have asymptotically that

$$\begin{aligned} |\operatorname{Im} f_+(h)| &\sim \text{const} \times z^{4/3} \quad \text{as} \quad z \to \infty \\ |\operatorname{Im} f_+(h)| &\sim \text{const} \times z^{3/2} \quad \text{as} \quad z \to 0^+ \end{aligned} \tag{9}$$

In order to compare $|\mathrm{Im}\, f(h)|$ to a metastable decay rate on the related stochastic process, we first suggest that it must be related to a decay rate "per unit volume." That is, if τ_n is the metastable lifetime for the "volume" n process and $r_n = 1/\tau_n$ is its decay rate, then in the region of h values for which $\mathrm{Im}\, f(h)$ is nonzero we should expect r_n/n to have a finite, nonzero limit which is (perhaps) related to $|\mathrm{Im}\, f_+(h)|$. This point will be discussed below in some detail, but for the time being we simply observe that in a more realistic system (such as the nearest neighbor Ising model) one knows that $f(h)$ [and thus the putative $f_+(h)$] is a free energy per unit volume and thus its imaginary part should be a "decay rate density" rather than a total decay rate. Moreover, one believes that in the thermodynamic limit for a short-range interaction model, the metastable decay rate is the same as the rate for forming critical droplets, which should be a finite rate per unit volume but infinite for the total (infinite) volume in the thermodynamic limit. Our object then in our one-dimensional model is to define the metastable decay rate r_n, to show that r_n/n has a finite, nonzero limit [in the region where $\mathrm{Im}\, f_+(h) \neq 0$], and to determine whether that limit is related to $|\mathrm{Im}\, f_+(h)|$.

We first determine the n dependence of ε_n. Let K_n be the Fokker–Planck generator $-\partial/\partial x^2 - n(\partial/\partial x)G'(x)$; in the region $h < 0$, we do various scaling transformations about the stable minimum of $G(x)$ located at some negative value $x_s = x_s(h)$. This will yield the asymptotics of the relaxation rate to equilibrium associated with small deviations from the stable minimum.

Letting $u = (x - x_s)\sqrt{n}$, we see that

$$\frac{1}{n}K_n = -\frac{\partial^2}{\partial u^2} - \frac{\partial}{\partial u}\left[Cu + O\left(\frac{1}{\sqrt{n}}\right)\right] \to \left(-\frac{\partial^2}{\partial u^2} - C\frac{\partial}{\partial u}u\right) \tag{10}$$

Thus K_n/n has a finite, nonzero limit as $n \to \infty$ in the rescaled variable u, and we therefore choose $\varepsilon_n = 1/n$.

For $-2/3 < h < 0$, the metastable decay rate can be defined in analogy with the critical droplet formation rate in a more realistic model as follows. We let $x_m = x_m(h)$ be the location of the local minimum of $G(x)$ (located at $x_m > 0$) and $x_d = x_d(h)$ be the location of the local maximum of $G(x)$ [located in (x_s, x_m)], and define for the stochastic process $X(t)$ and any initial position $X(0) = x > x_d$,

$$V(x, t) = \mathrm{Prob}(X(t') \neq x_d \qquad \forall t' \in [0, t] \mid X(0) = x) \tag{11}$$

It is known from the theory of diffusion processes (e.g., see Ref. 5) that $V(x, t)$ is the solution of the following partial differential equation with a Dirichlet boundary condition at $x = x_d$:

$$\begin{aligned} &\frac{\partial V}{\partial t} = \varepsilon_n\left[\frac{\partial^2}{\partial x^2} - nG'(x)\frac{\partial}{\partial x}\right]V; \qquad t > 0, \quad x \in (x_d, \infty) \\ &V(x, 0) = 1, \quad x \in (x_d, \infty); \qquad V(x_d, t) = 0, \quad t > 0 \end{aligned} \tag{12}$$

Thus, by expanding $V(x, t)$ in an eigenfunction expansion, it is clear that for any $x > x_d$, $V(x, t) \sim \exp(-r_n t)$, where

$$r_n = \text{minimum eigenvalue of } J_n$$

where

$$J_n = \varepsilon_n[-\partial^2/\partial x^2 + nG'(x)\,\partial/\partial x] \qquad \text{on } (x_d, \infty)$$

with a Dirichlet boundary condition at $x = x_d$. Clearly r_n is a reasonable definition for the metastable decay rate.

For $h \leqslant -2/3$, the definition of a reasonable r_n is somewhat more complicated since the local maximum for $G(x)$ no longer exists. Before resolving this point, we discuss the n dependence of r_n in the region $-2/3 < h < 0$. Now J_n is self-adjoint on

$$\mathscr{H} = L^2\{(x_d, \infty), \exp[-nG(x)]\,dx\}$$

and is unitarily equivalent to the Schrödinger operator

$$\tilde{J}_n = \varepsilon_n\left\{-\frac{\partial^2}{\partial x^2} + \frac{n^2}{4}[G'(x)]^2 - \frac{n}{2}G''(x)\right\} \qquad \text{on } L^2[(x_d, \infty), dx]$$

with a Dirichlet boundary condition at x_d. A standard WKB approximation suggests then that

$$r_n = \frac{n\varepsilon_n}{4\sqrt{\pi}}[-G''(x_d)G''(x_m)]^{1/2} \exp\{n[G(x_m) - G(x_d)]\} \tag{13}$$

and thus that $r_n \sim \exp(-n\Delta)$, where $\Delta = G(x_d) - G(x_m) > 0$. Thus r_n/n goes rapidly to zero, which is consistent with that fact that $\operatorname{Im} f_+(h) \equiv 0$ for $-2/3 < h < 0$ since f_+ is analytic for $h > -2/3$.

We now treat the situation for $h \leqslant -2/3$ since (somewhat paradoxically) this transpinodal region for our one-dimensional (as for a Curie–Weiss) model seems closer to the conjectured situation in a nearest neighbor Ising model for h slightly negative. There are now no longer any clearly defined values of x_m and x_d, so we consider more generally for $x' < x$

$$V(x, x', t) = \text{Prob}(X(t') \neq x' \qquad \forall t' \in [0, t] \mid X(0) = x) \tag{14}$$

The decay rate for making a transition from x to x' is then the rate constant in the asymptotic decay of $V(x, x', t)$:

$$r_n(x, x') = -\lim_{t \to \infty}(1/t) \log V(x, x', t) \tag{15}$$

For h slightly less than $-2/3$, we expect that if we choose x' appropriately, then r_n/n will have a nonzero, finite limit which will be independent of x and x'

and this limit will define the ("infinite volume") metastable decay rate ("per unit volume").

From the discussion above we see that $r_n(x, x')$ is the minimum eigenvalue of

$$\tilde{J}_n(x') = \varepsilon_n\left\{-\frac{\partial^2}{\partial x^2} + \left[\frac{n}{2}G'(x)\right]^2 - \frac{n}{2}G''(x)\right\} \quad \text{on } L^2((x', \infty), dx) \quad (16)$$

with a Dirichlet boundary condition at $x = x'$, so that, with $\varepsilon_n = 1/n$, $r_n(x, x')/n$ is the minimum eigenvalue of

$$\bar{J}_n(x') = \frac{1}{n^2}\left\{-\frac{\partial^2}{\partial x^2} + \left[\frac{n}{2}G'(x)\right]^2 - \frac{n}{2}G''(x)\right\} \quad \text{on } L^2((x', \infty), dx) \quad (17)$$

with a Dirichlet boundary condition at $x = x'$.

Clearly, as $n \to \infty$, we have

$$r_n(x, x')/n \to \inf_{x' < u < \infty} \tfrac{1}{4}[G'(u)]^2 = \inf_{x' < u < \infty} \tfrac{1}{4}(\tfrac{1}{3}u^3 - u - h) \equiv r(x') \quad (18)$$

For $h \geqslant -2/3$ and $x' \leqslant x_m(h)$, we have [as discussed above for $x' = x_d(h)$] that $r(x') = 0$ since by definition $G'(u) = 0$ for $u = x_m(h)$. On the other hand, for $h < -2/3$ and $x' > x_s(h)$, we have $r(x') > 0$, since now the only real zero of $G'(u)$ is at $u = x_s(h)$. In order to have $r(x')$ independent of x' we need that $[G'(u)]^2$ attain its minimum on $[x', \infty)$ in the interior of the interval. This interior minimum clearly occurs at $u = +1$. Thus we must have $x' < 1$ and further we must have $[G'(x')]^2 > [G'(1)]^2$, which is easily seen to imply that $x' > -2$. Thus for $-2 < x' < 1$ we find

$$r_n(x, x')/n \to r(x') = \inf_{x' < u < \infty} \tfrac{1}{4}[G'(u)]^2 = \tfrac{1}{4}[G'(1)]^2 = \tfrac{1}{4}(-h - \tfrac{2}{3})^2 \quad (19)$$

so that the metastable decay rate per unit volume for $h = -\frac{2}{3} - z$ is a well-defined function of h, say $\gamma(h)$, independent of x', and

$$\gamma(h) = \gamma(-\tfrac{2}{3} - z) = \tfrac{1}{4}z^2 \quad (20)$$

According to Ref. 1, the decay rate $\gamma(h)$ and the quantity $|\mathrm{Im}\, f_+(h)|$ given in Eq. (9) are not identical, but differ by a factor "kappa" (in Langer's notation). In our model this factor (up to constants) is G'' evaluated at the local maximum of G in the metastable range of h; transpinodally, where G has no such local maximum, we analytically continue and evaluate G'' at the appropriate root $\bar{x}$ of Eq. (8). Since $|G''(\bar{x})| = 2\sqrt{z} + O(z)$, we see that $\gamma(h)$ and $|G''(\bar{x})|\ \mathrm{Im}\, f_+(h)$ have the same h dependence, confirming the expectations of Ref. 1 (see also Refs. 6 and 7). Note that agreement obtains only to leading order in z.

There is some further evidence that can be obtained from our simple one-dimensional model linking the nonvanishing imaginary part of the free energy and the nonvanishing of the metastable decay rate. We first note that the analytic continuation of the free energy can be obtained by doing a change of contour in the complex x-plane in the integral defining Z_n. Namely, if we let C denote a contour which comes in from the upper half plane (say, along the positive imaginary axis), meets the real axis at $x_d(h)$, and then leaves along the positive real axis, then for $\operatorname{Im} h > 0$

$$f_+(h) = \lim_{n\to\infty} (-1/n) \log \int_C e^{-nG(z)}\, dz \tag{21}$$

This is the point of view of Refs. 6 and 8. Thus it is natural to define for finite n,

$$f_{n+} = -\frac{1}{n} \log \int_C e^{-nG(z)}\, dz$$

We next consider the situation when $G(z) = G_n(z)$ with $h = h_n \to -(\frac{2}{3})^+$ in an appropriate way so that $\operatorname{Im} nf_{n+}$ has a finite, nonzero limit (of course, both of the corresponding *densities* vanish). By scaling arguments, one has that if $z_n = 1 + wn^{-1/3}$ and $h = -\frac{2}{3} + \theta n^{-2/3}$, then

$$n[G_n(z_n) - G(1)] \to \tfrac{1}{3}w^3 - \theta w \equiv B(w)$$

and thus

$$\operatorname{Im} nf_{n+} = -\arg \int_C e^{-nG(z_n)}\, dz_n \to \arg \int_{C'} e^{-B(w)}\, dw \tag{22}$$

where C' is an appropriate contour coming in from the upper half plane (say along the ray $\arg w = 2\pi/3$) and leaving along the positive real axis. On the other hand, we have a total metastable lifetime $r_n(x_m(h_n), x_d(h_n))$, the minimum eigenvalue of $J_n = \varepsilon_n[-\partial^2/\partial x^2 + nG_n'(x)\,\partial/\partial x]$ with Dirichlet boundary condition at $x' = x_d(h_n)$. By a similar scaling argument we find that if we choose $\varepsilon_n = n^{-2/3}$, then

$$r_n \to \text{minimum eigenvalue of } \hat{J}$$

where

$$\hat{J} = -\partial^2/\partial w^2 + B'(w)\,\partial/\partial w \tag{23}$$

with a Dirichlet boundary condition at $w_d(\theta) = [\text{location of local maximum of } B(w)] = -\sqrt{\theta}$. The reason ε_n is taken proportional to $n^{-2/3}$ rather than n^{-1} is because we choose the time scale so that the metastable (rather than the stable) relaxation time has a finite, nonzero limit. This is necessary because $x_m(h_n) - x_d(h_n) \to 0$ in this case.

To compare (22) and (23), consider the situation for $\theta \gg 1$. Applied to the right-hand side of (22), the method of stationary phase gives

$$\lim|\mathrm{Im}\, nf_{n+}| \sim \tfrac{1}{2}\exp(-\tfrac{4}{3}\theta^{3/2}) \tag{24}$$

Note that the quantity in the exponent is just $B(\sqrt{\theta}) - B(-\sqrt{\theta})$, where $\pm\sqrt{\theta}$ are the locations of the minimum and maximum of B. On the other hand, r_n can be estimated by WKB methods as in Eq. (13), yielding

$$\lim r_n \sim \tfrac{1}{2}(\theta/\pi)^{1/2}\exp(-\tfrac{4}{3}\theta^{3/2}) \tag{25}$$

To compare (24) and (25) we again require the factor "kappa" of Ref. 1, here simply equal to B'' evaluated at the local maximum. This is seen to be $B''(-\sqrt{\theta}) = -2\sqrt{\theta}$, and we find that the two methods agree not only on the dominant exponential behavior, but on finer details (the θ dependence of the "prefactor") as well.

4. CURIE–WEISS MODEL

The Hamiltonian of Eq. (3) can be written

$$H_n = U(k) = -(2k-n)^2/2n - h(2k-n) \tag{26}$$

with k the number of spins pointing "up" ($\sigma_i = 1$). It is also convenient to define the magnetization per unit volume $x = \sum_i \sigma_i/n = (2k/n) - 1$. In equilibrium the probability of finding k spins up is

$$p(k) = Z_n^{-1}\binom{n}{k}\exp[-\beta U(k)] \equiv Z_n^{-1}\exp[-\beta n a_n(x)] \tag{27}$$

with Z_n the partition function

$$Z_n = \sum_{k=0}^{n}\binom{n}{k}\exp[-\beta U(k)] \tag{28}$$

and $T = 1/\beta$. By Laplace's method

$$\begin{aligned} f(h) &= \lim \frac{-1}{\beta n}\log\sum_{k=0}^{n} e^{-\beta n a_n(x)} \\ &= \lim \frac{-1}{\beta n}\log\frac{n}{2}\int_{-1}^{1} dx\, e^{-\beta n a(x)} = \min_{-1\le x\le 1} a(x) \end{aligned} \tag{29}$$

with $a(x)$ the limit of $a_n(x)$ as $n \to \infty$. The function $a(x)$ is

$$a(x) = T\left(\frac{1+x}{2}\log\frac{1+x}{2} + \frac{1-x}{2}\log\frac{1-x}{2}\right) - \frac{1}{2}x^2 - hx \tag{30}$$

[It can also be shown that the minimum of a and the minimum of A of Eq. (4) give the same free energy.] The value of x at which a attains its minimum satisfies $a'(\bar{x}) = 0$ and as in the one-dimensional model the analytic continuation of f is obtained by evaluating f at (possibly complex) points $\bar{x}$ even when such points do not yield the absolute minimum of f. For $h > 0$ we start from the largest positive root of $a'(\bar{x}) = 0$, this $\bar{x}$ being the magnetization in the stable state. Continuing to $h < 0$ when $T < 1$, the imaginary part of the continued free energy is zero so long as $a'(\bar{x})$ has a real, positive root. $\bar{x}$ becomes complex past the spinodal value of h

$$h_{\text{sp}} = -(1 - T)^{1/2} + T \tanh^{-1}(1 - T)^{1/2} \tag{31}$$

For h near h_{sp} the behavior of a and therefore f is to leading order the same as derived above for the one-dimensional model. It is thus easy to show that

$$|\text{Im}\, f| \sim |h - h_{\text{sp}}|^{3/2}, \qquad h < h_{\text{sp}} < 0, \qquad |h - h_{\text{sp}}| \text{ small} \tag{32}$$

For $h \to \infty$ we find $\bar{x} \sim -h \pm i\pi/2\beta$ and

$$|\text{Im}\, f| = h\pi/2\beta, \qquad h \to -\infty, \quad h \text{ real} \tag{33}$$

Because for $h \to -\infty$, $\text{Re}\, \bar{x} \sim -h \gg 1$ the magnetization is far from any possible physical value and one does not expect $\text{Im}\, f$ to have much significance.

There is a well-studied stochastic evolution associated with the Curie–Weiss model. Because the energy depends only on the total number of up spins, the spin flip dynamics becomes a Markov chain on the integers 0, 1,..., n with the following transition probabilities (see Ref. 2):

$$T_{k,k+1} = \alpha \frac{n-k}{n} \exp\left\{-\frac{1}{2}\beta[U(k+1) - U(k)]\right\} \qquad \text{for } 0 \leqslant k \leqslant n-1 \tag{34}$$

$$T_{k,k-1} = \alpha \frac{k}{n} \exp\left\{-\frac{1}{2}\beta[U(k-1) - U(k)]\right\} \qquad \text{for } 1 \leqslant k \leqslant n \tag{35}$$

$$T_{kk} = 1 - T_{k,k+1} - T_{k,k-1} \qquad \text{for } 0 \leqslant k \leqslant n \tag{36}$$

where T_{ij} is the probability for going from i spins up to j spins up and α is small enough for T_{jj} to be positive for all j. All T_{ij} not given by (34)–(36) are zero. Time units are chosen so that n steps (or spin flip attempts) are taken per second. If $p(k, \tau)$ is the probability of finding the system with k spins up after τ steps (and therefore at time τ/n), the master equation is

$$p(k, \tau + 1) = \sum_{j=0}^{n} p(j, \tau) T_{jk} \tag{37}$$

The lifetime of the metastable state of this system has been studied by

Griffiths *et al.*[2] by going over (to some extent) to the continuum limits of k and t. They themselves point out the hazards of this procedure. The problem is the rapid variation of p with k. In particular, to get a Fokker–Planck equation from (37) one would like to consider a probability function

$$P(x, t) = p(\tfrac{1}{2}n(1 + x), nt)$$

and expand P in a series

$$P\left(x + \frac{2}{n}, t\right) = p(k + 1, nt) = P(x, t) + \frac{\partial P}{\partial x}\frac{2}{n} + \frac{1}{2}\frac{\partial^2 P}{\partial x^2}\left(\frac{2}{n}\right)^2 + \cdots$$

However, derivatives of P with respect to x are themselves of the order of n [compare the equilibrium distribution, Eq. (27)], so that successive terms in the series do not obviously decrease. For this reason we shall do all our calculations on the discrete system, providing a rigorous bound on the decay rate for $|h| < |h_{sp}|$ and obtaining the exact n dependence of the decay rate in the transpinodal region.

As above, we define lifetime in terms of first passage time. For some fixed L let ${}_Lv(j, k, \tau)$ be the probability that after τ steps a system has k spins up, given that it initially had j spins up, and with the additional condition that at no time τ' $(0 \leqslant \tau' \leqslant \tau)$ did it have exactly L spins up $(j, k > L)$ (L is a taboo state in the language of Ref. 9). To study ${}_Lv(j, k, \tau)$ we define a modified transition matrix. Let $\tilde{T}_{ab}$ be the same as T_{ab} except for two elements. These two elements are

$$\tilde{T}_{L,L+1} = 0 \tag{38}$$

$$\tilde{T}_{LL} = 1 - \tilde{T}_{L,L-1} = T_{LL} + T_{L,L+1} \tag{39}$$

$\tilde{T}$ is a stochastic matrix. Under $\tilde{T}$ a system reaching the state L can never go back to $L + 1$. It follows that

$${}_Lv(j, k, \tau + 1) = \sum_{i=L+1}^{n} {}_Lv(j, i, \tau)\tilde{T}_{ik} \tag{40}$$

with the initial condition ${}_Lv(j, k, 0) = \delta_{jk}$. The total probability of not having undergone a first passage through L by step τ is just ${}_Lv(j, \tau)$, the sum over k $(L + 1 \leqslant k \leqslant n)$ of ${}_Lv(j, k, \tau)$.

The similarity of Eq. (40) to the continuum version of the first passage problem, namely Eq. (12), is evident. It is thus clear that the asymptotic decay properties of a system confined to $L < k \leqslant n$ are given by the largest eigenvalue of the $J \times J$ matrix

$$Y_{ij} = \tilde{T}_{n-j+1,n-i+1}, \qquad i, j = 1, \ldots, J; \quad J = n - L \tag{41}$$

Calling this eigenvalue λ, and recalling that there are n spin flip attempts per

second, we have that $\lambda^n = \exp(-\Gamma)$, with Γ the decay rate. The decay rate per unit volume is therefore

$$\Gamma/n = -\log \lambda \tag{42}$$

The matrix Y is not a stochastic matrix, because the sum of the elements in its Jth column do not add to unity; in fact

$$Y_{JJ} = \tilde{T}_{L+1,L+1} = 1 - T_{L+1,L} - T_{L+1,L+2}$$
$$Y_{J-1,J} = \tilde{T}_{L+1,L+2} = T_{L+1,L+2}$$

with no other nonzero entries in column J. The matrix

$$(Y^0)_{ij} = Y_{ij} + T_{L+1,L}\delta_{Ji}\delta_{Jj} \tag{43}$$

is stochastic. Because Y^0 is stochastic, its largest eigenvalue is 1. Since $Y^0 - Y$ is a nonnegative diagonal matrix, the largest eigenvalue of Y is equal to or less than one. Furthermore, by the Frobenius theorem, λ, the largest eigenvalue of Y, is nondegenerate and the associated eigenvector has all positive entries (we also use the fact that Y is irreducible: every state can be reached from every other state).

Although Y is not Hermitian, the detailed balance condition built into T_{ij} ensures that Y is unitarily equivalent to a Hermitian matrix X (just as J_n and $\tilde{J}_n$ were related in Section 3). Specifically, let

$$S = \text{diag}([p(n)]^{-1/2}, [p(n-1)]^{-1/2}, \ldots, [p(L+1)]^{-1/2})$$

[with $p(j)$ given by (27)] be a diagonal $J \times J$ matrix and let

$$X = SYS^{-1} \tag{44}$$

Then X is Hermitian and for any vector ξ

$$\lambda(\xi, \xi) \geqslant (\xi, X\xi) \tag{45}$$

with

$$(\xi, \eta) = \sum_{j=1}^{J} \xi_j^* \eta_j$$

A bound on Γ similar to the estimate given in Ref. 2, but which makes no appeal to a continuum approximation to the master equation, can be immediately obtained from (45). Let

$$\xi = \begin{pmatrix} p(n)^{1/2} \\ \vdots \\ p(L+1)^{1/2} \end{pmatrix} \tag{46}$$

Then (45) yields

$$\lambda \sum_{j=L+1}^{n} p(j) \geqslant \sum_{j=L+1}^{n} p(j) - p(L+1)T_{L+1,L} \tag{47}$$

We have the rigorous bound

$$1-\lambda \leqslant p(L+1)T_{L+1,L}\Big/\sum_{j=L+1}^{n} p(j)$$

$$= \alpha\binom{n-1}{L}e^{-\beta[U(L)+U(L+1)]/2}\Big/\sum_{j=L+1}^{n}\binom{n}{j}e^{-\beta U(j)} \tag{48}$$

For $0 > h > h_{sp}, a(x)$ has a minimum at some $\bar{x} > 0$ and we take L such that $x_L < \bar{x}$. Then Stirling's approximation and the Laplace method for integrals yield

$$\Gamma = O(\exp\{-\beta n[a(x_L) - a(\bar{x})]\}) \tag{49}$$

The constant implicit in the asymptotic relation is also easy to evaluate.

Equation (49) establishes that for $|h| < |h_{sp}|$, $\lim_{n\to\infty}(\Gamma/n)$ is zero, in conformity with the vanishing of the imaginary part of f.

In the transpinodal region ($h < h_{sp} < 0$) a more useful bound is obtained by letting ξ [of Eq. (45)] be $\xi_i = 1$ for $i = \nu_1, \ldots, \nu_2 - 1$ and zero otherwise, with $\nu = \nu_2 - \nu_1 \gg 1$. Then by (45)

$$\lambda\nu \geqslant \sum_{j=\nu_1}^{\nu_2-1}(X_{j,j-1} + X_{jj} + X_{j,j+1}) + O(1)$$

the $O(1)$ terms being of the form X_{ν_1-1,ν_1} arising from the edges of the sum. It follows that

$$(1-\lambda)/\alpha \leqslant (1/\alpha)\left\{1 - \min_{\nu_1 \leqslant j < \nu_2}(X_{j,j-1} + X_{jj} + X_{j,j+1}) + O(1/\nu)\right\} \tag{50}$$

For large ν, (50) can be replaced by its continuum version [with $O(1/n) < O(1/\nu) = o(1)$ errors] to yield

$$\lim_{n\to\infty}(1/\alpha)(1-\lambda) \leqslant \max_{x_1 \leqslant x \leqslant x_2} \tfrac{1}{2}[\psi(x)]^2 \tag{51}$$

with x_1 and x_2 corresponding to ν_2 and ν_1, respectively, and

$$\psi(x) \equiv (1+x)^{1/2}\exp[-\tfrac{1}{2}\beta(x+h)] - (1-x)^{1/2}\exp[\tfrac{1}{2}\beta(x+h)] \tag{52}$$

Since x_1 and x_2 are arbitrary points to the right of x_L, we minimize (51) over choices of x_1, x_2, obtaining

$$\lim_{n\to\infty}(1/\alpha)(1-\lambda) \leqslant \min_{x_L \leqslant x} \tfrac{1}{2}[\psi(x)]^2 \tag{53}$$

We next develop an upper bound for λ.

Consider a matrix of the form

$$H_1 = \begin{pmatrix} a_1 & b_1 & & & \\ b_1 & a_2 & b_2 & & 0 \\ & \ddots & \ddots & \ddots & \\ & & \ddots & \ddots & b_{M-1} \\ 0 & & & b_{M-1} & a_M \end{pmatrix} \tag{54}$$

with a_i real and $b_i \geqslant 0$ and define $b_0 = b_M = 0$. If the largest eigenvalue of H_1 is λ, then from

$$(x, H_1 x) = \sum_{i=1}^{M} |x_i|^2 (a_i + b_i + b_{i-1}) - \sum_{i=1}^{M-1} b_i |x_{i+1} - x_i|^2 \tag{55}$$

it is obvious that

$$(x, H_1 x) \leqslant \left[\max_{1 \leqslant i \leqslant M} (a_i + b_i + b_{i-1}) \right] \sum |x_i|^2$$

and thus

$$\lambda \leqslant \max_{1 \leqslant i \leqslant M} (a_i + b_i + b_{i-1})$$

Now return to the matrix X of Eq. (44). The matrix X is of the form H_1 of Eq. (54), so that we have the rigorous bound for λ

$$\lambda \leqslant \max_i (X_{ii} + 2X_{i,i+1}) \tag{56}$$

For $i = J$ the term $2X_{i,i+1}$ is replaced by $X_{i-1,i}$ in (56). Taking the continuum limit of this inequality gives

$$(1/\alpha)(1 - \lambda) \geqslant \tfrac{1}{2} \min_{x \geqslant x_L} [\psi(x)]^2 + O(1/n) \tag{57}$$

[the same ψ as Eq. (52)]. Equations (53) and (57) yield the result

$$\lim_{n \to \infty} (1/\alpha)(1 - \lambda) = \tfrac{1}{2} \min_{x \geqslant x_L} [\psi(x)]^2 \tag{58}$$

The properties of ψ are related to those of a. When $a' = 0$, $\psi = 0$ and simultaneous vanishing of ψ and ψ' occurs for $h = h_{sp}$. For h near h_{sp} (<0) and at that x (>0) such that $\psi' = 0$, Eq. (58) gives

$$(1/\alpha)(1 - \lambda) = \tfrac{1}{2} T^{-3/2} (h - h_{sp})^2 \tag{59}$$

The resemblance of (59) to (20) is not accidental, as many of our discrete process arguments have continuum analogs. The relation between the decay rate (59) and the imaginary part of the continued free energy (32) (for small

$|h - h_{sp}|$) is the same as that obtained above for the "one-dimensional" model, namely they differ by a factor $|h - h_{sp}|^{1/2}$. Again, as shown explicitly above, the second derivative of the "potential" $a(x)$ at its continued extremum provides this factor.

The foregoing results can be generalized to dynamical systems in which two or more spin flips can occur in a single time step, i.e., the transition probabilities $T_{k,k+j}$ are nonzero for $j > 1$. A form consistent with detailed balance is

$$\begin{aligned} T_{k,k+j} &= \alpha_j[(n-k)(n-k-1)\cdots(n-k-j+1)/n^j] \\ &\quad \times \exp\{-\tfrac{1}{2}\beta[U(k+j) - U(k)]\} \qquad \text{for} \quad 0 \leqslant k, \quad k+j \leqslant n \\ T_{k,k-j} &= \alpha_j[(k+1)\cdots(k+j)/n^j] \\ &\quad \times \exp\{-\tfrac{1}{2}\beta[U(k-j) - U(k)]\} \qquad \text{for} \quad 0 \leqslant k-j, \quad k \leqslant n \end{aligned} \tag{60}$$

$$T_{kk} = 1 - \sum_{j \geqslant 1} (T_{k,k+j} + T_{k,k-j}) \qquad \text{for} \quad 0 \leqslant k \leqslant n$$

Using this T, the matrix X is defined as above and

$$\lim(1 - \lambda) = \lim \min_k \sum_{j \geqslant 1} (T_{k,k+j} + T_{k,k-j} - 2X_{k,k+j})$$

For example, if the α_j have a Poisson distribution form

$$\alpha_j = \alpha_0 e^{-\rho}\rho^j/j!, \qquad \rho > 0, \quad j \geqslant 0$$

then

$$\lim[(1 - \lambda)/\alpha_0] = \min e^{-\rho}(e^{\rho u^2/2} - 2e^{\rho uv/2} + e^{\rho v^2/2})$$

with

$$u = (1 + x)^{1/2} e^{-\beta(x+h)/2}, \qquad v = (1 - x)^{1/2} e^{\beta(x+h)/2}$$

The dependence of $1 - \lambda$ on $h - h_{sp}$ given in (59) is not affected by this generalization, although the coefficient multiplying the $(h - h_{sp})^2$ term is changed. This result is of some interest, since one of the questions our work raises is the extent to which our conclusions depend on the specific dynamical model. Another point is that our discrete methods allow easy and rigorous generalizations to various dynamics such as those of Eq. (60).

We remark finally that there is a continuous-time stochastic dynamics closely related to the discrete-time process defined by (34)–(36), in which (37) is replaced by

$$\frac{d}{dt} p(k, t) = \sum_{j=0}^{n} p(j, t)[T_{jk} - \delta_{jk}]$$

It is easy to show that our discrete-time analysis of the decay rate implies that in the continuous-time context we also have

$$\Gamma/n \to \tfrac{1}{2}\alpha \min_{x \geq x_L} [\psi(x)]^2$$

5. CONCLUSIONS

We know no a priori reason for the imaginary part of the analytically continued free energy to be proportional to the decay rate for a metastable state, although the analogy to quantum mechanics makes the idea plausible. Within the droplet model, however, Langer calculated both the analytic continuation[6] and the decay rate[8,1] and found them to differ only in a factor ("kappa") which is a property of the saddle point in free energy through which the system passes on its way to the stable state. In this paper we have provided rigorous verification of his results in some simple models. It must be said, though, that the need to identify the factor "kappa" detracts from the generality of the results. While we did not need to invoke a droplet model, we nevertheless had to identify a potential in order to evaluate "kappa"—it would have been preferable if the factor had emerged as a property of the stochastic process or of the free energy continuation.

With the factor "kappa," agreement holds to leading order near the singularity (h_{sp}), but not necessarily away from there. We can show, however, in the case of the Curie–Weiss model that the agreement is to some extent independent of the details of the spin flip dynamics. Specifically, our method allows calculation of decay rates in the case of many simultaneous spin flips, and agreement persists.

Our model systems illustrate another phenomenon that occurs in realistic metastable behavior. No matter how close λ (the largest eigenvalue of the restriction of $\tilde{T}$) is to one, so long as $\lim_{n\to\infty} \lambda < 1$ the lifetime of the system as a whole [$\sim -1/(n \log \lambda)$] goes to zero. On the other hand, the time needed to go from x_j to x_L cannot be less than $(x_j - x_L)/2$ [equal $n(x_j - x_L)/2$ steps divided by n steps per second], so that for sufficiently large n the eigenvalue λ (which remains perfectly well defined) ceases to govern the system's evolution. [Mathematically, if a spectral decomposition of $\tilde{T}$ is inserted in (40), a relatively long time will elapse before the largest eigenvalue dominates the sum.] It follows that for any h there is some n beyond which the metastable state (or decay bottleneck) ceases to dominate the relaxation.

What is happening is that there are several time scales in the problem and they do not all have the same n dependence. These scales are: (1) microscopic [$\Delta x = O(1/\sqrt{n})$] fluctuations about the stable state [our demand that this time be $O(1)$ fixed ε_n above], (2) microscopic fluctuations about the metastable

state (if there is one), (3) escape from the metastable state (critical droplets, free energy barriers, etc.), (4) macroscopic changes in the system [$\Delta x = O(1)$]. If the macroscopic relaxation takes places on the same time scale as microscopic fluctuations (time scale 1) (as it does in our models),[4] then macroscopic relaxation will appear to be deterministic. In our one-dimensional model, for example, the system heads toward x_s with a definite drift velocity. Looked at in this way, the point x_m simply represents a minimum in the drift velocity. Of course for any finite n, an h can be chosen close enough to h_{sp} (but $|h| > |h_{sp}|$, so that the system spends a long time at x_m. But with increasing n the metastable escape time scale (time scale 2) must become less than that of macroscopic relaxation.

In this respect our models reflect the behavior of more realistic systems. Consider, for example, the two-dimensional Ising model. The imaginary part of the free energy or the largest eigenvalue of the truncated master equation may be perfectly well-defined quantities for $n \to \infty$. Nevertheless, these quantities will only convey dynamical information up to a certain system size. It seems to us that this may be the best compromise one could hope for in the quest for a mathematical idealization of metastability: quantities which are well defined in the thermodynamic limit but whose application to large systems is limited. Physical or laboratory metastability then occurs because the system sizes for which the ordinary (macroscopic, deterministic) relaxation is longer than metastable relaxation are so large, even on the scale of 10^{24} constituents, that many macroscopic systems are governed by the metastable evolution. We are certainly not the first to enunciate the view that metastability, insofar as it is characterized by long lifetimes, is an inherently finite system phenomenon; but we believe our simple models show how this is not inconsistent with the existence of certain mathematical idealizations which are perfectly well defined in the thermodynamic limit (and hence can be associated with an ideal concept of the metastable system) but whose use for dynamical description is limited by system size.

An "experimental" example of the transition from metastable relaxation to ordinary relaxation in the Ising model is given by Stoll and Schneider.[11] They studied the n dependence of lifetime and found that indeed as system size grew the lifetime went from inverse volume dependence to volume independence.[5] At the largest n values they indicate[11] that critical (and larger) droplets form quickly and most of the relaxation is taken up with the linking of the droplets, a process we would consider macroscopic deterministic relaxation, not related to the phenomenon of metastability, and having relaxation time independent of system size.

[4] The coincidence of time scales 1 and 4 would seem to be related to the fluctuation–dissipation theorem.

[5] They have a third region of very small volumes, but this does not concern us here.

The imprecision implicit in the foregoing "compromise" definition of metastability is in some ways analogous to that which enters the description of unstable states or particles in quantum mechanics. The idealized concept of "a pole in the S matrix" is more or less useful as a characterization of an unstable state as that pole is closer or farther from the real axis. For our metastable state, although there may be a range of volumes for which good measurements of the free energy can be made, one cannot in principle get arbitrary accuracy, since a sufficiently large volume destroys the metastable state. In the same way one can never measure the location of the pole in the S matrix—one can only estimate its position more precisely for poles closer to the axis. In both situations, however, although the quantities are not directly measurable, they are knowable by analytic continuation, in one case from real energy scattering shifts, in the other from stable free energies.

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